

Title of post

Generating hyperactive Pd-species in the bulk from Pd-complexes or Pd nanoparticles for the Suzuki cross-coupling reaction.

General information

Date of publication: 27/07/2018

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Modalities of application: To apply, please address a motivation letter together with a Curriculum Vitae to the contact. References from previous working position will be helpful.

Type of Contract: ANR project HYPERCAT, CDD

Expected start date: 1st October 2018

Proportion of work: full-time over 18 months

Remuneration: CNRS legal basis

Context of the study

Suzuki reactions are of increasing importance for organic synthesis representing ca. 10% of a 3 million patents in pharmaceuticals. Due to its impact, Akira Suzuki (with R. F. Heck and E.-I. Negishi) was awarded the 2010 Nobel Prize in Chemistry. Most of the researches dedicated to this reaction concern homogeneous catalysis, describing the discovery of new ligands allowing higher activity or selectivity. Except sporadic examples, no study relates the nature and concentration of the active Pd-species. Three forms of the catalytic species may exist or co-exist: true homogeneous, nanoparticles in solution, and true heterogeneous. For industrial applications, two options can be followed: find hyperactive species in solution that will not poison the products, or try to heterogenize Pd-catalysts on a solid surface and expect a heterogeneous mechanism.

In the project, the use of various Pd-catalysts (NPs or TMC, supports, size, ligands...) associated to appropriate reactors (fixed-bed + empty tube) and analyses (TEM, ETEM, ICP/MS, SAXS...) will allow to gain information about the nature of the active species in solution (complexes or NPs). The development of a model taking into account possible contribution of the solid catalyst and that of species in solution will clearly give an answer on whether a heterogeneous Suzuki coupling is possible or not.

To understand the nature of the active Pd-species in Suzuki reaction (mono-atomic, diatomic, colloids or NPs Pd-species...), and how to generate them from a palladium precursor, several molecular pre-catalysts (next to Pd NPs prepared by other partners) as homogeneous Pd-complexes or supported (grafted) Pd-complexes will be synthesized. The prepared materials will be evaluated in benchmark Suzuki reaction (i.e. iodo-acetophenone with phenyl-boronic acid). The generation of hyperactive species during the reaction will be evaluated under various operating conditions in two different reactors: a batch reactor, and a continuous compartmented reactor. Pd elemental analyses, coupled to the measured activity (TOF) will define whether a system is able to generate hyperactive species.

Activities

Pd-catalysts based on bidentate ligands, from which we expect more or less Pd decoordination, will be prepared and fully characterized by spectroscopic techniques (NMR and IR). As key step could rely on Pd-decoordination to generate in the bulk active species (mono-atomic Pd species to small Pd-particles), complexes based on P-P, P-N and N-N ligands (Figure 1) were selected. It is expected, an easy decoordination for P-P ligands to relative stable Pd-complexes using N-N ligands under the reaction conditions[1-3]. We believe that the rate of Pd-release in the bulk media can be, hopefully, controlled by the nature of the ligands. This area was little studied for the Suzuki reaction, compared to Heck cross-coupling. To get deeper insights on the way Pd could be released from these complexes, immobilization on metal-oxide supports like silica, titania or zirconia is planned. The selected ligands will be modified to ensure covalent anchoring by introducing alkoxysilyl for silica (and related) supports or alkoxyphosphonate, phosphonic acids or carboxylic acids moieties for titanium or zirconium oxides [4-7].

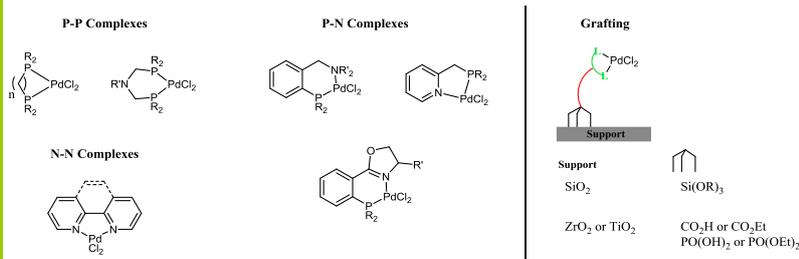


Figure 1: Representative synthesis of supported metallic NPs on silica using an organometallic precursor

complex, or grafting the final Pd-complex. The second approach presents the advantage of ensuring, after grafting, the integrity of the complexes by NMR analyses and avoiding adsorption of "free" palladium species onto the support.

The ligand modifications should be implemented during syntheses. With the modified ligands in hand, two approaches will be evaluated: grafting the ligand before preparing the corresponding Pd-

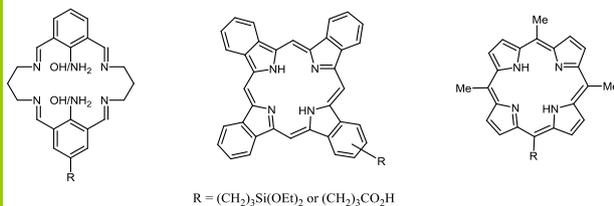


Figure 2: Examples of TAM ligands

For catch/release purposes, covalently grafted macrocyclic tetra-azo ligands (TAM) like porphyrin, phthalocyanines and other associated ligands (See Figure 2 for examples), known for providing Pd based catalysts with good to high activity, will be immobilized onto a support. Focus will be made on TAM ligands as we expect

interesting properties for catching and releasing from/in the reaction mixture dissolved active Pd-species. Like for Pd-complexes described above, these ligands will be modified to ensure covalent immobilization. Next to characterization by a set of spectroscopic techniques, UV-vis spectroscopy will be used when using TAM ligands to follow catch/release properties of Pd-species in solution.

Skills

The candidate should have a strong experience in organometallic synthesis of Transition-Metal complexes associated to good knowledge of associated characterization techniques. Experience in working under inert atmosphere will be highly appreciated.

Context

This research project will be conducted in CDFA team of IRCELYON. IRCELYON includes 5 research teams working in the area of clean and renewable energies, bioresources, air and water remediation, fossil energy, surface science, reactors and chemical engineering, and materials for catalysis (see <http://www.ircelyon.univ-lyon1.fr>). IRCELYON possesses its own internal scientific platform to perform chemical and textural characterizations of catalysts. CFDA team possess all equipment for analyzing reaction mixtures without requiring external services.

Constraints and risks

This work is a part of the larger ANR project HYPERCAT, developed in close collaboration with LGPC and C2P2 laboratories located in Lyon.

Regular meeting with the partner are expected, at least every 3 months.

Regular research reports (twice a year) should be delivered by the candidate.

Supplementary information

Application should be addressed by e-mail only.

Closing date for sending applications: 15/10/2018