

# Catalysis with Nanoparticles and Magnetic Fields

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Magnetic nanoparticles display both interesting core physical properties and interesting surface chemical properties. The composition of the particles allows to modulate their magnetic properties in terms of saturation magnetization, magnetic anisotropy and Curie temperature and hence heating power. Thus magnetic nanoparticles heat when submitted to an alternating magnetic field. Magnetic heating is instantaneous and in principle the best way to transform electrical energy into heat. Iron seemed interesting both for its magnetic and catalytic properties. For the preparation of high quality, unoxidized Fe NPs we have searched for many different precursors but with limited success. The iron bis(amide)  $\{\text{Fe}[\text{N}(\text{TMS})_2]_2\}_2$  opened the door to a new chemistry of iron NPs including iron (0), iron carbides and iron alloys.

We have developed in Toulouse a new generation of iron based nanoparticles (NPs) of unprecedented heating power. We have prepared iron carbide particles by carbidization of preformed monodisperse Fe(0) nanoparticles under a CO/H<sub>2</sub> atmosphere at 150°C. They consist essentially of crystalline Fe<sub>2.2</sub>C, display a SAR (heating power) of up to 3.3 kW/g and are able to hydrogenate CO<sub>2</sub> into methane in a flow reactor after addition of a catalytic Ru or Ni layer and excitation by an alternating magnetic field. Iron Cobalt NPs have been prepared from  $\{\text{Fe}[\text{N}(\text{TMS})_2]_2\}_2$  and the relative  $\{\text{Co}[\text{N}(\text{TMS})_2]_2\}_2$ , also first synthesized by Prof Andersen. These soft magnetic bimetallic FeCo NPs with a high Curie Temperature allow performing high temperature catalytic reactions such as propane dehydrogenation or methane and propane dry reforming. Iron nickel nanoparticles have been synthesized from iron amide and nickel amidinate precursors and found very active for CO<sub>2</sub> hydrogenation. In addition, submitting nanoparticles of iron carbide or iron nickel to magnetic heating in solution leads to local overheating and to perform under a low H<sub>2</sub> pressure difficult reactions such as hydrodeoxygenation of biomass derived platform molecules.

The lecture will briefly present the synthesis of the particles, their magnetic properties, their surface modification to deposit a catalytic layer and their catalytic properties for CO<sub>2</sub> hydrogenation in a flow reactor and high temperature catalysis. Further developments of the technique in solution or for electrochemical reactions will also be described.

## Biography:



Bruno Chaudret is a specialist of organometallic and “nano” chemistry. After a PhD with Sir G Wilkinson (Imperial College, London), he developed in the early 80s the synthesis of hydride and dihydrogen complexes and investigated by NMR their exchange processes which follow classical or quantum-mechanical pathways. These studies have been extended to the coordination of other simple groups such as C-H and Si-H, and led to a creative chemistry as well as to new catalytic processes. In the early 90s, Bruno Chaudret developed an organometallic method for the synthesis of metal or metal oxide nanoparticles. The mild conditions used allowed the control of the particle size and size distribution together with that of the surface species present on the

nanoparticles (hydrides, organic or inorganic molecules). The presence, dynamics and reactivity of surface species has been monitored by various NMR techniques. Due to their clean surfaces, the particles exhibit physical (e.g. magnetic) properties similar to those found in high-vacuum. According to the reaction conditions, the synthesis allows the formation of precise shapes (spheres, cubes, rods, wires, urchins, fractal structures) which may assemble into two- or three-dimensional super-crystals for particles diameters between 1 and 15 nm. These new nano-objects display interesting properties in various domains such as catalysis, magnetism, optics, micro- and nanoelectronics and have led to several applications in micro-electronics including the industrial production of gas sensors.

The present interest of Bruno Chaudret concerns first the chemistry of mono- and bimetallic nanoparticles for catalytic reactions including hydrodeoxygenation of biomass derived molecules and late stage labellisation of biomolecules with deuterium or tritium through C-H activation. The main research project is the use of magnetic induction in catalysis. The project involves the synthesis of magnetic nanoparticles acting both as heating element and catalyst for reactions in solution and in the solid state. This includes CO<sub>2</sub> hydrogenation for which a pilot plant is being built.

He is the research director of the CNRS and Director of the « Laboratoire de Physique et Chimie des Nano-Objets (LPCNO UMR INSA-CNRS- UPS 5215) » and the Institut National des Sciences Appliquées (INSA) Toulouse. He is author of 500 articles in refereed journals and 22 patents (2 licenced patents - 1 industrial development and production of gas sensors (MiCS)). He has been principal research of many scientific international and national project, to select some from the last 5 years (H2020-FET-Open FLIX (2019-2024), H2020- ITN Isotopics (2015-2020), ANR (French Research Agency), France-Germany MOCANANO (2012-2016), ANR Tanopol 2015-2019), ANR Hy-Wally (2016-2020), Region Midi-Pyrénées/Industry Hydromet (2015-2019), Ministry of industry / ST-Microelectronics (2005-2019)...). He has also gained two ERC Adv grants, Nanosonwing 2010-2015 (Co-I; PI Prof. Piet van Leewen) and MONACAT 2016-2021 as PI. He has codirected 42 PhD student (all Université de Toulouse), 8 PhD of international co-tutelle and 40 Postdocs. He has received many awards (e.g. French Chemical Society, Silver medal CNRS, Miguel Catalan Award, RSEQ, Spanish Chemical Society, Seaborg Lecture, University of California Berkeley, USA, Elected at the French Academy of Sciences, Gay-Lussac-Humboldt Award, Alexander von Humboldt Foundation, Germany, EastChem Visiting Professor (Saint-Andrews, Edinburgh), UK, Sir Geoffrey Wilkinson Prize & Lectureship, Royal Society of Chemistry, UK, Grand Prix Pierre Süe; Award, Société Chimique de France, French Chemical Society, Elected at the Academia European, Paolo Chini Lecture, Italian Chemical Society, Chevalier dans l'ordre de la Légion d'Honneur, Wittig-Grignard Award, DGCH, German Chemical Society , Chevalier dans l'ordre des Palmes Académiques).