Advanced Hyperpolarized Solid-State NMR Methods for Structure Elucidation of Supported Catalysts Caught in the Act

Développement de Nouvelles Méthodes de RMN Hyperpolarisée pour la Détermination Structurale de Catalyseurs Supportés en Action

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Thesis project: Solid-state NMR spectroscopy is a powerful technique for characterizing inorganic and hybrid materials, that offers the possibility to directly investigate both the bulk (silica and/or alumina) and surface functionalities (e.g., adsorbates, grafted molecules, organic fragments, etc.). In applications such as catalysis, having a precise understanding of the structure of surface species is critical, since one of the most powerful ways to develop systems with improved properties is through the determination of structure-activity relationships. However, the sensitivity of NMR methods poses a major limit for the investigation of surface species. During the past two decades, Dynamic Nuclear Polarization (DNP) has emerged as a unique technique to enhance the NMR spectra of both liquids and solids. In a DNP experiment, the large polarization of unpaired electrons is transferred to the neighboring nuclei via the microwave irradiation of the EPR spectrum at low temperature (typically 100 K), leading to NMR signal enhancements of several orders of magnitude.

A few years ago, we have demonstrated that DNP could be used to drastically enhance the solid-state magic angle spinning NMR signal of organometallic fragments incorporated in porous silica-based materials and to obtain, in an expeditious way, detailed structural information on surface species that were previously not amenable to solid-state NMR spectroscopy (1). We have shown how DNP could yield up to a 200-fold increase in the NMR sensitivity of the organic functionalities of hybrid silica materials as well as on a wide range of materials like Metal Organic frameworks and Alumina frameworks (2). These remarkable results have opened new, previously inconceivable, possibilities to investigate surface species in sophisticated systems of high fundamental and industrial relevance, and clearly heralded DNP as a key technique in the field of materials in the next several years.

In this context, we and our collaborators have achieved a major step forward in 2017 with the demonstration that the full three-dimensional (3D) structure of a model Pt complex anchored on an amorphous silica surface could be determined by DNP surface enhanced NMR spectroscopy (3). The increase in the NMR sensitivity of the surface fragment provided by DNP enabled the implementation of a series of multidimensional and multi-nuclear $^{13}$C-$^{15}$N and $^{29}$Si-$^{15}$N NMR experiments providing quantitative structural restraints. We have recently shown that the methodology could be extended to determine selectively the 3D structure of the active sites among a variety of surface species in Iridium-based catalysts (4).

The central objective of this PhD project is to further extend the DNP NMR methodology so as to tackle new structural features of relevant supported catalysts, and to monitor real-time structural changes in the course of the catalytic reaction. Ru-NHC will be targeted as they are highly active supported catalysts in olefin metathesis (5). More specifically, we will target the conformation of the surface complexes at different stages of the synthetic pathway, characterize the location of the halogen counter ion, and

![Schematic structure of the Ru-NHC catalyst](image-url)
investigate the surface structure of reaction intermediates that appear during the catalytic reaction. This will be achieved by implementing and developing new DNP NMR methods allowing for the quantitative measurement of inter-atomic distances and dihedral angles in combination with new specific labelling schemes in order to constrain the three-dimensional structure of the organometallic fragments and elucidate their interaction with the support. We will also examine the NMR spectral signature of the halogen atoms present in the coordination sphere of the supported metal center (labelled X in the figure) as they are known to modulate the catalytic activity. Finally, pseudo operando NMR experiments will be run in conditions mimicking the catalytic processes to observe intermediates/resting states during the olefin metathesis reactions.

The project will address several research areas from (i) experimental work towards the development of NMR methods under DNP to unravel the structure and coordination sphere of metal centers, (ii) the implementation of numerical protocols to analyse the data and calculate surface structures and (iii) the investigation and characterization of new generation of polarizing agents and formulations compatible with highly reactive materials.

The project will be carried out at the unique European High-Field NMR facility in Lyon, using state of the art equipment and methods, and in collaboration with leading groups in materials science (notably at CPE Lyon). The project is firmly anchored at the interface between the chemistry of materials and the physics of spin dynamics. If you want pursue your research training at the heart of a top-level laboratory, in a young, friendly and truly international atmosphere, join us!

Principle of DNP NMR on surfaces and the high-field NMR magnet and DNP instrumentation that will be used in the project

References: