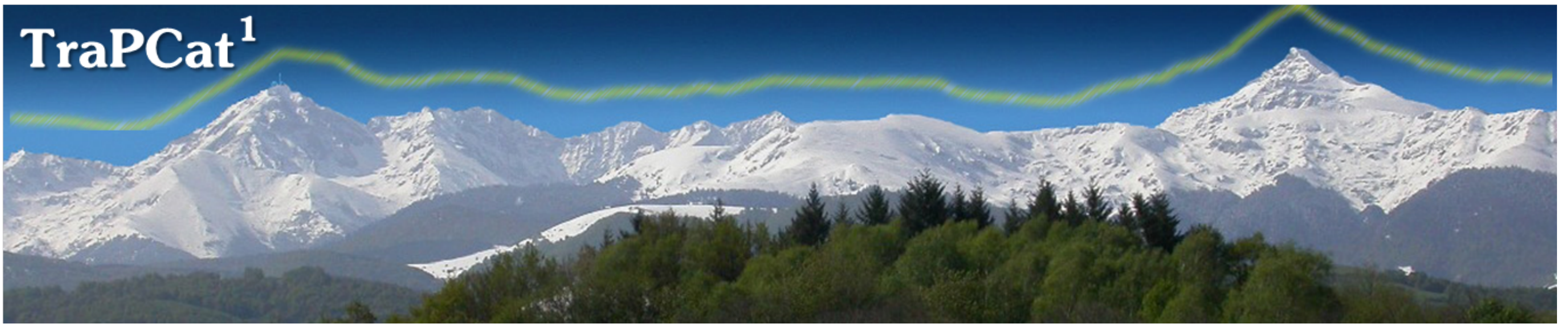

1st Trans Pyrenean Meeting in Catalysis

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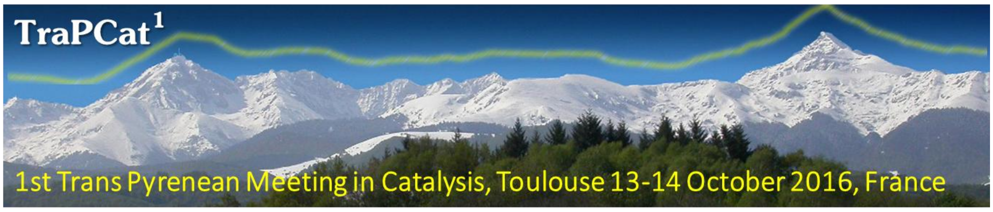

Pd-catalyzed Suzuki–Miyaura cross-coupling using a PdNPs-based catalytic membrane

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Catalytic membranes are of great interest since they act both as a separation layer and as catalyst. [1] Most studies have targeted inorganic membranes made from ceramic or metals that can operate at elevated temperatures and that are in general more resistant to harsh environments. However, for reactions under mild conditions, polymeric membranes present some advantages over inorganic membranes such as low cost, better transport mechanisms through the membranes due to their better diffusivity and solubility of the reactants. Concerning the catalyst, the choice of palladium nanoparticles PdNPs is based on the reaction conditions allowed by the polymeric membrane (temperature up to 150°C) and their proven efficacy on C-C coupling and selective double bound in hydrogenation reactions.

Metal nanoparticles tend to aggregate in the absence of stabilizing agents which leads to a loss of catalytic reactivity. To overcome the problem of aggregation of nanoparticles, we propose the use of polymers to stabilize them. [2] Polymers are interesting stabilizers due to the steric bulk of their framework as well as their role on the size control of nanoparticles.Our approach consists on modifying the surface of a polymeric membrane support via photo-induced radical polymerization of vinyl and acrylic monomers. The resulting grafted polymers allow the incorporation and stabilization of PdNPs by intermatrix synthesis.

Catalytic membranes with different grafted layer structure and nature have been successfully prepared using flat sheet membranes. Two model reactions have been tested: (i) Suzuki-Miyaura cross-coupling between 1-iodo-4-nitrobenzene and phenylboronic acid and (ii). reduction of p-nitrophenol to p-aminophenol in the presence of sodium borohydride. Reactions were carried out by filtering the solution containing the reactants through the catalytic membranes. 100% conversions and 100% selectivities for both reactions were achieved after short residence times (less than a minute). No leaching or deactivation of the PdNPs was detected after several runs. Experiments from present and previous works [3],[4], shown that catalytic membranes are much more efficient when compared to batch reactors or colloidal nanoparticle systems.

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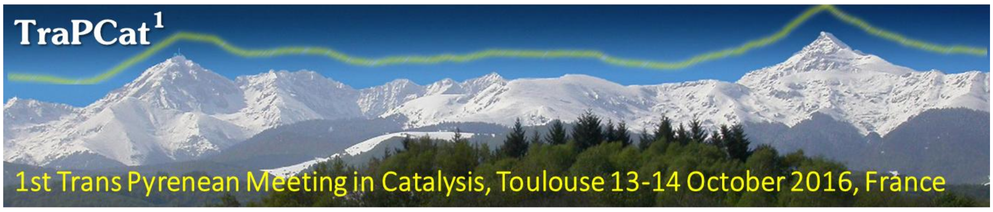

Measuring Which Ligand Does Best in Difficult C–C Couplings

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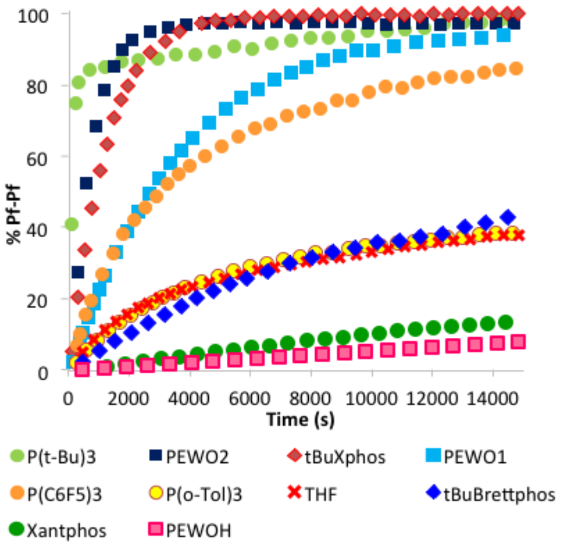
Reductive elimination is one of the most decisive step in Pd catalysed cross-coupling reactions because it is typically irreversible and this pulls forward the whole catalytic cycle.[1,2]Through several years valuable knowledge about reductive elimination have been developed mostly based on theoretical studies of the barriers for the different pathways it could take.[3,4] This work develops an experimental system to test ligand ability to promote difficult coupling processes.



A Pdcomplex,*cis*-[Pd(C_6F_5)$_2$(THF)$_2$],[5](**1**) is an excellent meter to easily evaluate the relative ability of different ligands to promote challenging couplings. It only requires monitoring the formation of the coupling product C_6F_5–C_6F_5 (**2**). Our protocol is useful to rank experimentally the ability of ligands to promote electronically difficult couplings as isolated from other steps; in addition, it happens to detect some side reactions.

Testing several common ligands used in Pd catalysis, this ability was ranked in the order P^{t}Bu$_3$> PEWO2 ≈ ^{t}BuXPhos>P(C_6F_5)$_3$ ≈ PEWO1 > P(*o*-Tol)$_3$ ≈ THF>>Xantphos ≈ PEWOH >> PPh$_3$ according to the coupling initial rates, whereas their efficiency in the long term is ranked ^{t}BuXPhos ≈ PtBu$_3$ ≈ PEWO2 > PEWO1 > P(C_6F_5)$_3$>> THF ≈ P(*o*-Tol)$_3$>Xantphos> PEWOH >> PPh$_3$.

The scale of relative $\Delta G^{\ddagger}$(Pf-Pf) values is hoped to help to the understanding of problems associated to difficult couplings. Other ligands may be incorporated in the future.

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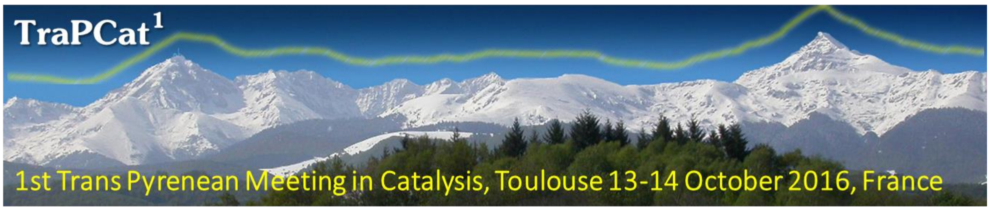

Activation of BH_3 by Phosphorus-Stabilized Geminal Dianions and Catalytic Reduction of CO_2

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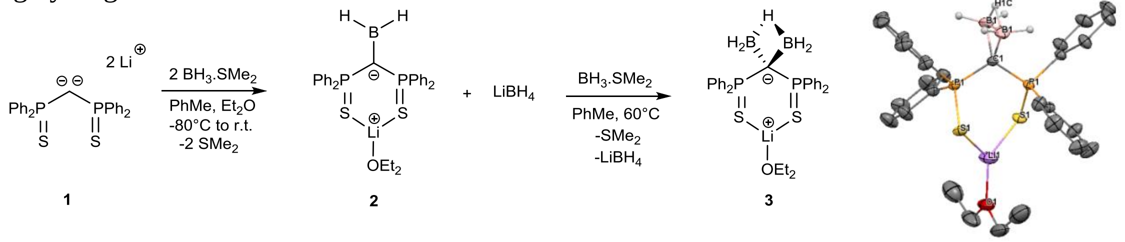
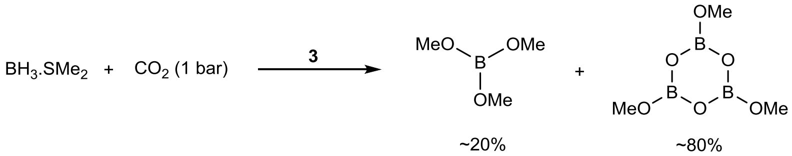
In the past years, geminal dianions stabilized by P(V) moieties have been particularly studied,[1] mainly for their use as precursors of carbenes complexes.[2,3] Indeed, the carbon center possesses two lone pairs which allow a double donation to metals *via* double σ + π interaction. The question was then asked: can the same double donation occur with main group elements? And if so, what would be the nature of the resulting bond.

Geminal dianion **1** was reacted with 2 equivalents of $BH_3.SMe_2$ to form a new compound **2** and $LiBH_4$. The crystal structure of **2** reveals a short C-B bond, consistent with a multiple bond character. This product further reacted with one equivalent of $BH_3.SMe_2$ to generate the diborane compound **3**. DFT calculations showed the dianionic moiety enhances the hydridic character of non-bridging hydrogens.



The use of CO_2 as a C1 carbon source for the production of fuels or chemicals has gained considerable interest in recent years.[4] However, this process is hampered by the high thermodynamic and kinetic stability of CO_2. A catalytic approach is then particularly attractive in order to achieve its reduction to formic acid and/or methanol under mild conditions.

Because of the strong hydridic character of the non-bridging hydrogens and the potential of forming geminal B-C bonds, we studied the activity of compound **3** in the catalytic hydroboration of CO_2, focusing on the use of $BH_3.SMe_2$ as reductant. Our system was found to be one of the most efficient catalyst for this transformation (TON up to 2799).[5]



The full account of this study will be presented.

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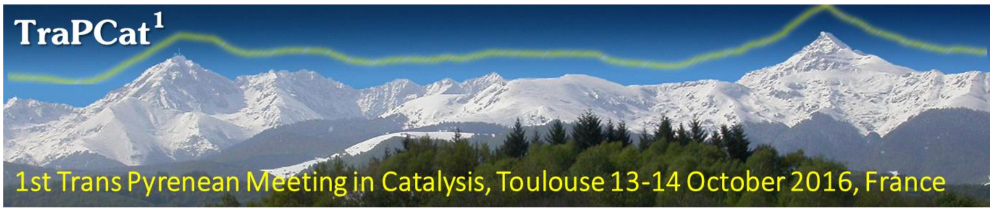

Iron based nanoparticles for the magnetically induced hydrogenation of carbon dioxide to methane

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To limit global warming and decrease the carbon footprint in the energy mix, electricity is increasingly produced from intermittent renewable resources. As a result, large scale and long term energy storage is required to face the unavoidable variations in electricity production. From this perspective, the chemical storage of energy through the Sabatier reaction (power to gas) is especially promising.

Our group recently evidenced the interest of magnetic induction to thermally activate suitable heterogeneous catalysts[1]. We present here the hydrogenation of CO_2 catalyzed by iron based nanoparticles through magnetically induced heating. The challenge of synthesizing nano-objects displaying both catalytic activity and appropriate magnetic properties was taken up by designing specific iron carbide nanoparticles. Based on an organometallic approach[2], the synthesis developed gives access to highly monodisperse and finely tunable iron carbide nanoparticles[3]. The size, carbon content and crystallographic organization of the NPs were proven to be critical parameters to obtain high specific absorption rates (SAR). In optimal conditions, SAR as high as 3000 W/g were measured (100 kHz, 47.4 mT). To our knowledge, this value is by far the highest ever reported for such mild conditions.

Subjected to an alternating magnetic field in a dedicated flow reactor, suitable iron carbide nanoparticles were proven to be catalytically active for the hydrogenation of CO_2 to hydrocarbons (Fig. 1). Interestingly, the catalytic activity of iron carbide nanoparticles can be tuned by functionalizing the NPs surface with different metals such as nickel and ruthenium.

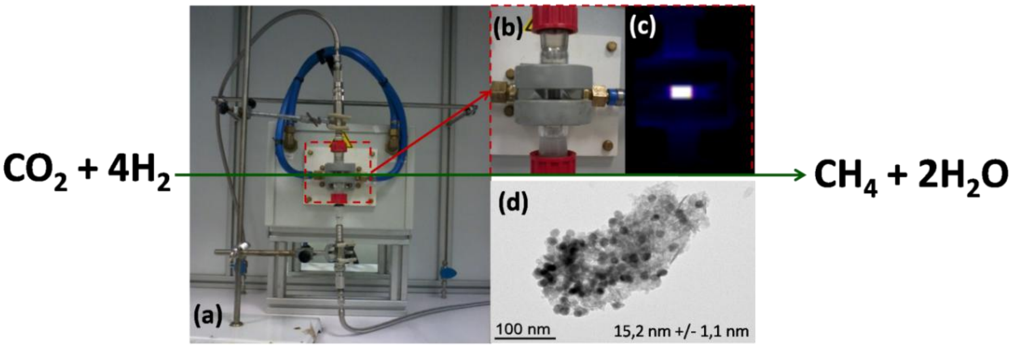

Figure 1: CO_2 hydrogenation set-up. a: Global view of the device constituted of a magnetic inductor and a flow reactor; b: Zoom on the part [coil + reactor containing the catalyst]; c: Thermal image ; d: TEM image of the supported catalyst.

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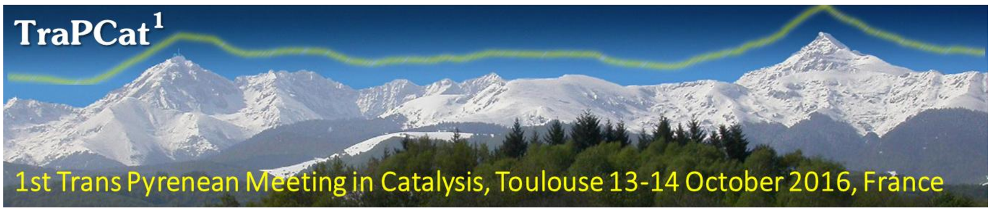

Investigating the surface sites active in nucleophilic addition on CO_2 from structure-activity relationships on pure ZrO_2 catalysts

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In the strategy to reduce CO_2 emission, the EU particularly promotes the Carbon Capture from the industrial exhausts. This capture will provide a huge stock of cheap, concentrated CO_2, which could be advantageously used as C1 building block, once we meet the scientific challenge of the CO_2 activation.

In this project, we focus on understanding the heterogeneous catalysis of the nucleophilic addition (A_N) of alcohols on CO_2. In the literature, the reaction intermediates were evidenced with IR spectroscopy[1,2] but the catalytic mechanism is still unclear. Our strategy aims at describing the active site from structure-activity relations built with a model system, the A_N of methanol on CO_2 catalyzed with pure zirconia, which produces dimethyl carbonate (DMC): $2\ MeOH + CO_2 = (OMe)_2CO + H_2O$

This study presents the synthesis, the characterization and the catalytic performances of pure zirconia catalysts with an unusual range of morphologies and catalytic activities. Beyond the classical techniques of post-synthesis characterization, we specifically probed the distribution of acido-basic surface sites (FTIR-probe molecules, methylbutynol [MBOH] model reaction[3]).To build our catalysts panel, we synthesized zirconia samples with three methods: classical precipitation (P), sol-gel (SG) route and an original synthesis from metallic alginate gels (algi).

The panel of ZrO_2 catalysts exhibits various specific surface areas and two crystal phases in varying proportions (Fig 1.a). With the *in-situ* IR spectroscopy, we investigated the adsorption structures at the catalyst surface for both reactants of the A_N reaction (CO_2 and methanol). With the catalytic MBOH reaction (Fig 1.b), we evidenced various distributions of acido-basic catalytic sites in our catalyst panel: basic, amphoteric, and acidic sites converted MBOH into distinct products with selectivities depending on the ratio of sites available on the surface. The catalytic performances in DMC synthesis will be discussed from those advanced characterization results so that we can propose original structure-activity relationships.

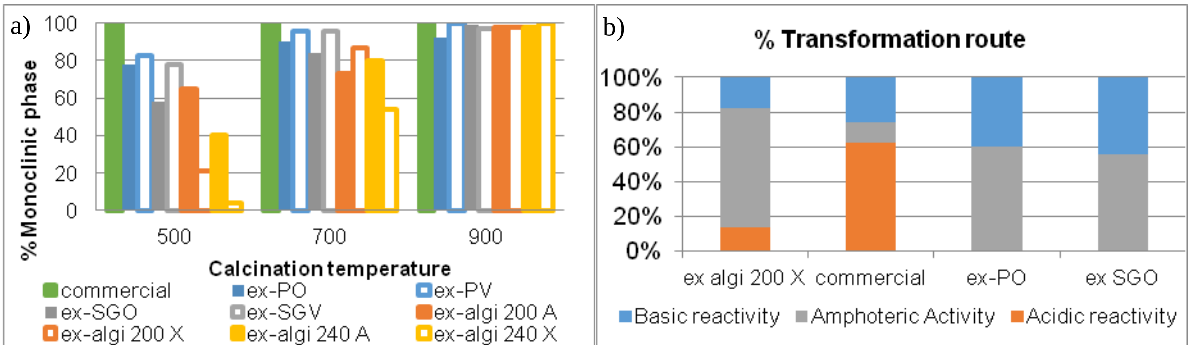

Figure 1. Influence of the synthesis route on the ZrO_2 physicochemical properties: a) Proportion of monoclinic phase in the ZrO_2 crystalline domains as a function of the drying method (oven, vacuum, aerogel, xerogel) and the calcinations temperature b) Acido-basic catalytic reactivities from the MBOH model reaction at 200°C for ZrO_2 calcined at 700°C.

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Efficient conversion of CO_2 to oxazolidinones with Indenediide Palladium Pincer Complexes

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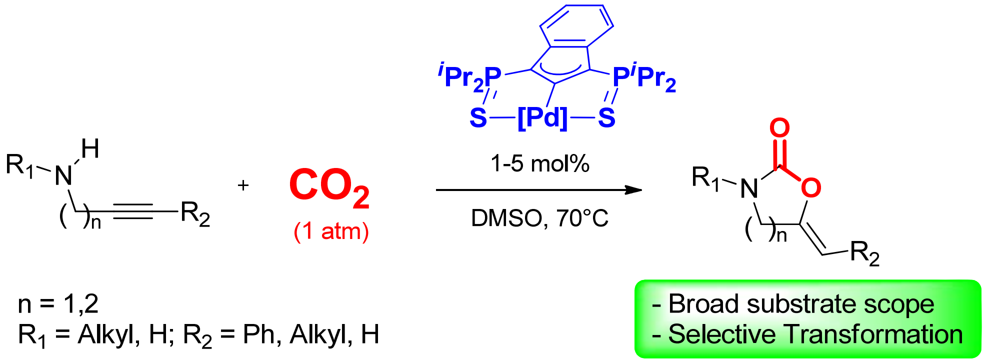
Since the pioneering work of Shvo and Noyori, impressive developments have been achieved in metal-ligand cooperative catalysis. Over the last two decades, spectacular progress has been achieved in this field using pincer complexes. In particular, the group of Milstein discovered an original aromatization/dearomatization process in pyridine-based pincer complexes.[1]

Recently, we described original indenediide Pd(II) pincer complexes (see figure) combining an electrophilic Pd center and an electron-rich ligand backbone.[2] The non-innocent character of the indenediide ligand has been applied in the catalytic intramolecular addition of carboxylic acids/amides to alkynes in absence of external base.[3] We have also demonstrated that the association with an organic proton shuttle could, namely catechol, enhance significantly the activity and selectivity of these pincer complexes.[4]

Encouraged by these results, we are currently seeking to expand the applications of these complexes to other valuable transformations. We have become interested on the use of CO_2 as C1 building block, and in particular on the construction of the oxazolidone motif via the cyclization of carbamic acids resulting from the fixation of CO_2 to alkynylamines. The results obtained show that the indenediide Pd(II) pincer complexes perform very efficiently, with a broad scope of substrates in terms of alkyne substitution, class of amine and ring-size.



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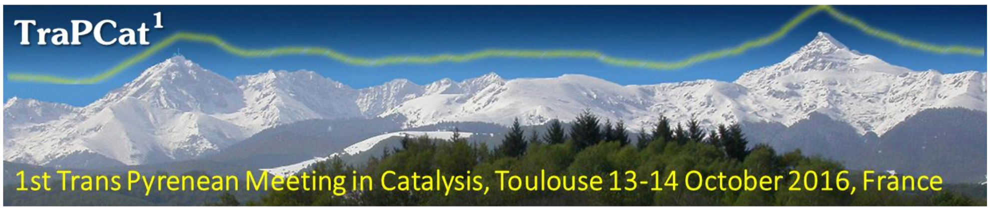

Synthesis of Ru-based nanoparticles as catalysts for energy related transformations

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Keywords: *water oxidation, ruthenium nanoparticles, immobilization*

Molecular hydrogen is a promising candidate for replacing fossil fuels as energy sources. However, its renewable and clean generation is still a great challenge. A particularly attractive solution is the production of this gas from water splitting (WS) by sunlight as driving force (Figure 1, right).[1] Therefore, an enormous progress has been recently made on the development of catalysts to speed up the involved semi-reactions; the oxidation of water to O_2 (WOC) and the reduction of protons to H_2 (PRC).

The decomposition of homogeneous species into heterogeneous systems of non-controlled size, composition and reactivity, is a common phenomenon in catalysis.[2] Particularly, several examples of *in situ* formed oxides and colloidal species acting as rugged, low-overpotential WOCs and PRCs have been recently reported.[3] However, the factors controlling their efficiency are still not rationally understood.

In this context, a family of Ru and RuO_2 NPs of different sizes stabilized by pyridine-based ligands, has been prepared by means of the organometallic approach (Figure 1, left),[4] and their WO activity when dispersed in aqueous solution or immobilized into ligand functionalized carbon-based supports have been analyzed.

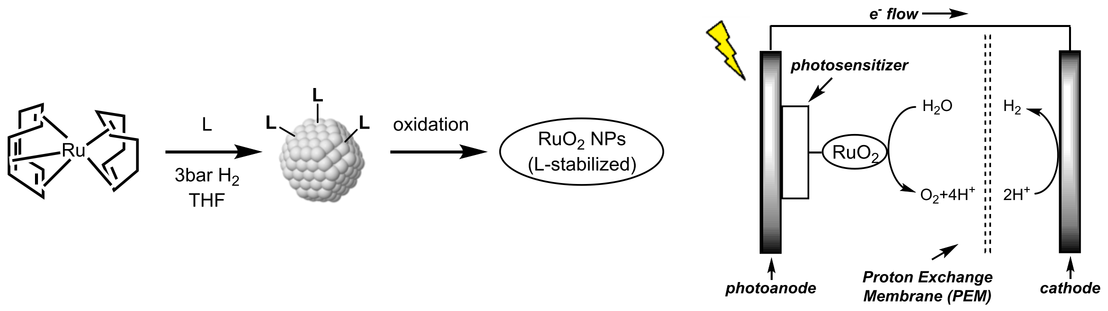

Figure 1. Left, synthesis of RuO_2 NPs by the organometallic approach; right, basic photoelectrochemical cell type with RuO_2 NPs as WOC.

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Selective catalytic hydrogenation of nitrobenzene over Ru@C_{60} nanocatalyst

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Carbon based materials have attracted much interest in heterogeneous catalysis.[1] Fullerene, among these carbon materials, have unique properties that make it as a promising unit for the construction of assemblies with metal nanoparticles. In the past decades, many researches have disclosed the preparation of transition metal fullerides that provide much possibility of metal nanoparticles and fullerene C_{60} self-assembly.[2] However, it is still a big challenge to synthesize defined metal@C_{60} nanostructures and to characterize them. Recently, Ru@C_{60} nanostructures decorated with small Ru nanoparticles (~1.5 nm) have been synthesized by decomposition of [Ru(COD)(COT)] (COD= 1, 5 cyclooctadiene, COT= 1, 3, 5-cyclooctatriene) in the presence of fullerene C_{60} under dihydrogen in our group (Figure 1). Several techniques (TEM in high resolution, scanning and electron tomography modes, IR, NMR, Raman, WAXS, EXAFS and XPS) together with theoretical calculations allowed us to have an insight into the structure of these Ru/C_{60} nanomaterials. Notably, significant charge transfer from ruthenium to fullerene has been evidenced by Raman spectrometry, XPS and DFT.

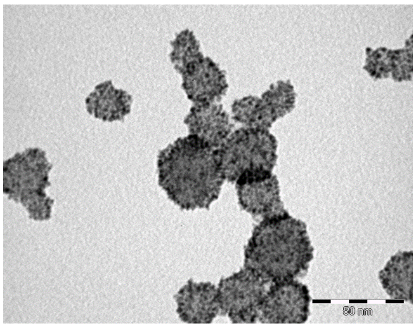
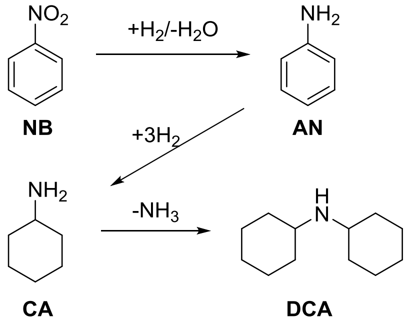


Figure 1: TEM image of Ru/C_{60} =10/1, scale bar 50nm



Scheme 1: Hydrogenation of nitrobenzene

It was found that the charge transfer from Ru to C_{60} in these Ru@C_{60} nanostrucures, can be attributed to strong electron accepting capability of C_{60}. The electrophilic character of Ru in these nanostructures can be interesting for catalytic reactivity. Our Ru@C_{60} nanocatalyst was studied in the chemoselective hydrogenation of nitrobenzene (Scheme 1).The use of electron deficient ruthenium nanoparticles supported on Ru fulleride nanospheres allows the successive and chemoselective hydrogenation of nitrobenzene(**NB**) first to aniline(**AN**) and then to cyclohexylamine(**CA**). DFT calculations allow to rationalize the stepwise hydrogenation, showing that -NO_2 group strongly interacts with the ruthenium surface under hydrogenation conditions.

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Influence of the Stabilizing Ligands in Ruthenium Nanoparticle Catalysis

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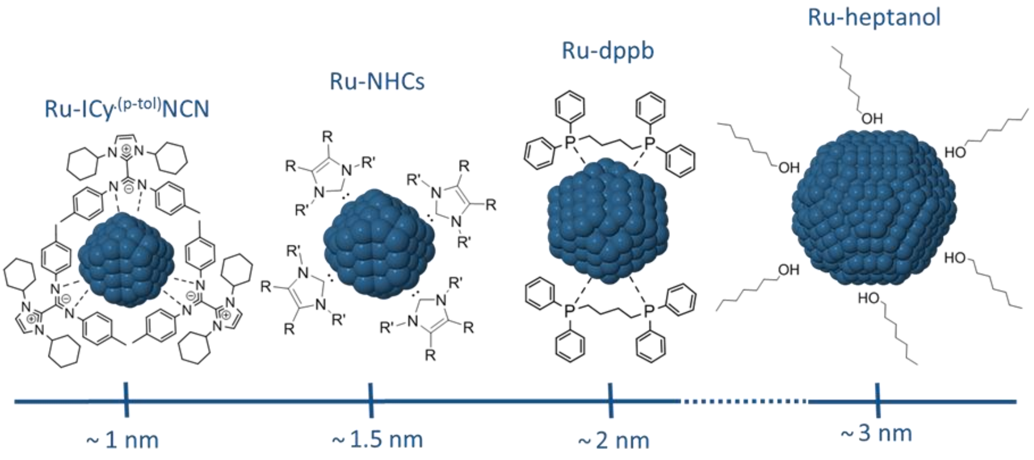
The interest of well-defined metal nanoparticles (MNPs) as catalysts has grown during the last twenty years, with applications in many catalytic processes, such as hydrogenation, oxidation, polymerization or C-C coupling reactions.[1] The great potential of MNPs in catalysis stems from their particular electronic configuration and high number of active sites, thus combining the benefits of homogeneous and heterogeneous catalysts.

After the first synthesis of polyvinylpyrrolidone-stabilized ruthenium NPs (Ru-PVP) in the early 90's using an organometallic approach,[2] this method has become very popular for the preparation of RuNPs.Apart from being a versatile metal in catalysis, ruthenium is able to coordinate to many types of ligands, such as alcohols, amines, phosphines, N-heterocyclic carbenes (NHCs) and amidinates forming part of betaines,whichallows us to study the influence of these ligands on the size and the activity of the resulting NPs (Figure 1).[3] For example, the amidinate formed by adding an NHC to a carbodiimide ($ICy^{\cdot(p\text{-}tol)}NCN$) is a very efficient ligand for the preparation of ultra-small RuNPs (~ 1 nm), which present a size selectivity for styrene hydrogenation.[4] Moreover, RuNPs stabilized by non-isolable chiral NHCs,synthesized through a new procedure, present interesting differences in selectivity in hydrogenation reactions.[5] Lastly, long-chain NHC-stabilized RuNPs are versatile catalysts for both oxidation and hydrogenation reactionsthat can even be performed successively in a one-pot fashion.[6] In the present communication we will analyze the effect of the ligands in the nanoparticle reactivity.



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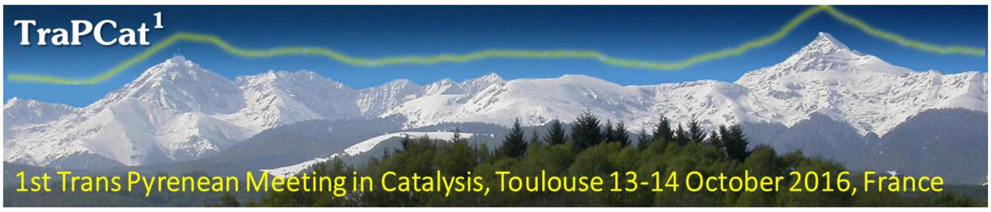

Supported lanthanide catalysts: Role of the grafting on the stereochemical outcome of different polymerization reactions.

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In the context of the research of low cost and environmentally benign catalytic systems, development of highly active and selective catalysts is of prime importance. From an industrial point of view, heterogeneous processes are advantageous because of the facile separation of the final products from the catalysts and the easy recycling of these catalysts. Moreover, the easier solid–liquid separation reduces the solvent consumption, which is in agreement with the constant demand for greener chemical processes. In the case of homogeneous catalysts, every entity can act as a single active site. This makes homogeneous catalysts more active and selective compared to heterogeneous catalysts. Therefore, a catalytic system, which takes the advantages of both homogeneous and heterogeneous catalysis, would greatly enhance the interest for industrial applications. One possibility to achieve this type of catalytic system is the use of supported catalysts.

Among the metals applied within the field of supported catalysis, rare-earth systems have been the subject of constant interest due to their high activity in several fields, such as in polymerization[1] and fine chemistry[2]. In this oral presentation we would like demonstrated through a theoretical/experimental approach that support effects can be used to change the stereochemical outcome of different polymerization reactions. Thus, we will try to shed light on the origin of the influence of catalyst grafting in different selective processes such as the β-butyrolactone ring opening polymerization or Methyl methacrylate polymerization mediated by supported lanthanide catalysts.

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Water Oxidation Catalysts based on Earth Abundant Metals

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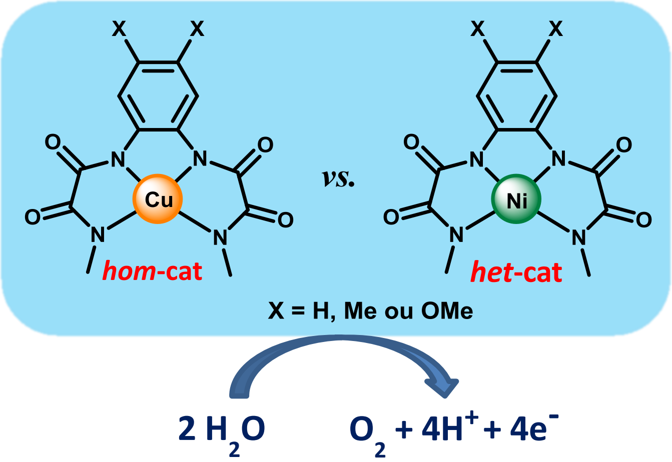
Water oxidation is a high energy process, involving a $4e^-/4H^+$ transfer. Recently, many efforts have been done in finding water oxidation catalysts (WOC) for lowering the overpotential, with higher stability.[1] However, the use of efficient catalysts based on earth abundant and cheap metals is required for potential application.[2]

First of all, in this work, we have explored the use of oxidatively rugged but redox active ligands to develop copper catalyst. Within this strategy, the ligand is capable of being oxidize and that could yield to active species avoiding high oxidation state in the metal center. As the electron-donating capacity at the aromatic ring increases, we observed a drastic decrease of the overpotential to a record low of 170 mV.

Later on, these ligands were combined with nickel to lead to a series of Ni(II) complexes. Theses complexes have shown to act as precursors for the formation of catalytic active film for water oxidation. This film has been deposited either by applying an anodic potential or by successive cyclic voltamogramms. The potential of electrodeposition was dependent on the chemical nature of the substituents. However, the resulting films characterized as nickel oxide have shown comparable activity for water oxidation catalysis independently of the Ni complexes precursors used.



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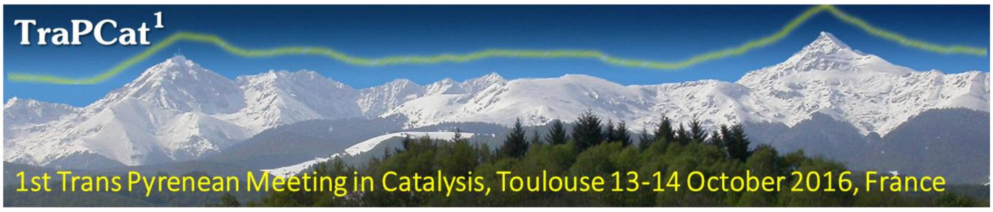

Development of a novel catalytic monolith reactor for three-phase hydrogenation reactions: from catalyst formulation to pilot scale reactor experimentation & modelling

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This study lies within the framework of the ‘Hydromore ANR’ project, which aims at developing innovative catalytic reactorsinspired from monolith technology and integrating*in situ* heat removal system. The proof of concept is made on the total hydrogenation of a bio-sourced olefin, alpha-pinene, and includes the development of an efficientcatalytic coating, the investigation of the reaction kinetics, the assessment of the proposed reactor design at pilot scale and its scale-up through multiscale and multiphysics modelling.

First part of the work was dedicated to catalyst screening, selection of the monolithmaterial (Al, Cu, Ni), mesoporous support (SiO_2, Al_2O_3, TiO_2), active metal type (Pd, Pt), precursor and content (0.5-3 wt%), as well as of the synthesis procedure on deposit anchoring, catalytic activity and stability upon recycling.The catalytic layers were prepared by dip-coating inaqueous colloidal dispersions, addition of metallic precursor in the sol-gel suspension or its impregnation onto preformed porous layer, and heat activation treatment. The catalytic tests were operated in a batch stirred autoclave reactor using either small coated platelets or powdered catalyst.Initial reaction rates were calculated from instantaneous gas consumption in a ballast tank feeding the reactor in H_2at constant pressure,and assessed through GC/FID analysis of liquid samples. Pd/$Al_2O_3$was found as the most promising catalyst as it yielded a well adherent deposit of 5-10 µm thickness on aluminum alloy processed by selective laser melting and its initial activity was proved to be four times as high as that of a commercial egg-shell catalyst due to high metal dispersion (Pd nanoparticles of ca. 1 nm).Strong deactivation wasalso prevented by a convenient treatment of the terpene oil.

The kinetic study performed with the powdered catalyst showed good reproducibility, expected first order behaviour with respect to the catalyst weight (i.e. no external mass transfer limitations) and activation energy of ca. 40 kJ/mol.

Based on these promising results, jacketed aluminium tubes of 2 mm internal diameter and 20 cm height were coated with the selected catalyst, leading to a 10 to 30 µm thick layer. Their activity was assessed on a continuous hydrogenation set-up operatinginthe Taylor flow regime. Pinene conversion was found stable after several hours of operation, reaching 10% at 20 bar and 140°C and 25% when temperature was increased to 160°C. This differential mode of operation allowed evaluating the extent of mass transfer limitations in the catalytic channel by comparison to autoclave reactor tests. Thissingle capillary configuration enabled a good control of fluid distribution and heat transfer, so that the reactor behaviour should be conveniently modelled through a unit cell approach (gas bubble surrounded by a liquid film and separated by two liquid half-slugs)accounting for hydrodynamics, gas-liquid and liquid-solid mass transfer and complex reaction kinetics.

The perspective of the work includes the comparison of the single tube experimental database to simulations made with COMSOL Multiphysics and the extension to a heat-exchanger monolith reactor comprising 84 parallel channels.

Iron(II) Catalyzed Hydrophosphination of Isocyanates

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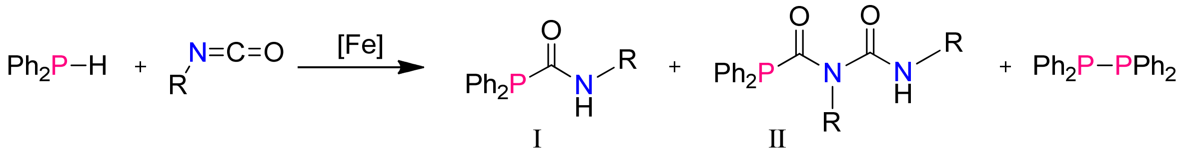
Organophosphorus compounds are a versatile class of chemicals which play key roles in organocatalysis, as ligands for transition metal complexes and as building blocks for medicinal and supramolecular chemistry.[1] Therefore, there has been a growing demand in the development of atom-economical routes for the preparation of functionalized phosphines. In particular, hydrophosphination is an attractive reaction which proceeds *via* P–H bond addition across a C–C/X (X = O, N, S) multiple bond.[2] However, this reaction can be synthetically challenging as a result of the coordination capability of both the starting phosphines and the resulting functionalized phosphines which can poison the catalyst. In addition most hydrophosphination catalysts contain precious metals with scarce availability and high toxicity.[2] Consequently there is a paramount necessity for the development of more sustainable methods with more economical and environmentally friendly metals such as iron.

In this context, we will show the first transition metal catalyzed hydrophosphination of isocyanates. For the catalyst we focus our attention on two- and three-coordinate Fe(II) *m*-terphenyl complexes due to the limited number of low-coordinate metal complexes in catalytic transformations.[3]



Furthermore, we have found that the reaction between organic isocyanates and diphenylphosphine produces phosphino carboxamides (I) as well as the unprecedented derivatives (II), where two isocyanates have inserted into the P–H bond. This result is rather surprising due to the absence in the literature of catalytic transformations for this new family of functionalized phosphines. This result can give us mechanistic insight into catalytic transformations with low-coordinate highly encumbered iron species.

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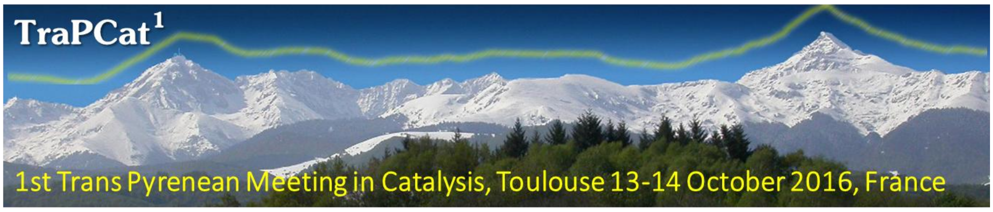

C-H functionalization of benzylthioethers catalyzed by Ru/Cu derivatives: synthetic scope and mechanistic possibilities

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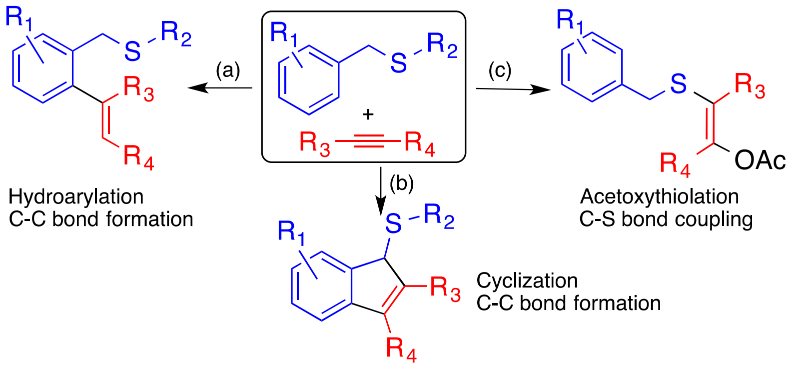
The site-selective activation of C-H bonds promoted by transition metals is currently one of the most powerful tools for the tailored building of complex organic molecules [1]. The selectivity required by the reaction is sometimes achieved according to electronic or steric biases. However, when two or more positions are very similar and their discrimination is not possible, the use of directing groups provides a general solution [2]. Due to this fact hundreds of directing groups are known, almost all of them based on N- and O-bonding atoms. In clear contrast the use of S-directing groups is scarce, in spite of the interest of many S-containing molecules, due to problems related with the deactivation of the catalysts after S-bonding.

In this contribution we show that the use of S-directing groups in Ru/Cu catalysis is perfectly compatible. We have studied the coupling of benzylthioethers with internal alkynes, and we found a highly versatile process. By fine tuning of the reaction conditions we have observed either the hydroarylation of the alkyne (only one C-H bond activation, path a) or the oxidative coupling of the arene and the alkyne (double C-H bond activation, path b) affording indene derivatives. On the other hand, when benzylmercaptane is used as starting material, the selective acetoxythiolation of the alkyne is observed (path c).

All these results have been rationalized on the basis of the respective reactions mechanisms, which have been fully determined by DFT methods.



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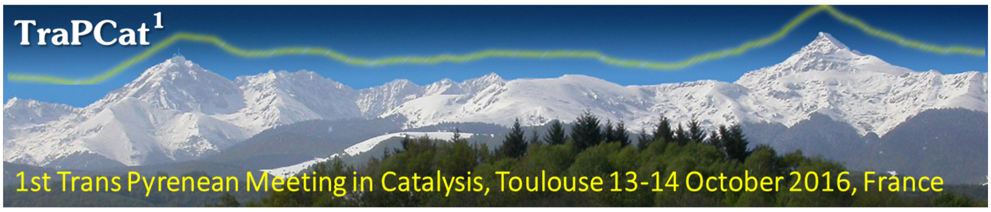

Terminal Ni(II) Azolate Complexes with Frustrated Lewis Pair-Type Reactivity: Some Applications in Catalysis

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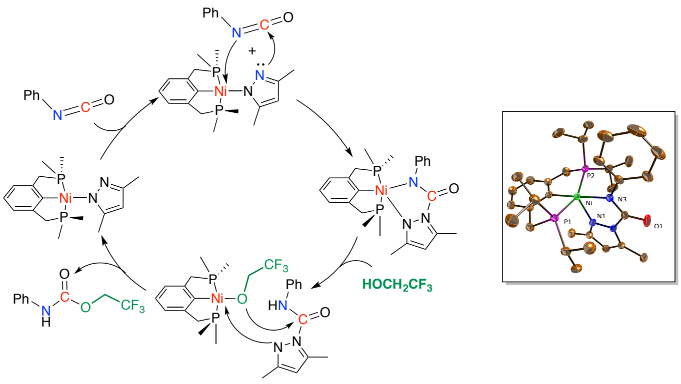
In this contribution we describe Ni(II) complexes containing pyrazolate ligands coordinated in terminal fashion through one of the nitrogen atoms, while the second is allowed to remain free and potentially reactive. In order to stabilize the monodentate coordination, the Ni(II) atom is confined in a PCP pincer scaffold. The key feature of these complexes is the presence of the basic N centre in the neighbourhood of the square-planar Ni(II) centre, which retains a residual Lewis acidity, at a distance comparable to the size of a chemical bond. This gives rise to a peculiar reactivity, reminiscent to that of frustrated Lewis pairs.[1] For example, such complexes add to unsaturated molecules such as heterocumulenes or activated alkynes, and can cleave C-O bonds of esters.

Whilst the original FLP concept involved metal-free systems, its application to transition metal-based systems is increasingly attracting attention.[2] Most of these organometallic FLP involve highly reactive zirconocene complexes. In contrast, the pincer Ni(II) complexes are thermally very robust and tolerant to the open atmosphere, which considerably facilitate their application in Catalysis. An example is the activation of phenylisocyanate for the addition of fluorinated alcohols of low nucleophilicity, shown in the Scheme.



Scheme 1.

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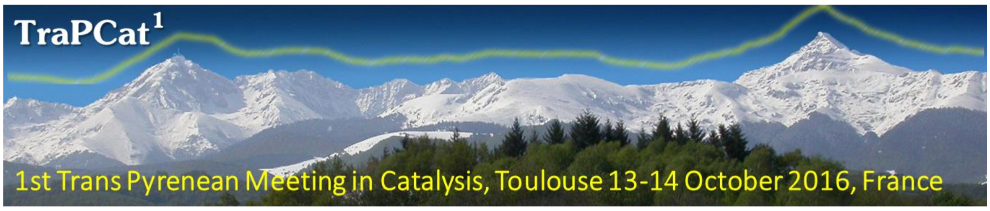

Assessing structure property relationships of biosourced dextrans.

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Due to their limited carbon footprint, polysaccharide-based materials are attractive alternatives to fossil carbon based polymers. However, their mechanical properties are still insufficient for most non-food uses. In order to explore their potential for applications as bioplastics, we have carried out the synthesis of a panel of α-glucans with different macromolecular structures, by using a battery of wild-type and engineered α-transglycosylases from the family 70 of Glycoside Hydrolases (CAZy GH70 ; http://www.cazy.org ; Lombard *et al.,* 2014). The use of enzymes for the *in vitro* synthesis of biosourced polymers indeed offers a better control of reaction conditions and consequently of product structure, compared to microbial synthesis. In order to investigate the relationships between the structure and the properties of such polymers, new dextrans with various molar masses and controlled architecture (α (1 → 2) or α (1 → 3) branched dextrans) were synthesized using both dextransucrases and branching enzymes. The macromolecular characteristics, crystalline structure, and thermal and mechanical properties of these new biopolymers have been studied compared to those of commercial dextrans. Macromolecular structures and particle size were determined using Asymmetrical flow field flow fractionation (AF4) coupled with multi-angle laser-light scattering (MALLS). Dextrans films were prepared by casting and mechanical properties were determined using a humidity-controlled dynamic mechanical analysis. The film crystallinity was determined by wide-angle X-ray scattering (WAXS). The physico-chemical properties were shown to be dependent on the molar mass, the type and the degree of branching. In particular, the mechanical properties of these polysaccharides, especially the storage modulus, are governed by specific structural characteristics. These results open new perspectives for the design of bio-based materials with plastic properties.

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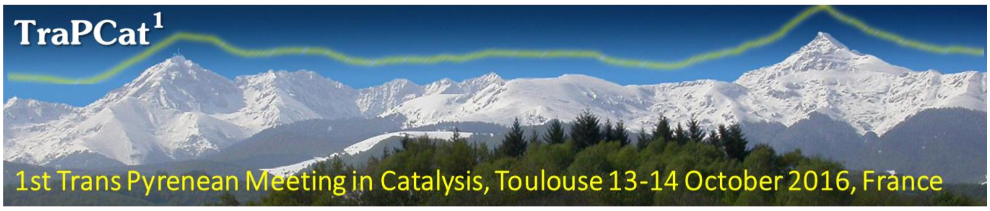

A trip toward light-switchable catalysis

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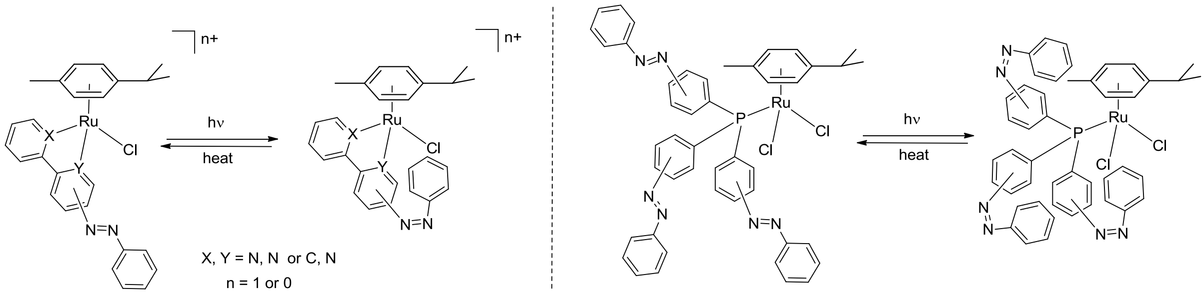
The development of photo-responsive compounds has become an intensive area of research in recent years. They are intended for the production of “smart chemical systems”, whose properties and/or functionality are sensitive to changes of the environment (light irradiation). Surprisingly, in spite of their importance and versatility, smart photo-responsive organometallics remain rather unexplored in comparison with their organic counterparts. One of the most evident strategies to construct photo-responsive metal complexes is the incorporation of organic photochromic units in the structure of their ligands. These photo-sensitive ligands, rather than acting as conventional spectators that tune the properties of their complexes, transform them into dynamic smart entities able to offer a functional response to an external stimulus. Certainly, one of the most challenging areas of application of such foto-sensitive organometallic systems would be the development of photo-switchable catalysts.

Driven by the importance of cyclometalated phenylpyridyl (ppy) and bipyridyl (bipy), and phosphine ligands in the construction of organometallic complexes, we developed a series of photochromic ppy,[1] bipy[2] and phosphine[3] ligands, that contain appended azobenzene fragments. In this communication, the synthesis, and photochromic behaviour of some of their Ru(II) and Ir(III) derivatives, as well as our efforts towards the development of photoswitchable catalysts will be presented.



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Buttressing Effect in N-Heterocyclic Carbenes: Formation of Highly Efficient Pd-Catalysts for the Buchwald-Hartwig Amination

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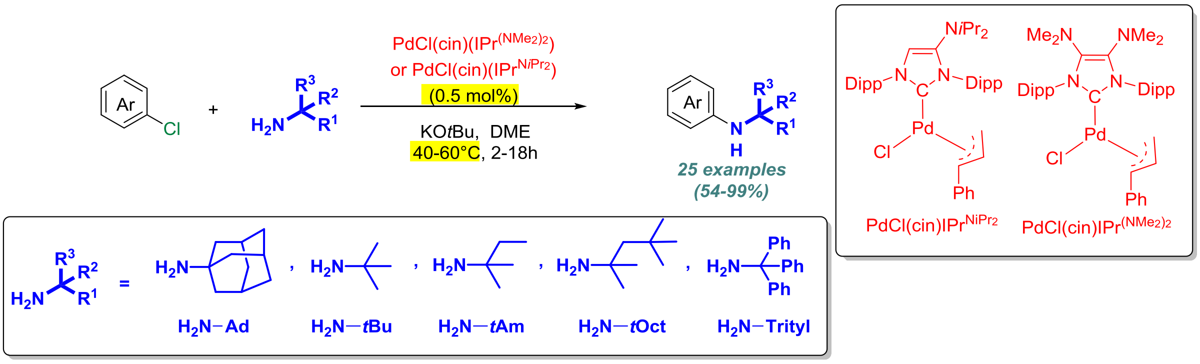
N-heterocyclic carbenes (NHCs) have gained considerable significance as ubiquitous ligands for the design of a variety of highly efficient transition-metal pre-catalysts.[1] Their intrinsic interest is both due to their high steric bulk, mainly determined by the nature of nitrogen wingtips, and their strong electronic donor properties.[2] Focusing on the benchmark example of the 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene ligand, IPr, exhibiting a known efficiency in Pd-catalyzed cross-coupling reactions,[3] we present herein a complete study on the optimization of the catalytic efficiency of Pd-NHC catalysts by incorporating dialkylamino and/or halogen groups on the backbone of the carbenic heterocycle, and provide evidences that those substituents exert a 'Buttress effect' on the NHC ligands leading to some of the very most efficient pre-catalysts for the Pd-catalyzed Buchwald-Hartwig amination reaction, in terms of catalyst activity and stability and scope of substrates.[4,5]

As illustrative example, this strategy allowed the highly challenging coupling of aryl chlorides with bulky primary amines under mild conditions (see figure).[5,6]



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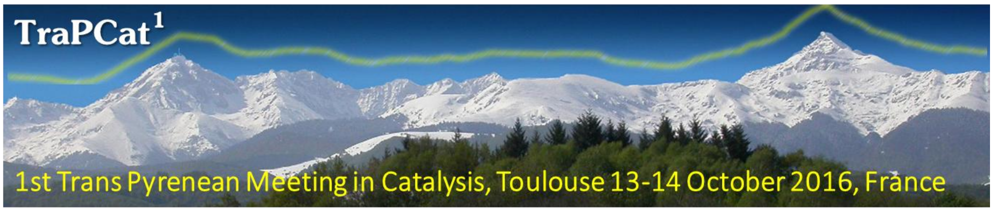

Palladium-Catalyzed Asymmetric Heck Reaction Using Chiral P,N-Ligand Library.

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Catalytic asymmetric carbon–carbon bond formation is one of the main objectives in modern synthetic organic chemistry. It is requiered in the synthesis of natural products, pharmaceuticals, and functional materials. One way to achieve the C-C bond is the asymmetric Pd-catalyzed intermolecular Heck coupling of an aryl or alkenyl halide or triflate to alkenes, a reaction known to be very versatile due to its high tolerance of functional groups.[1]

Plenty of chiral bidentate phosphine ligands have been applied for intramolecular Heck reactions as well as oxazoline-phosphine ligands.[2] However, the intermolecular version has been less studied. There are therefore few examples of diphosphine and phosphine-oxazoline ligands that provide high regio- and enantioselectivities, being the low reaction rates and the low substrate versatility are common limitations for all of them.

Our group discovered that introducing a biaryl phosphite moiety in the ligand design is advantageous, overcoming the common limitations for the intermolecular Heck reaction. Thus, the use of phosphite-oxazoline ligands provided excellent activities (because of the greater π-acceptor ability of phosphite rather than phosphine) and regio- and enantioselectivities in the palladium Heck coupling of different substrates and triflate sources.[3] In this communication, we will present the successful application of new phosphite-oxazoline ligands in the Pd-catalyzed asymmetric intermolecular Heck reaction of several substrates and triflate sources.

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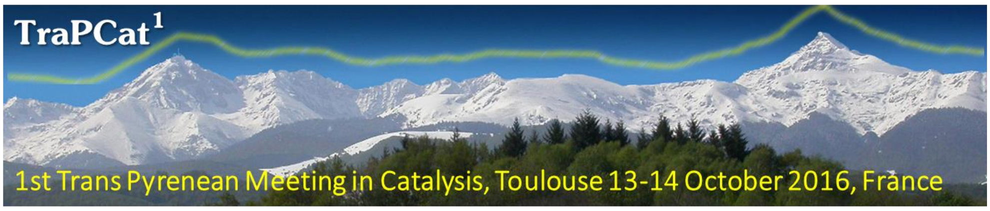

Catalytically Active Water-Soluble Palladium Nanoparticles Stabilized by Coordination of N-Heterocyclic Carbene Ligands to Their Surface, Evidenced by Knight Shift in Solid State NMR

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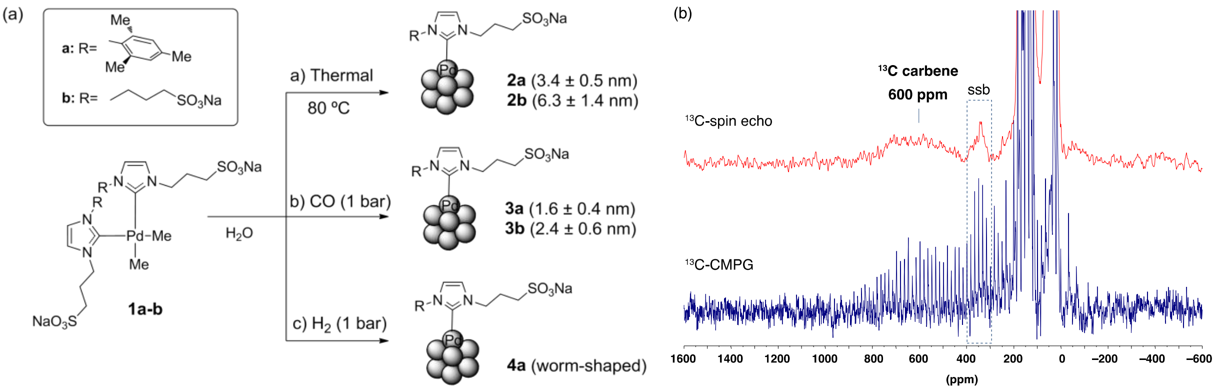
Metallic nanoparticles (MNPs) dispersed in aqueous media are interesting for their different applications in catalysis, including green catalysis.[1] Understanding of the surface estabilization of the MNPs is essential for the comprehension of their catalytic activity. In recent years, some examples of water-soluble MNPs stabilized with NHCs directly coordinated to the surface have been reported.[2]

In this work, we report the synthesis of water-soluble PdNPs with different shapes and sizes, that were obtained by thermal decomposition or reduction with CO or H_2 of dimethyl NHC Pd(II) complexes. NMR studies in solution helped to elucidate the organometallic intermediates and organic decomposition products involved in the reduction of the Pd(II) precursors. The sizes of the NPs are dependent of the organometallic precursor and the synthetic method employed (Figure a). For nanoparticles containing ^{13}C-labeled NHC ligands, the resonance of the carbene carbon was located at 600 ppm as a consequence of Knight shift (Figure b). Knight shifts are characteristic of large MNPs that display bands in their electronic structure.[3] In addition to metal nuclei, the ^{13}C NMR resonances of surface-adsorbed molecules can also be Knight shifted due to the mixing of their molecular orbitals with metal conduction bands. Their observation is therefore an evidence of the coordination of the NHC ligand to the surface of the nanoparticle. Despite the coordination of the NHC ligands, which gave a high stability of the systems in water, the surface of the PdNPs was still accessible for catalysis, as we successfully tested the NPs as recyclable catalysts for the chemoselective hydrogenation of styrene.



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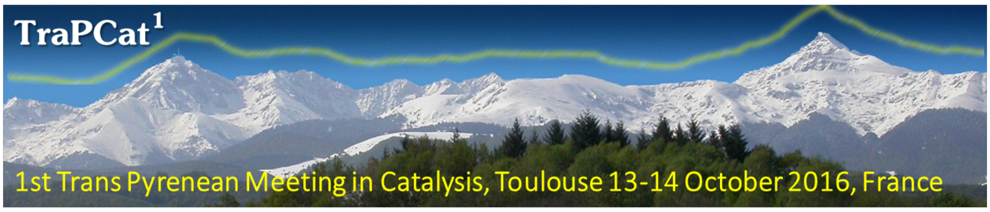

ACIDIC AND METAL-DOPED ZEOLITES - GREEN CATALYSTS FOR ORGANIC SYNTHESIS

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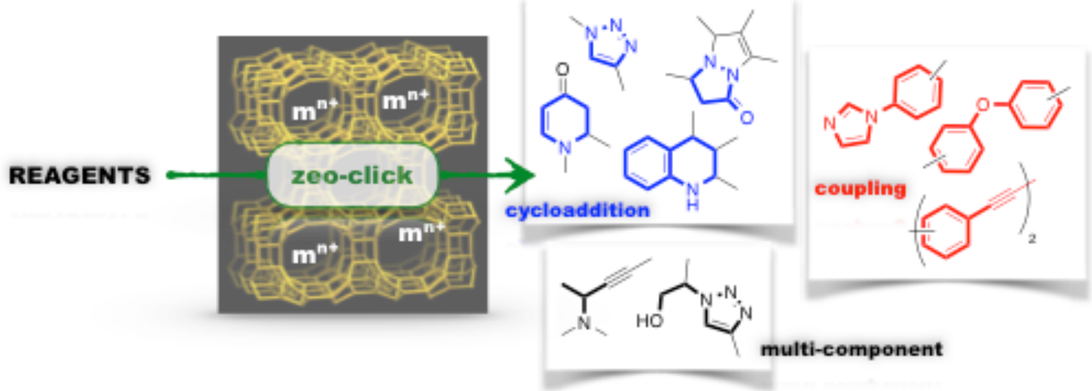
Homogeneous catalysis, notably with the advent of transition metal catalysis, led to remarkable progress and spectacular achievements in organic synthesis.[1] However, within the 'Green Chemistry' context,[2] the replacement of standard homogeneous catalysts by heterogeneous alternatives has become in the last decade a major challenge in industry and academia.[3]

Within this context of "greening" organic synthesis, we are looking for precisely new classes of heterogeneous catalysts fulfilling the following criteria i) easy-to-prepare, easy-to-handle, easy-to-recover and if possible recyclable, ii) fit for use to generate relevant organic compounds quickly and reliably by joining appropriate units together, iii) fit for the broadest possible palette of organic reactions without the need for additional reagents (*ie,* ligand, additive, …).

Acidic zeolites as well as metal-doped zeolites **m**-zeo, combining the properties of zeolites (heterogeneous solid support, size and shape selectivities) with those of metal ions known for their properties in homogeneous catalysis, proved to fulfill all targeted criteria. Depending on the nature of the cation (**m** = proton or transition metal), zeolitic materials were thus shown to promote various archetypal organic transformations, from cycloaddition reactions (*ie,* Huisgen, Dorn and Diels-Alder reactions),[4] through coupling reactions (*ie,* Glaser, Chan-Lam and Ullmann-type reactions)[5] to multi-component reactions[6]. Overall, the simplicity of use and the broad scope of applications of such catalysts enabled us to introduce the "zeo-click" heterogeneous approach.[7]

If this proposal of oral communication is received favorably, we wish to report on representative results featuring the relevance of these catalysts for organic synthesis.



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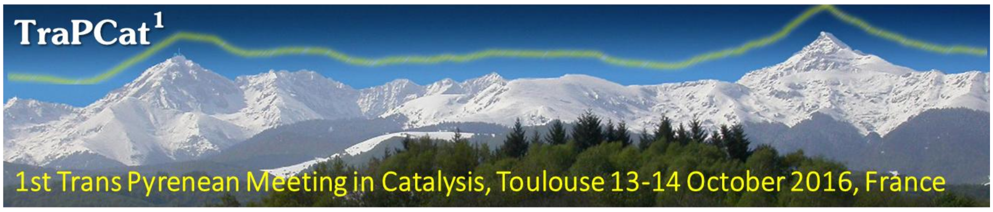

P,X chiral ferrocenyl ligands grafted on inorganic supports: synthesis, characterization and preliminary catalytic results

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Our group has developed various chiral PO[1], PN[2], PS[3] or P(NHC)[4] ferrocenyl phosphines for asymmetric catalysis (hydrogenation, allylic substitution, Suzuki-Miyaura coupling,…).[5] PS ligands, for example, have demonstrated good efficiency in asymmetric hydrogenation (Figure 1).

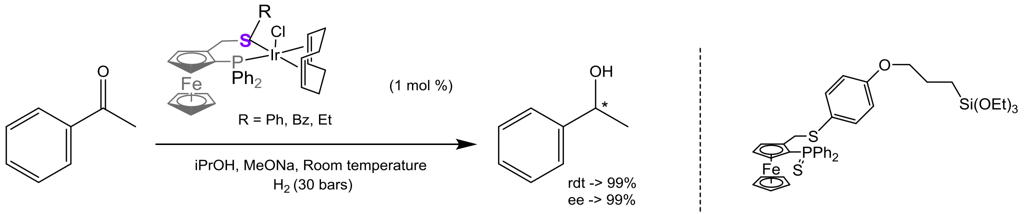

Figure 1: a) homogéneous asymmetric hydrogenation with PS ferrocenic ligand (left). b) functionalized chiral PS ferrocenyl ligand for immobilization on solide support (right).

We are now investigating the heterogenization of these catalytic systems by grafting functionalized PX ferrocenyl ligand on inorganic support, such as hydroxyapatite [6] (HAP) which is a new support or mesoporous MCM41. The synthesis and characterization of the functionalized ligands, their grafting and the preliminary catalytic results with the new catalytic materials, in particular in asymmetric hydrogenation reactions, will be presented.

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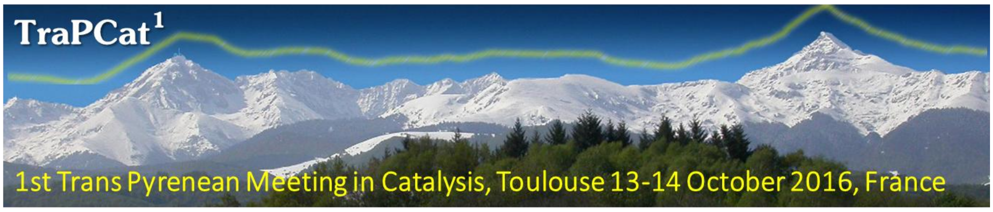

Study of model cobalt catalysts for Fischer Tropsch

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Fischer–Tropsch synthesis (FTS) is a technically proven and economically viable route for the conversion of coal, biomass, and natural gas to hydrocarbon fuels. This process attracts a lot of attention as the petroleum resources are decreasing. Even though this process is known since 1923, the reaction mechanism and the deactivation process are still unclear. [1] Cobalt is currently one of the best adapted metals for this reaction since it presents an optimal trade-off between price and catalytic performance. The crystal structure (*fcc*or *hcp*) seems to play a role on the catalyst performances. [2] In addition, Co catalysts typically lose about half their activity within a few months, so the definition of highly stable Co catalyst is of paramount importance. [3]

The controlled decomposition of an organometallic cobalt precursor in the presence of stabilizing agents allows the synthesis of size and shape controlled Co nano-objects in solution. Furthermore, cobalt nano-objects can be epitaxially grown by the same solution chemistry approach directly on metal surfaces. [4] Based on these results, we have developed an innovative catalyst by cobalt heterogeneous overgrowth on pre-existing Co nanoparticles of a conventional Fischer-Tropsch catalyst. Our method allows the growth of Co nanowires, of *hcp* structure, which starts from several nucleation sites of the surface of the pre-existing Co *fcc* nanoparticles leading to urchin-like shaped cobalt nano-objects embedded in the porosity of a silica-alumina support (Fig. 1). [5]

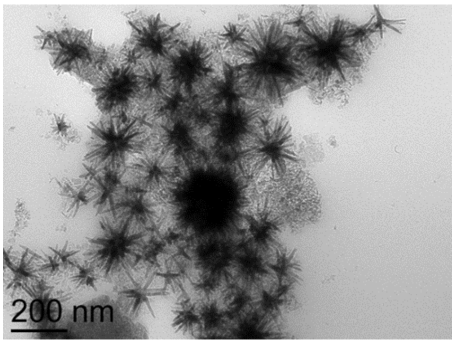

Fig. 1. TEM picture of urchain-shaped cobalt embedded in a silica alumina support model

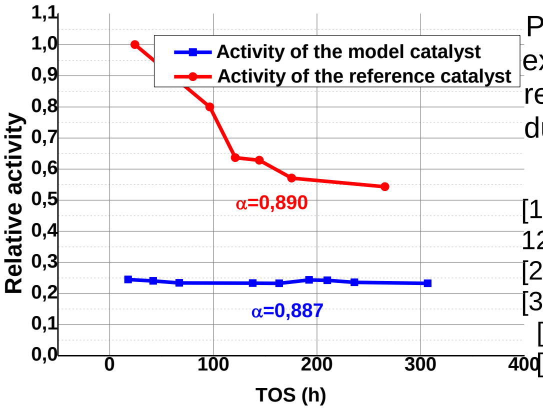

Fig. 2. FTS slurry catalytic test of the model catalyst compared to a reference catalyst

Preliminary catalytic results show that this catalyst exhibits a very high stability (Fig. 2) compared to a reference catalyst with the same loading of cobalt during a 300 hours run.

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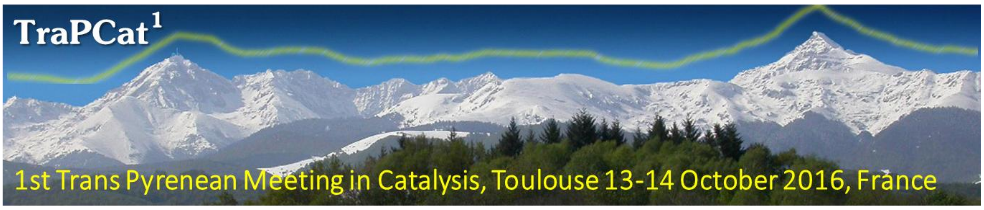

Photocatalytic H_2 production from ethanol$_{(aq)}$ solutions over Pt/anatase TiO_2: the effect of by-products in the H_2 production rate

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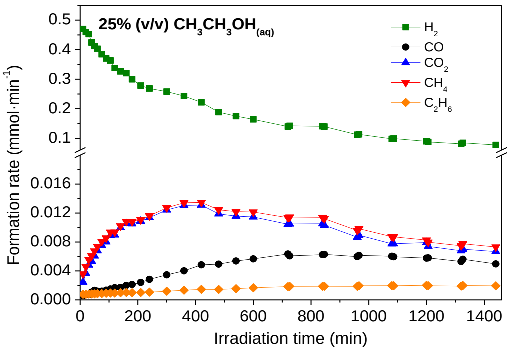
The use of fossil feedstock for H_2 production could be diminished by the use of biomass-derived sources. In this context, the photocatalytic H_2 production from bio-ethanol is of particular interest. However, the oxidation of ethanol proceeds by successive steps and several C-containing products can be obtained. We have studied the influence of morphological and structural characteristics of TiO_2 and Pt/TiO_2 catalysts in the degradation and photoreforming of ethanol$_{(aq)}$[1]. Besides H_2, different amounts of intermediate oxidized products such as acetaldehyde, acetic acid and 2,3-butanediol among others were obtained. Here we report the study of photocatalytic transformation of these main by-products in order to better understand the reaction pathways for the photocatalytic formation of H_2 and oxygenate-derived compounds over Pt/anatase TiO_2 catalysts. The effect of ethanol and acetaldehyde concentration in the formation rate of H_2 is analyzed. Moreover, the photocatalytic transformation of other by-products is studied. Characterization of the fresh, used, and reduced photocatalyst was carried out using CO chemisorption followed by DRIFTS.



The Figure shows the rate of formation of gaseous products over Pt/anatase TiO_2 as a function of the irradiation time. High H_2/CO_x ratios were obtained when the photocatalytic transformation of ethanol$_{(aq)}$ solutions were carried out over Pt/anatase TiO_2. The main pathways were the dehydrogenation of ethanol to acetaldehyde and the coupling of two α-hydroxyethyl radicals forming 2,3-butanediol; the later is favored by the increase of ethanol concentration. The presence of partially oxidized products in the reaction medium, acetaldehyde, 2,3-butanediol and acetic acid produced a decrease of the H_2 formation rate. From acetaldehyde, a main reaction pathway is its decomposition to CH_4 and CO. The photoirradiation of an acetic acid$_{(aq)}$ solution mainly leads to its decomposition forming CO_2 and CH_4. Ethanol is produced by photoirradiation of acetaldehyde and 2,3-butanediol aqueous solutions over the Pt/anatase TiO_2. The DRIFTS results indicate that under photoreaction, Pt species are reduced and CO could compete with other adsorbates for coordination on Pt^0 centres.

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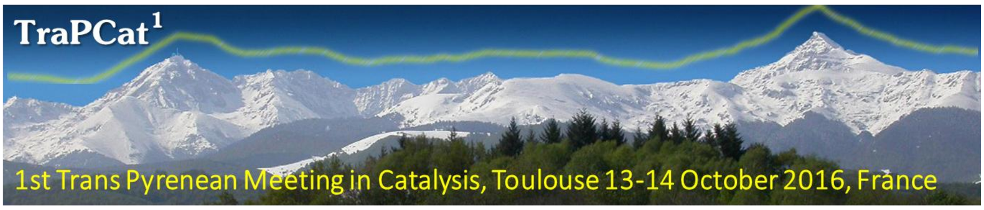

Multicomponent CuZnO-based catalysts for H_2 production from methanol steam reforming. The effect of Ga_2O_3, Al_2O_3 and ZrO_2

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The addition of different components to CuZnO-based catalysts can improve the catalytic performance of the systems in the hydrogenation of CO_2 to methanol. We have recently reported $CuZnOGa_2O_3$ catalysts in which the intimate association between highly dispersed copper species and strong basic sites on ZnO in the presence of small Ga_2O_3 particles is related with their performance in the methanol production from CO_2/H_2[1]. We have also recently demonstrated that the catalytic behavior of Cu/ZnO in the methanol steam reforming (MSR) process for the production of hydrogen can be improved by the addition of Ga_2O_3[2]. In the present work, we study the effect of the presence Al_2O_3 and ZrO_2 in $CuOZnOGa_2O_3$ catalysts for the MSR process. For this end, $CuOZnOGa_2O_3M_xO_y$ (M=Al, Zr), $CuOZnOGa_2O_3$ and CuOZnO catalysts were prepared by a sol-gel method using aqueous solutions of nitrate salts and ethylenidiamine and tetraaceticethylendiamine acid. The samples were dried and calcined at 500 ºC.

Fresh catalysts were characterized using XRD, Raman spectroscopy, N_2 physisorption, N_2O chemisorption, TPR and CO_2 adsorption followed by TG-calorimetry. The catalytic behavior of calcined catalysts in the MSR was studied at atmospheric pressure in the temperature range of 275-240 °C, under GHSV in the range of 2,200-4,400 h^{-1} with molar ratio water/methanol=1.

The BET surface area of calcined samples was in the order: $CuOZnO<CuOZnOGa_2O_3<CuOZnOGa_2O_3M_xO_y$ (M=Al, Zr). The Cu dispersion (D_{Cu}) of the multicomponent catalysts was always higher than that of CuZn and ZrO_2-containing catalysts showed higher D_{Cu} than $CuOZnOGa_2O_3Al_2O_3$. Moreover, the presence of ZrO_2 favours the reducibility of CuO and increase the CO_2 adsorption capacity. In all cases, H_2 and CO_2 were the main products of the MSR, the H_2/CO_2 ratio obtained was close to 3. The characterization of post-reaction catalysts showed that under MSR conditions CuO was reduced to Cu.

The high performance of $CuOZnOGa_2O_3ZrO_2$ catalysts were related with their characteristics. $CuOZnOGa_2O_3ZrO_2$ produced a higher amount of H_2 that the other catalysts. Raman spectroscopy and TPO experiments did not allow detect carbonaceous deposits on $CuOZnOGa_2O_3ZrO_2$ after reaction.

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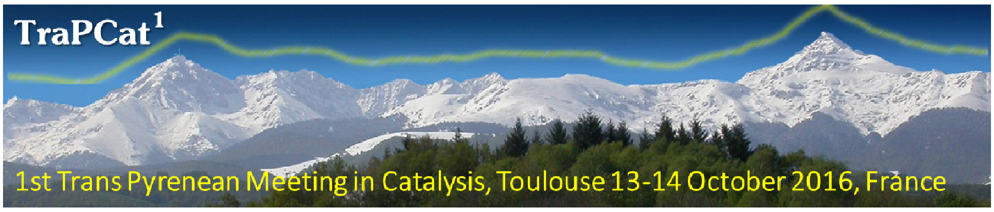

Ethylene to propylene by one-pot catalytic cascade reactions

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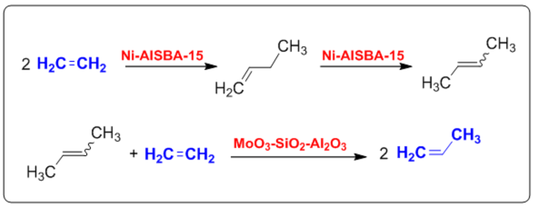
In this study we propose an original method for converting ethylene to propylene involving cascade reactions, using two robust and highly active heterogeneous catalysts developed in our Institute [1-3]. In a single flow reactor and under identical conditions, ethylene was first selectively dimerized/isomerized over a Ni-based catalyst to form 2-butenes, which reacted then with the excess of ethylene over a Mo-based catalyst to produce propylene (Scheme 1). Two consecutive catalyst beds consisting of Ni-AlSBA-15 (Si/Al = 7; 2.6 wt% Ni) and MoO_3–SiO_2–Al_2O_3 (Si/Al = 14; 6.5 wt% Mo) respectively, were placed in the reactor. The following parameters were chosen for conducting the dimerization-metathesis reactions: T = 80 °C and p = 3.0 MPa. WHSV was 16.5 h^{-1} for the oligomerization catalyst (0.15 g) and 5 h^{-1} for the metathesis catalyst (0.50 g).



Scheme 1. Ethylene to propene by cascade reactions

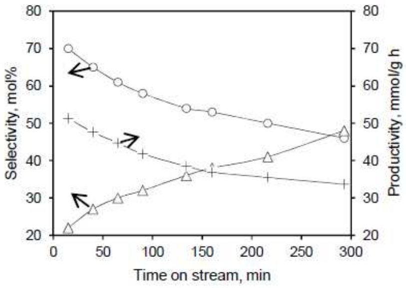


Figure 1. Selectivity to propylene (o), butenes (Δ) and productivity in propylene (+)

In the presence of the two catalysts, beside C4, C6 and C8 olefins, propylene, pentenes and heptenes were also formed. The selectivity to C3 and C4 was > 90% and the selectivity profiles as a function of time on stream are given in Figure 1. The selectivity to propylene decreased progressively from 70 to 46 % over the first 5 h on stream. The selectivity to butenes increased from 22 to 48 %. The conversion of ethylene was of 40±2% throughout the reaction period. The productivity in propylene is also reported in Figure 1. Although it decreased from 51.3 to 33.7 mmol g^{-1} h^{-1} with the time on stream, these values are remarkably high.

For the conversion of ethylene to propylene we proposed a general mechanism consisting in three catalytic cycles: the first one is based on coordination chemistry on Ni sites (dimerization of ethylene to form 1-butene), the second one is based on acid catalysis (double bond isomerization, to form 2-butenes) and the third one (cross-metathesis) occurs over the Mo sites, according to a Chauvin mechanism [2].

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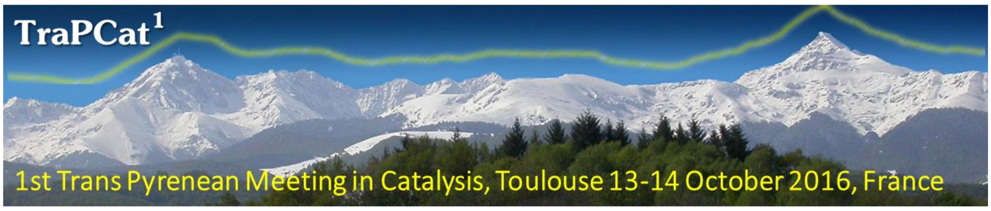

Few layer graphene/carbon nanotube hybrids produced using oxide spinel catalysts

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Graphene is an extremely versatile 2D material for nanotechnology applications due to its excellent physical and chemical properties. Hybrids based on graphene take advantage of these properties to create functional 3D materials by anchoring other nanomaterials on graphene. Among the different additives, carbon nanotubes (CNTs) are among the most studied. The high aspect ratio in combination with electrical conductivity and mechanical properties implies that they can function as an effective connector material between the graphene sheets creating 3D nanostructures with improved functional properties. Indeed, synergy has already been reported between CNTs and graphene or few-layered graphene (FLG) for application in energy, catalysis, and electronics [1]. Due to their chemical similarity, there is a significant interaction between CNTs and graphene, which means that the properties of the hybrid depend significantly on the preparation method including the assembling technique used. Catalytic chemical vapour deposition (CVD) preparation of CNT-FLG hybrids consists of mixing catalysts that separately produce FLG or CNTs [2]. Here, we report a single step preparation of CNT/FLG hybrid materials by a fluidized bed CVD process using a single catalyst, an Al-doped cobalt ferrite oxide powder.

Different $Al_xCo_{1-x}Fe_2O_4$ (x = 0.025–0.10) catalysts were prepared using the citrate-nitrate gel combustion method. CVD synthesis was carried out at 650°C in a horizontal fixed bed reactor using ethylene as the carbon precursor. The yield of the reaction was calculated by the parameter $\xi = g_{hybrid}/g_{cat.}$. The samples were characterized by TEM, XRD, Raman spectroscopy, TGA, and N_2 adsorption-desorption measurements.

Al doping of the cobalt ferrite in the 0.01–0.025 mol range led to the formation of a uniform hybrid, wherein both the FLG thickness and the CNT diameter could be controlled by changing the reaction conditions. Only FLG was obtained when $CoFe_2O_4$ was used as catalyst. However, the introduction of even small amounts of Al to this catalyst induced the production of CNTs. For catalysts with higher Al content (e.g. $AlCoFeO_4$), CNTs were selectively produced. Hence, there is a small window ($Al_xCo_{1-x}Fe_2O_4$, x < 0.05), where both CNTs and FLG can be obtained using a single catalyst. BET surface areas of these hybrids increased with increasing CNT content. X-ray diffractograms indicated that d_{002} for the hybrid was different from that for FLG or CNT, indicating a close contact between both constituents of the hybrid. Hence, the materials reported in this study could be a useful steppingstone for the single catalyst-based preparation of CNT/FLG hybrid materials.

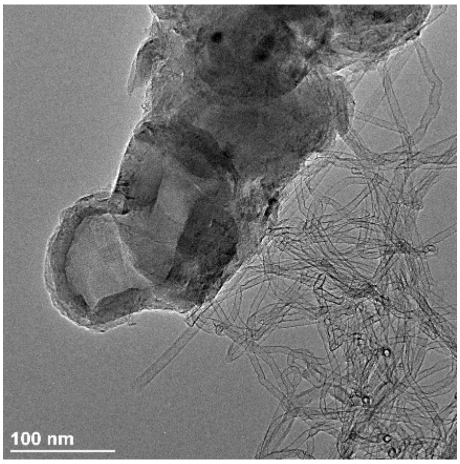

Figure 1. TEM micrograph of the hybrid material obtained with $Al_{0.025}Co_{0.975}Fe_2O_4$.

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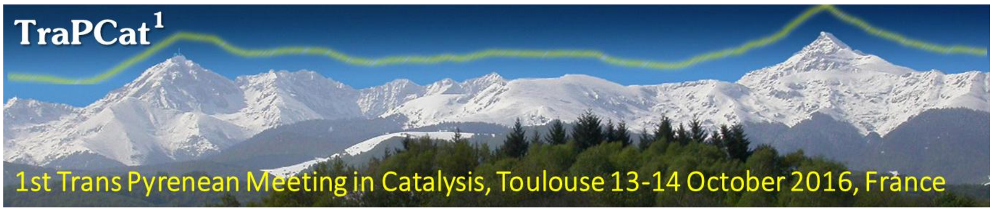

Regeneration of coked catalysts by an oxidation process using ozone

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Approximately 80% of industrial processes currently use heterogeneous catalysts because of their various advantages. However, their major drawback is deactivation which can occur over variable time scales (from seconds to several years). This phenomenon can be generated by several mechanisms[1]: poisoning (chemisorption of impurities or by-products on active sites), fouling (carbon or coke deposition which blocks the porosity) and/or degradation (chemical, physical or mechanical). Our work focuses on the regeneration of a zeolite catalyst from industry which is generally deactivated by fouling with coke deposition[2].

The most common process to remove coke is combustion, generally carried out with air or oxygen under severe conditions (400°C - 600°C). The aim of our work is to study the possibility of replacing this high energy consuming process by an oxidation process with milder conditions[3,4]. Thus, first studies were run with coked zeolite extrudates. Their regeneration was achieved by oxidation with ozone at low temperatures, between 50°C and 200°C. The effects of temperature, time on stream and inlet concentration of ozone on carbon removal efficiency were studied. Moreover, experiments have been led using air or pure dioxygen to produce ozone. Thanks to elementary analysis, it has been possible to calculate the carbon removal on the coked zeolites and then determine the efficiency of the process. It has also been shown that by-products containing nitrogen could remain on the regenerated catalyst when air is used to produce ozone.BET analysis provides precise parameters of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The total specific surface area in m^2/g, the pore size distribution and the total pore volume (micropores and mesopores) have been evaluated on coked and regenerated samples. Finally, adsorption isotherms using a model molecule such as methylene blue have also been carried out, which has shownthat adsorption capacities are much higher on regenerated zeolites compared to coked zeolites.

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N-heterocyclic Carbenes for Stabilisation of nanoparticles and their application in catalysis

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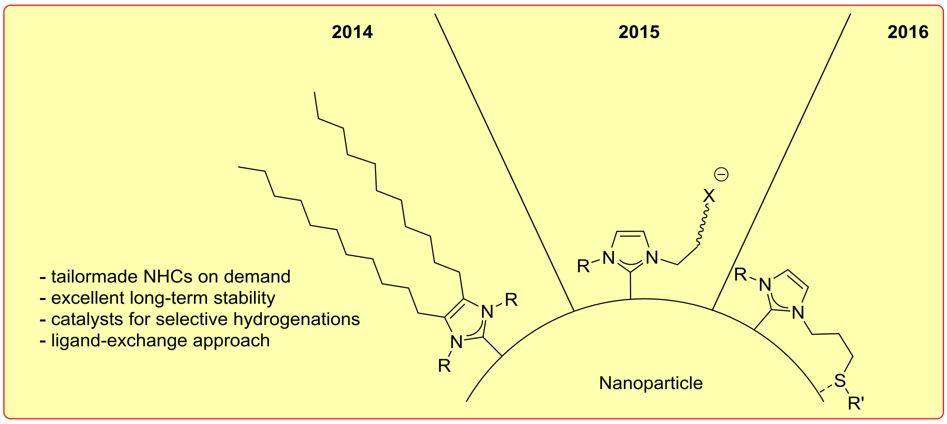
N-heterocyclic carbenes (NHCs) are well established ligands in organometallic chemistry, which results from their electron-rich character and directed steric demand towards the metal leading to strong transition metal to carbon bonds. Additionally, the synthesis of NHCs enables a diverse structural variation and therefore adaption of the required characteristics. [1] Due to their unique properties and the vast variety NHCs have emerged as an excellent ligand class for surface stabilization and modification. [2]



Recently, we developed a variety of NHC-ligands for the stabilization of different nanoparticles (for example Pd and Au). The NHC stabilized nanoparticles were synthesized from well-defined thioether stabilized nanoparticles *via* a powerful ligand-exchange approach. All of the fully characterized nanoparticles showed good long-term stability and promising reactivity in catalysis. Installing long alkyl chains in the backbone of the NHCs provided stable nanoparticles due to steric repulsion with the opportunity to add different substituents at the nitrogen positions on demand (2014). [3] An alternative stabilizing motif, electrostatic repulsion, was achieved by introducing charged groups at the end of a side chain of a NHC resulting in water-soluble nanoparticles (2015). [4] A combinatorial approach is given with a modular, bidentate NHC-thioether-hybrid system, which imparts an easy synthesis of different kinds of ligands with the required properties depending on the substituent attached to the thioether moiety (2016). [5]

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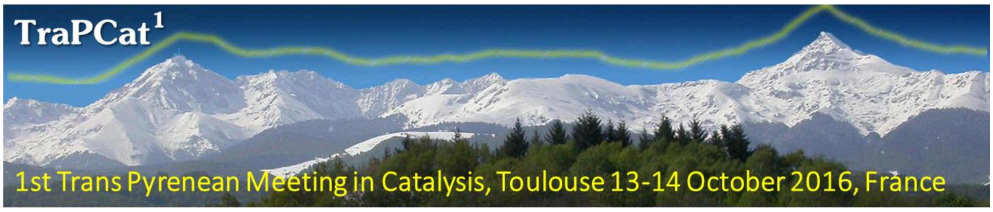

Base-free oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylicacid over graphenic materials supported Rucatalysts

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2,5-furandicarboxylic acid (FDCA) is a chemical building block from biomass. It can be used as alternativemonomer to potentially replace terephthalic acid which is involved in the production of polyethylene terephthalate (PET).[1] FDCA is usually obtained by catalytic oxidation of hydroxymethylfurfural (HMF). It should be remarked that in most of the reported reaction procedures a base additiveisrequired[2], so onlyvery few reports of using base-free catalysts have been reported.[3–5] This is probably related with the stabilization of FDCA as a salt.

In this communication we describe the synthesis and characterization of reduced graphene oxide (rGO) and N-doped reduced graphene oxide (NrGO),which have been applied as support of ruthenium nanoparticles (NPs). Furthermore these catalytic materials have been evaluated in the base-free aqueous-phase oxidation of HMF to yield FDCA.

NrGO and rGO were obtained via thermal treatment of graphite oxide (GO) in a vertical quartz reactor. GO was synthesized from natural graphite powder following a modification of the Brodie’s method.[6]rGO was preparedunder flow of nitrogen and NrGO in flowing NH_3. Catalysts were prepared by the incipient wetness impregnation technique in order to obtain samples with ruthenium loading of 4 wt.%. The catalysts were characterized using X-ray diffraction (XRD), N_2 adsorption (BET), elemental analysis,and transmission electronic microscopy (TEM).

Oxidation tests of HMFto FDCAwere carried out at 100 °C and 10 bar of air in a batch reactor during 24 hours, all of the catalysts were activated beforereaction at 350° C for 2 h under flowing hydrogen gas and the products were analyzed by HPLC.

It has been evidenced that surface areas of the reduced OGs depend on the grain sizes of the natural graphitesused in the OGpreparations. In the case of NrGO sample the contentin nitrogen varies between2and 4 wt.%depending with the treated GO material. The structureand sizes of the Ru NPs were studied by XRD and by TEM. The majority of the Ru particles are among 3-6 nm in sizes showing highly dispersed Ru NPs.

Under our experimental reaction conditions, the highest HMF conversion (99.3%) is achieved using 4%Ru/NrGO as catalyst with a selectivity toFDCAclose to53.0%, while with 4%Ru/rGO catalyst the conversion is near 75% with a selectivity to FDCA below 10%. These results reveal the important role of thebasic surface nitrogen heteroatoms exposed on the NrGO support,whichcertainly participate in the reaction througha bifunctional mechanism.

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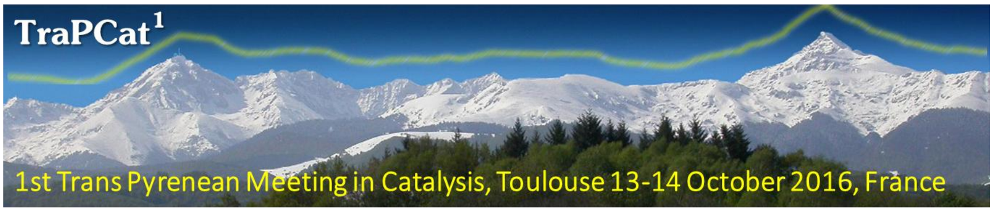

Influence of support carbonaceous doped nitrogen materials in catalysis hydrotreatment

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Carbonaceous materials have been used due to their high versatility ina broad range of applications, such as separations, energy storage or catalysis. Applicability is related to the possibility to design and modulate properties such as chemical composition, surface properties, porosity, etc. In this sense, it is possible to prepare nitrogen doped carbons with a chemical composition of the surface that can lead to improved catalytic activity [1]. This study introduces the possibility to design and prepare porous carbons with nitrogen functionalities, and check their behaviouras supports for Pd hydrotreatment catalysts. 4-chlorophenol, a pollutant that represents a serious problem in wastewater from industry due to high toxicity and a poor biodegrabilitywas considered as target compound [2, 3].

Carbon materials were prepared by infiltration of a mixture of carbonaceous precursor and nitrogen doping agent (resol resin and 1,1-phenanthroline, respectively) in a mesoporous silica template (MSU-F). They were thermally treated (700 ºC, 1 h, N_2flow) and the silica template was removed. Metal nanoparticles, the active phase of the catalyst, were prepared by thewet impregnation method (~1.2% Pd w.). The doped carbons and catalysts were characterized by different techniques including elemental analysis, N_2 adsorption-desorption isotherm, electron transmission microscopy, X-ray photoelectron spectroscopy and chemisorption of CO. The doped carbons showed spongy morphology, with high surface area and pore volume, especially for those with higher contents of nitrogen, although no differences were observed in the type of nitrogen functionalities. The active was homogeneously dispersed in all cases thanks to doping.

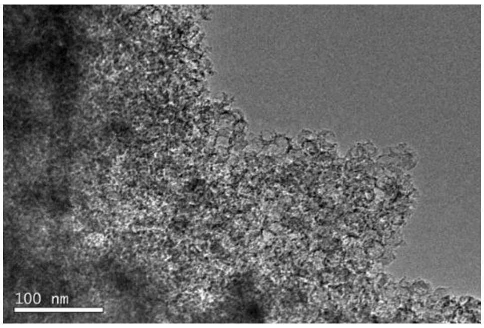

Figure 1. Micrograph of nitrogen doped carbon.

The hydrotreatment for the removal of 4-chlorophenol was carried out using constant hydrogen flow (50 mL/min) and stirring. Reaction temperatures (30, 50, 70 ºC) were selected in order to calculate kinetics constants and the corresponding activations energies by Arrhenius equation. Reaction samples were analysed by gas chromatography with an injector flame detector at different times of reaction. The results showed differences in the behaviour of the doped carbon depending on the quantity of nitrogen atoms in the carbonaceous support. Higher activities were found in the reactions were catalystswith doped carbon support were used. Theactivity also increasedwith the reaction temperature more noticeably when the catalysts were prepared with supports includingin theirstructure N atoms. Thisindicatesan important decrease in the activation energy in the hydrodechlorination reaction from non-doped carbon to doped carbon supports. Therefore, doped carbons as supports can facilitate the hydrodechlorination reaction decreasing the necessary energy required to start the reaction.

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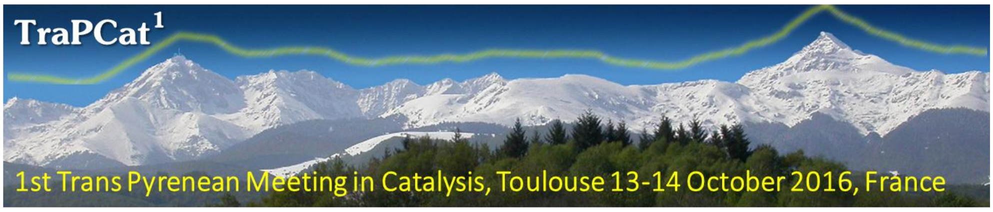

Apatitic calcium phosphates with grafted aminopropyltriethoxysilane: Synthesis, characterization and preliminary catalytic results

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Chiral ligands for homogenous asymmetric catalysis have received considerable attention over the last decades and numerous catalytic systems allowing high-efficiency reactions have been reported. However, only a few examples have been developed into industrial processes. Among the various solutions, immobilization of the catalyst on a solid support (powder) using a "molecular chain" enabling its recycling by a simple filtration is a great challenge that meets both industrial and academic chemist's expectations [1, 2]. The use of apatitic calcium phosphates (a biocompatible synthetic materials in aqueous media) as inorganic catalyst support is a virtually unexplored field. In the present work, we report the grafting of different crystallised stoichiometric hydroxyapatites differing by the drying method (freeze-dried (HAP) and dried at 100°C (HAPD), and nanocrystalline apatite (NCA)) with aminopropyltriethoxysilane (APTES) in toluene (Figure 1). The nature of the alkoxysilane/apatitic surface interaction has been studied by various techniques (FTIR spectroscopy, Raman, NMR, XRD, SEM, TEM, etc.) [3]. APTES grafted on HAP support has been used as anchor for a phosphine-ether ligand. Preliminary catalytic results with phosphine ligand anchored on HAP surface in the Suzuki-Miyaura reaction will be presented.

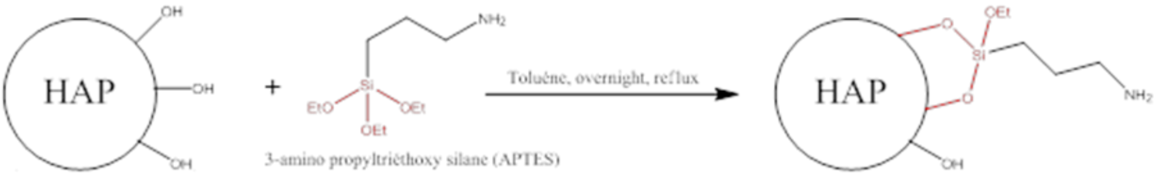

Figure 1: Grafting of aminopropyltriethoxysilane (APTES) on HAP support.

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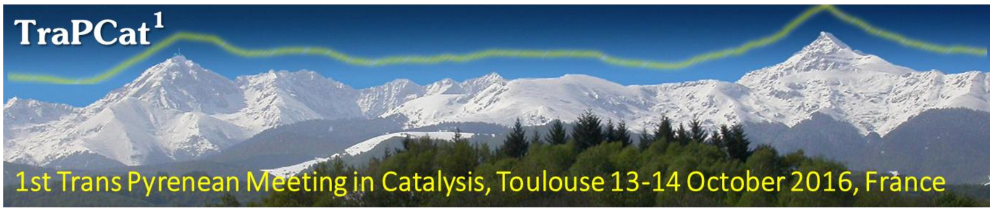

Catalytic Conversion of Carbon Dioxide using new Immobilized N-Heterocyclic Carbene based Catalysts

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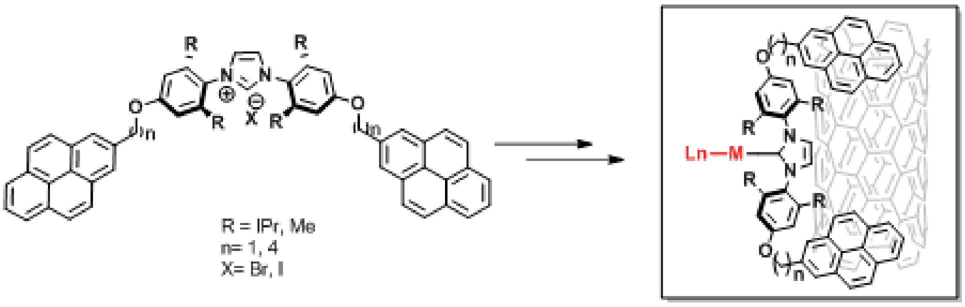
One of the current aims in Catalysis is to combine the advantageous of Homogeneous and Heterogeneous catalysis.[1] Tremendous research efforts are continuously directed towards the development of new systems that merge the high selectivity and activity observed in Homogeneous Catalysis and the recyclability that offers Heterogeneous catalysis.[2] One powerful approach to overcome this challenge is to immobilize homogeneous catalyst on a solid support. The application of these immobilized homogeneous catalysts in conjunction with continuous flow techniques could represent an efficient synthetic methodology to address practical application in Chemical and Pharmaceutical industries.[3]

The immobilization of Homogeneous Catalyst has been achieved via covalent attachment onto solid supports.[1] However, this approach usually required additional synthetic manipulations and significant structural perturbations of the parent catalysts skeletons.[4] As an alternative, non-covalent interactions appear as an ideal strategy to obtain supported catalyst without chemical modifications of the homogeneous catalyst or the solid support.[5]

Herein we report the synthesis and characterization of new pyrene tagged N- Heterocyclic Carbenes ligands and their coordination to metal fragments. The Heterogenization of these metal complexes is performed using carbon supports through π-π stacking interactions.[5] The catalytic performance and recycling of these new hybrid materials have been studied in the production of fine chemical using CO_2.



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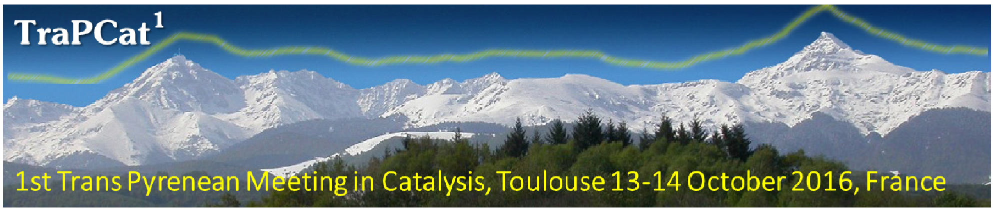

Anionic N-Heterocyclic Carbene Complexes of Gold(I) as Precatalysts for Silver-Free Cycloisomerization of Enynes.

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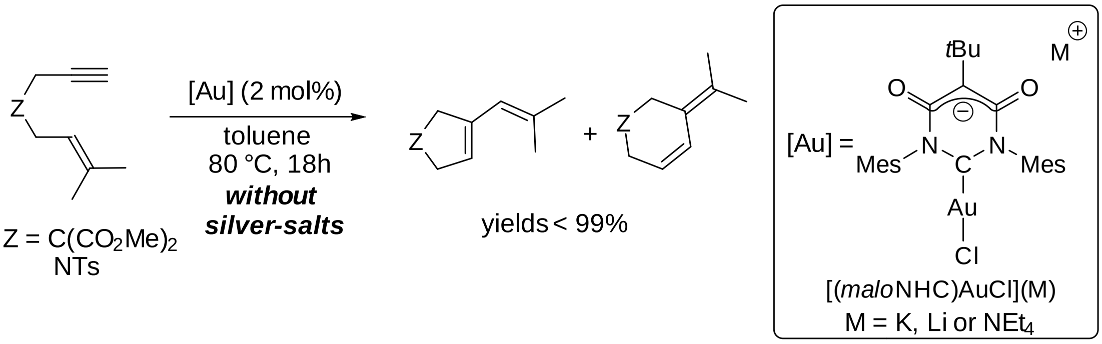
Over the last few years, gold(I) catalysis has gained considerable significance in organic synthesis, since it comprises atom-economic and highly efficient processes for the transformation of relatively simple substrates into valuable, highly complex molecular architectures.[1]

The active species $[LAu]^+$ involved in all these reactions is often generated in situ by reaction of LAuCl complexes with silver salts to extract the chlorido ligand. However, it was shown that the presence of silver salts is not so innocent in gold(I) catalyzed reactions and can lead to the formation of side-products.[2] Among the gold(I) catalytic systems that do not involve silver salts developed up to now, the use of zwitterionic complexes supported by anionic L-type ligands has appeared to be very promising.[3]

In this context, we present herein a new family of anionic gold(I) complexes of general formula [(*malo*NHC)AuCl](M), based on anionic N-heterocyclic carbenes incorporating a malonate backbone *malo*NHC$^-$ previously developed in our group. We will discuss about their synthesis, their characterization, and their use as precatalysts in cycloisomerization reactions of 1,6-enynes. Particularly, we will evidence that the anionic gold(I) complexes can enable self-release of the soluble zwitterionic catalytically active species [(*malo*NHC)$^-$Au]$^+$ into the solution with concomitant formation of MCl salts.[4]



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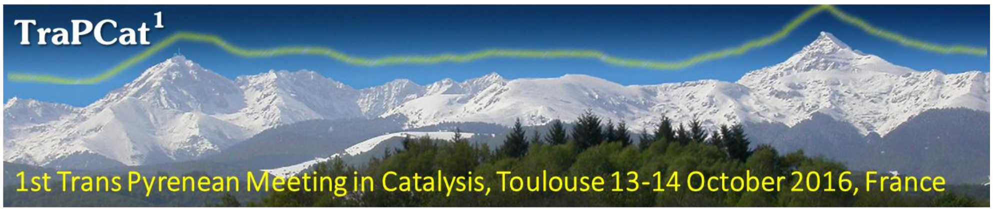

Reduction and functionalization of CO_2 through a bis(boryl)acetal intermediate

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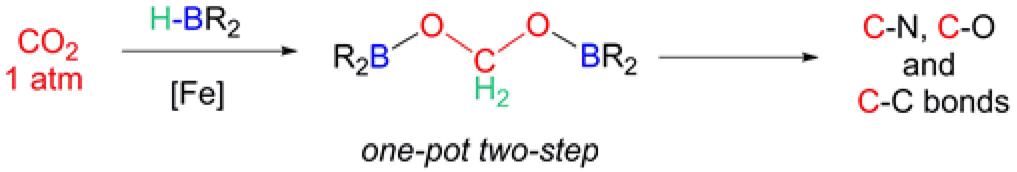
CO_2 is an attractive source of carbon: it is an abundant and rather non-toxic molecule. Despite its thermodynamicstability, it has been reduced in HCOOH, CO, CH_3OH and CH_4undermild conditions.[1]Our team recently completed this C1 list by the characterization and the selective trapping of HCHO, usingpolyhydride ruthenium catalysts.[2] The next challenge consists in transforming CO_2 into more elaborated molecules, while using earth abundant catalyst.

I will present the selective hydroboration of CO_2 into bis(boryl)acetalunder very mildconditions (25°C, 1atm of CO_2, 1h). This 4 electrons reduction is very efficiently catalysed by a dihydride iron complex. The subsequent transformation of the generated bis(boryl)acetal affords a large variety of products featuring C-N, C-O and even C-C bonds.[3]



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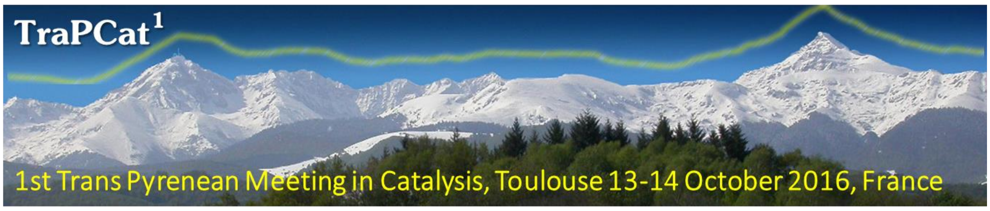

Dendritic phosphine complexes for redox-switchable catalysis

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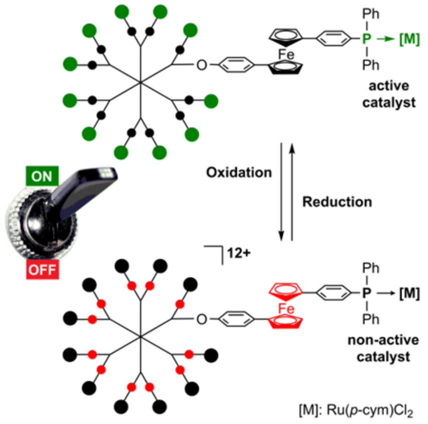
Redox-switchable catalysis (RSC) is a field of growing importance, in which the catalytic efficiency of a coordinated metal centre can be influenced *in situ* by a redox-active functionality to which it is linked.[1,2] RSC has been applied to several areas of homogeneous catalysis, but no report had involved the use of dendritic ligands for RSC before our work. Dendrimers are hyperbranched macromolecules having a precisely defined structure.[3] The nature of the internal structure can be an important parameter,[4] and the phosphorhydrazone dendrimers that we synthesize since a long time[5] are particularly suitable for catalysis.[6] The grafting of catalytic entities as terminal functions of dendrimers induces a high local catalyst concentration that may cause a positive dendritic effect.

We have already synthesized dendrimers decorated by phosphine ligands for the complexation of $RuCl_2$(*p*-cymene), and use them for catalysing the isomerization of 1-octen-3-ol to 3-octanone.[7] We have also synthesized various types of dendrimers incorporating ferrocenes in their structure, for studying their electrochemical redox properties.[8] Association of ferrocenes and phosphine complexes of $RuCl_2$(*p*-cymene) in a single dendritic entity has been carried out recently. These dendrimers have been used also for catalysing the isomerization of 1-octen-3-ol to 3-octanone.[9] Furthermore, the rate of this catalysed reaction can be finely tuned by playing with the redox properties of the ferrocene. The catalysis is switched off when the ferrocene is oxidized, and it is switched on when the ferrocenium is reduced. This is the very first example of redox switchable catalysis with a dendrimer.[10]



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Synthesis of γ-aminobutyric esters via rhodium catalyzed hydroaminomethylation of acrylates.

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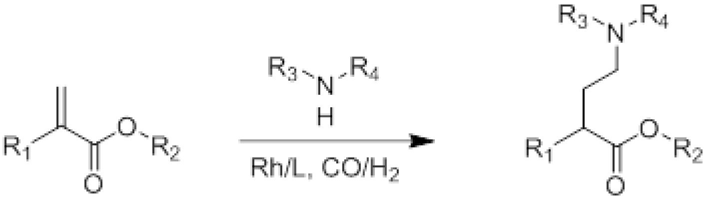
The efficient and selective synthesis of amines using easily available and abundant precursors is a long-standing goal of chemical research, since they are powerful building blocks for the synthesis of pharmaceutical and agrochemical products.[1] Among amine containing molecules, γ-aminobutyric acids (GABA) have attracted considerable attention since it plays an important role in reducing neuronal excitability. Moreover, this scaffold is present in several natural products. [2]

Only a system has been developed to obtain a large scope of GABA motif. However, such system is not catalytic, islimited to non-easily available reagents and requires the use of an excess of amine. [3]

In this context, rhodium catalyzed hydroaminomethylation is an attractive reaction for the synthesis of GABA motifs since it allows the productionof amines with high atom economy.[4]In this process, the challenge mainly lies in the design of a catalytic system that combines of high chemo- and regioselectivity.[5]

In this work, we report the synthesis of γ-aminobutyric esters via rhodiumcatalysedhydroaminomethylation of acrylates with different amines. Optimisation of the conditionsand screening of phosphorus ligands were tested in order to control the regio- and chemoselectivity of the process to obtain the desired products.



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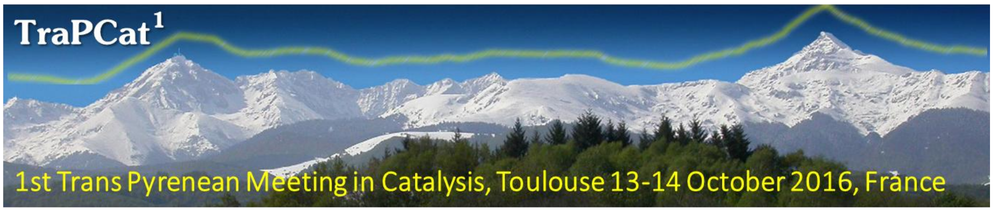

Platinum-Catalysed Intermolecular Addition of Carbonyl Compounds to 1,6-Enynes: Investigation of a new reaction pathway

Odile Dechy-Cabaret,[1,2] Kévin Fourmy,[1,2] Mohamed El Louz,[1,2] Sonia Mallet-Ladeira,[1,2] Jean-Claude Daran,[1,2] Maryse Gouygou[1,2]

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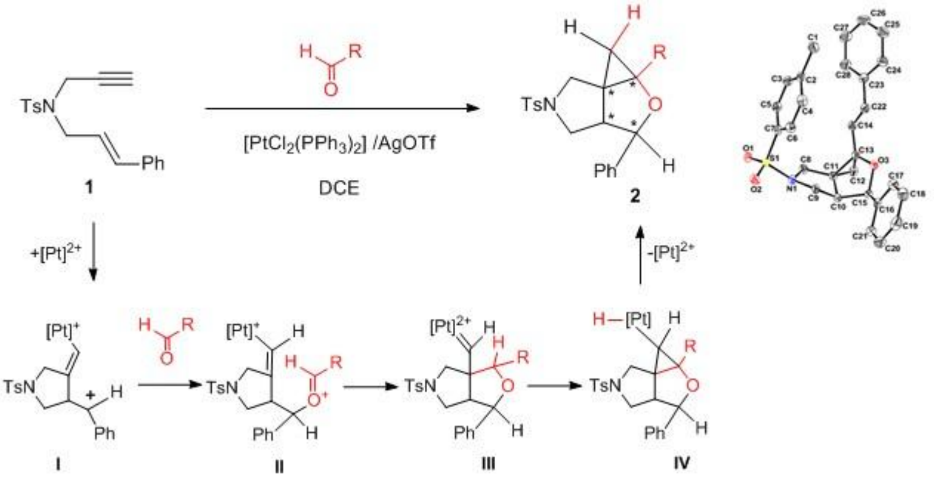
In recent years, gold- or platinum-catalysed cycloisomerisations of 1,6-enynes have attracted considerable attention since they represent powerful synthetic tools for the construction of cyclic and heterocyclic moieties. Skeletal rearrangements take place in the absence of an additional reactant by 6-*endo-dig* or a 5-*exo-dig* cyclisation processes via cyclopropyl-metallocarbenoid intermediates whereas tandem cycloisomerisation/addition reaction occurs in the presence of hetero- or carbo-nucleophiles by addition on these key intermediates.Carbonyl compounds also act as nucleophiles in intra-[1]and inter-molecular[2]tandem cycloisomerisation/addition reactions.

Following our work on platinum-phosphole complexes for 1,6-enyne cycloisomerisations,[3] we have developed the Pt(II)-catalysed intermolecular addition of aldehydes to 1,6-enynes **1** that provides new tricyclic compounds **2** bearing four stereogenic centers created with high diastereoselectivity.[4]



This new tricyclic compound may derive from Pt-carbeneintermediate **III** by addition of aldehyde on the stabilized homoallylic/benzylic cation **I**. The subsequent reaction proceeds by 1,3-insertion of **III** into the CH bond in α-position to the oxygen atom, as confirmed by deuterationexperiments, followed by elimination of the metal fragment to afford cyclopropane compounds **2**.

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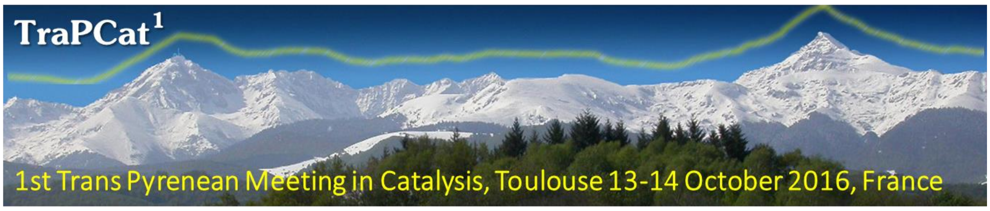

[N,P]-pyrrole $PdCl_2$ complexes catalyzed the formation of dibenzo-α-pyrone and lactam analogues

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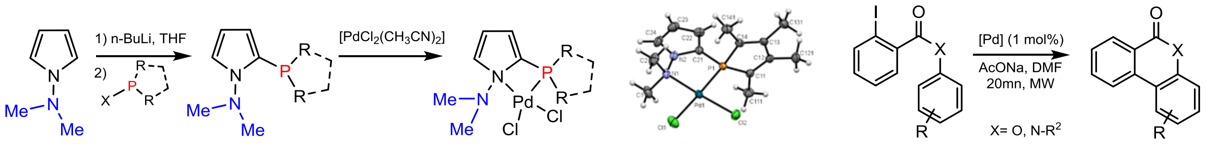
Dibenzo-α-pyrones and their derivatives are an important structural motif currently extended in several natural products[1] with important biological properties. A diversity of methodologies exists for building a dibenzo-α-pyranone motif,[2] however, synthetic strategies mainly based on palladium-catalyzed reactions have a crucial role in its obtainment. In particular, direct intramolecular arylation has been chosen as powerful synthetic protocol to obtain this kind of structural motifs,[3] due to its effectiveness in the coupling on encumbered substrates and its versatile application in the synthesis of complex natural products. In this context, the development of novel palladium-catalyzed approaches for the C-H direct functionalization of arenes for the preparation of such compounds using very low catalyst loadings, which would provide a cost-effective and environmentally attractive procedure, continues being an important challenge.

In attempt to explore and to better understand the scope of direct intramolecular arylation for obtaining a variety of dibenzo-α-pyrone and lactame analogues, we have developed the synthesis of a novel family of ligands [N,P] including pyrrole as the framework and different phosphine or phosphole units as phosphorus donors.[4]



The palladium complexes obtained from these ligands were used as catalytic precursor on direct arylation of a variety esters and amides, using microwaves as energy source, to obtain both benzopyranones and phenanthridinones.[4]

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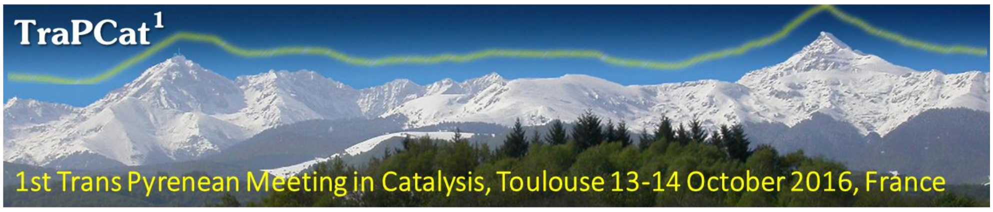

Influence of the Second Coordination Sphere in Oxidation Catalysis

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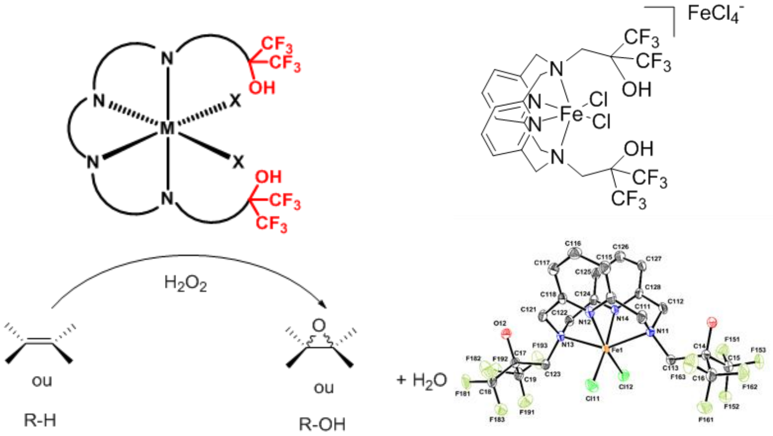
Oxidation reactions represent a core industrial technology for the conversion of chemical feedstock, such as alkanes and alkenes, into valuable chemicals such as epoxides, diols, and alcohols for example. In order to develop an environmentally friendly chemistry, oxidation catalysts that are efficient and selective under mild conditions are needed. In Nature, monooxygenase metalloenzymes are able to activate molecular oxygen and to transfer oxygen atoms to a substrate. This is mainly due to an intramolecular hydrogen bonding network and protonation steps, both participating in the O_2activation but also facilitating access to high-valent species responsible for the oxidation process. However, few synthetic systems take into account the second coordination sphere for the development of oxidation catalysts.[1] Thus, our approach is to introduce a well-defined second coordination sphere around the metal center to facilitate hydrogen peroxide activation by the metal complex and thus more easily access high-valent species able to transfer specifically an oxygen atom to a substrate. We focused on the known ability of fluorinated alcohols to activate H_2O_2 via an H-bonding network.[2] Thus, ligands decorated in the second coordination sphere by hydroxyl groups that have F substituents in their proximity are being developed, in order to combine the H-bonding network in the second coordination sphere with the metal center for H_2O_2 and/or O_2 activation. This strategy is being explored for Fe and Mn catalysts using neutral multidentate N-based ligands.



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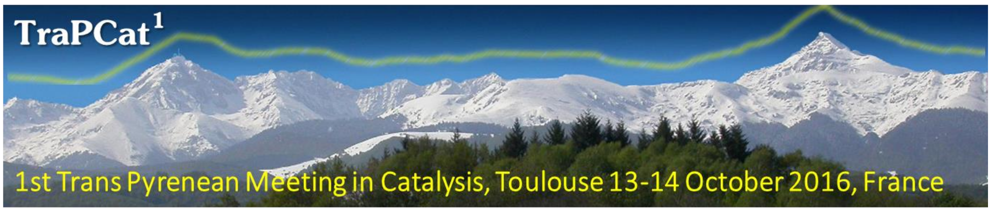

Oxocyclohexadienyl piano stool complexes for sustainable catalysis

M. Kechaou-Perrot,[1,2] L. Vendier, [1,2] S. Bastin,[1,2] J.-M. Sotiropoulos,[3] K. Miqueu,[3] L. Menéndez-Rodríguez,[4] P. Crochet,[4] V. Cadierno,[4] A. Igau*,[1,2]

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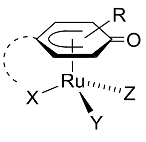
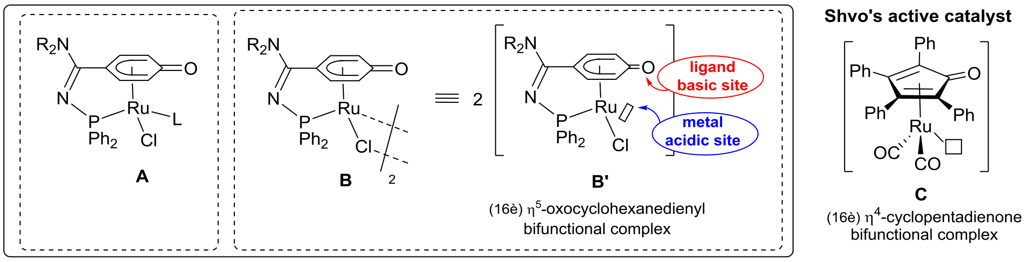


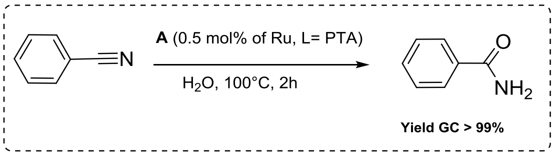
I

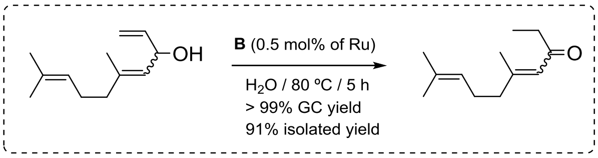
Within the family of 6-membered rings coordinated in an η^n-hapto mode to a transition metal, η^5-oxocyclohexadienyl ligands have been little studied. To the best of our knowledge there is no example of piano-stool ruthenium complex **I** with an η^5-oxocyclohexadienyl as ligand which has been tested in catalysis before our studies.[1] Indeed, half-sandwich Ru-based η^5-oxocyclohexadienyl complexes are very scarce and their corresponding tethered complexes unknown.

We recently succeeded to set up a straightforward preparation of unprecedented tethered η^5-oxocyclohexadienyl piano-stool mono metallic **A** and dimeric bridged-chloride **B** ruthenium(II) complexes. [2] Depending on the L-type ligand in **A** grafted on the metal, these new complexes are able to be air and water stable. Complexes **B** are precursors for η^5-oxocyclohexadienyl 16è complexes **B'**, which can be considered as the homologue of Shvo monometallic 5-membered ring η^4-cyclopentadieone active complex **C**. Computational studies have been carried out on complexes **A** and **B**. The calculations clearly indicated that the structure for **B** is strongly preferred compared to the bridged-oxygen isomer.



Our pioneering tests in catalysis with η^5-oxocyclohexadienyl piano-stool complexes showed that the monomeric complexes **A** (L= PTA) are robust and effective nitrile hydration catalysts.[3] The dimeric Ru(II) complexes **B** performed, under mild conditions, the base-free redox isomerization of allylic alcohols.[2]





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DESIGN OF CHIRAL PHOSPHORUS CONTAINING CALIX[4]ARENES AND THEIR USE IN ASYMMETRIC CATALYSIS

Andrii Karpus,[1,2,3] Oleksandr Yesypenko,[4] Vyacheslav Boiko,[4] Vitaly Kalchenko,[4] Rinaldo Poli,[1,2] Jean-Claude Daran,[1,2] Zoia Voitenko,[3] Eric Manoury[1,2]

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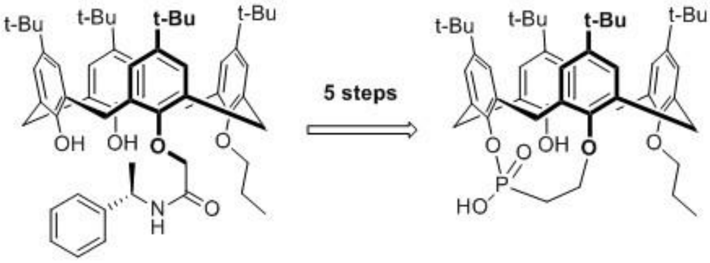
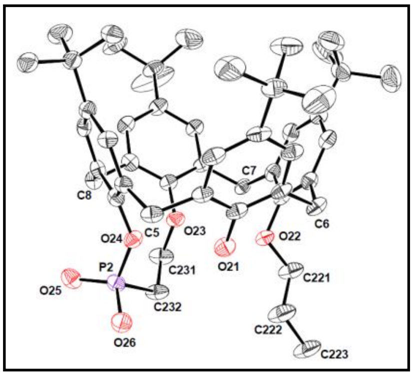
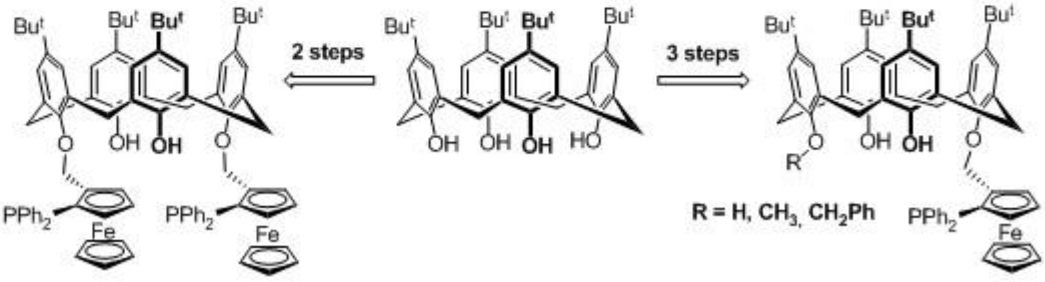
Chiral phosphoric acids have shown their potential in organocatalysis for a wide range of reaction and substrates, such as the asymmetric protonation of prochiralenolates, ketenes or ketene imines[1] or the organocatalytic asymmetric hydrolysis of epoxides[2]. Inspired by these results, a new optically pure chiral phosphoric acid bearing an inherently planar chiral calix[4]arene with ABCH substitution pattern was synthesized in 7 steps from *p*-*tert*-butylcalix[4]arene, with an overall 15.5 % yield and tested as an organocatalyst[3].





The synthesis and use in asymmetric catalysis of ferrocene-containing chiral enantiomerically pure calixarene derivatives and their use in asymmetric catalysis will also be presented. Initial tests with these new"pocket"-like ligands were carried out in the asymmetric allylic substitution reaction, showing good catalytic activities and enantioselectivities (ee up to 86 %).



AK thanks the French Embassy in Ukraine and the "InstitutUniversitaire de France (IUF)" for support.

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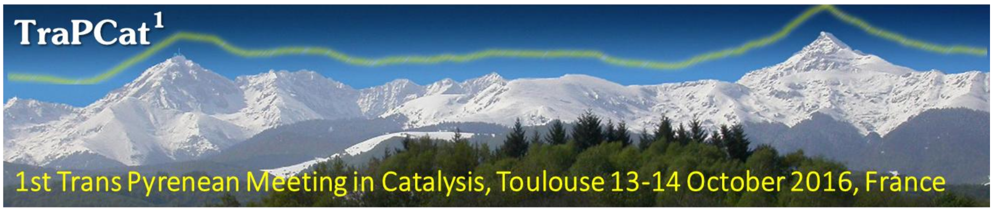

The use of Dendritic Phosphoramidite Ligands for Enantioselective Rh-catalyzed [2+2+2] Cycloaddition Reactions.

L. Garcia,[1,2] A. Roglans,[1] A. Pla-Quintana,[1] R. Laurent,[2] J-P. Majoral,[2] A.-M. Caminade[2]

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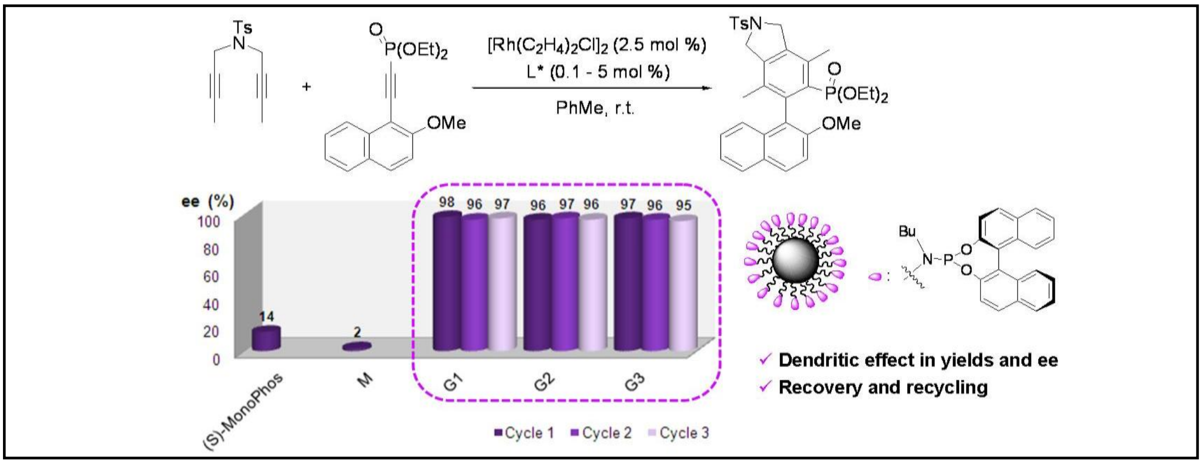
Dendrimers[1], nano-objects with astonishing applications in areas ranging from biology to material science, have also been successfully applied in catalysis. The precise incorporation of ligands in the different domains of the dendrimeric structure has enabled the complexation of metals leading to good catalysts in a number of reactions, which can furthermore be easily recovered and reused. In some cases, positive dendrimeric effects[2] have been observed with the enhancement of the activity and/or selectivity by using dendrimeric catalysts instead of monomeric catalysts.

We have grafted phosphoramidite ligands[3] at the surface of phosphorus dendrimers from generation 1 to 3. These new materials have been found to be highly effective catalysts for the rhodium(I) catalyzed [2+2+2] cycloaddition reaction of three alkynes[4].

A strong multivalent effect is observed both in the activity and enantiodiscrimination leading to axially chiral biaryl compounds: near quantitative yields and ee up to 99% with dendrimeric ligands were obtained compared to moderate yield and ee less than 15% with monomeric ligands. Moreover, the dendrimeric catalyst can be recovered and reused in these alkyne cycloadditions with no significant reduction in the yields and enantioselectivities obtained for three consecutive cycles[5].



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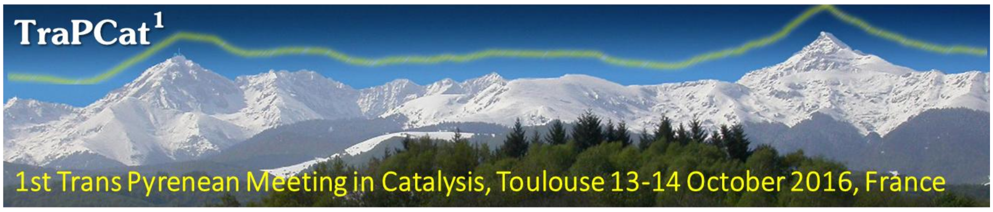

Oxidation-Promoted Activation of a Ferrocene C-H by a Rhodium Complex

A. Labande,[1,2] N. Debono,[1,2] A. Sournia-Saquet,[1,2] J.-C. Daran, [1,2] and R. Poli [1,2,3]

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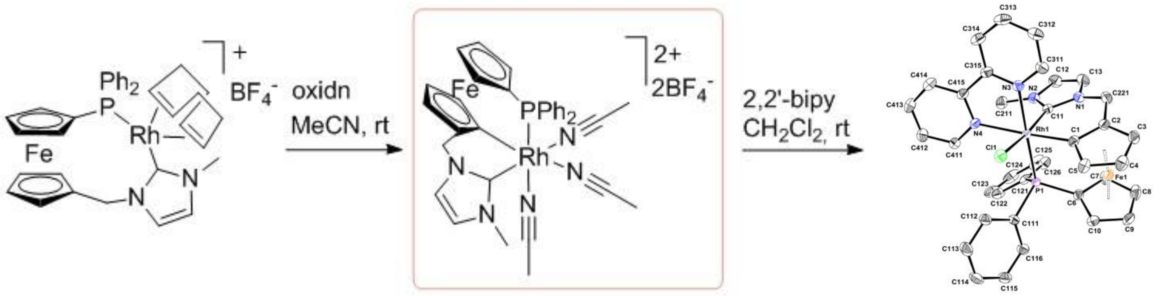
Cyclometalation on rhodium complexes via C–H activation has been well known for decades, especially with the use of pincer ligands.[1] However, very few examples describe the C–H activation by oxidative addition on rhodium(I) complexes with PCP pincer ligands bearing a ferrocenyl unit in place of a phenyl.[2] In this presentation, we report the activation of a ferrocene C-H bond on rhodium initiated by ferrocene oxidation and followed by electron transfer from rhodium to ferrocenium, eventually leading to a planar chiral rhodium(III) complex.[3]



We have investigated the behaviour of a rhodium(I) complex bearing a chelating phosphine/N-heterocyclic carbene ligand with an electroactive ferrocenyl group directly linked to the phosphorus atom. The initial chemical or electrochemical oxidation of ferrocene to ferrocenium is followed by a two-electron transfer from rhodium to ferrocenium and subsequent reorganisation of the coordination sphere around rhodium. Following this reorganisation, we observe the activation of a ferrocene C-H bond and the formation of a rhodacycle. The planar chiral rhodium(III) complex thus formed is very stable and preliminary catalytic tests showed that it is active for the Grignard-type arylation of 4-nitrobenzaldehyde via C–H activation of 2-phenylpyridine.

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Core-shell Phosphine-Containing Polymers AsNanoreactors for Biphasic Catalysis

A. E. Manoury,[1]B. S. Chen,[1]C. A.Joumaa, D. F. Gayet,[1]E. R. Poli,[1]F. X. Zhang,[2]G. W. Zhang,[2]H. M. Lansalot,[2]I. F. D'Agosto,[2]J. B. Charleux,[2]K. A. Cardozo,[1,3]L. E. Lobry, M. L. Barthe,[3]N. C. Julcour,[3]O. J.-F. Blanco,[3 P.]H. Delmas[3]

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Catalyst recovery and recycling is one very important aspect of the application of catalytic technology, with a strong impact on energy efficiency, industrial economy, and the environment (waste production). We will present our first results on a new approach for efficient biphasic catalysis using water to confine the catalyst, based on the catalyst covalent linking to the hydrophobic core of well-defined amphiphilic nanosized core-shell polymers. These polymers (see figure 1) have been efficiently synthesized by RAFT polymerization in aqueous dispersion. The core-shell functionalized polymers were efficiently usedin the rhodium-catalyzedhydroformylationof 1-octene under aqueous biphasic conditions The catalyst could be recycled several times by simple decantation with low Rh leaching. A mechanism for Rh leaching will be proposed. The first results in the iridium and rhodium-catalyzedhydrogenation of alkenes under aqueous biphasic conditions using the same nanoreactorswill be also presented.

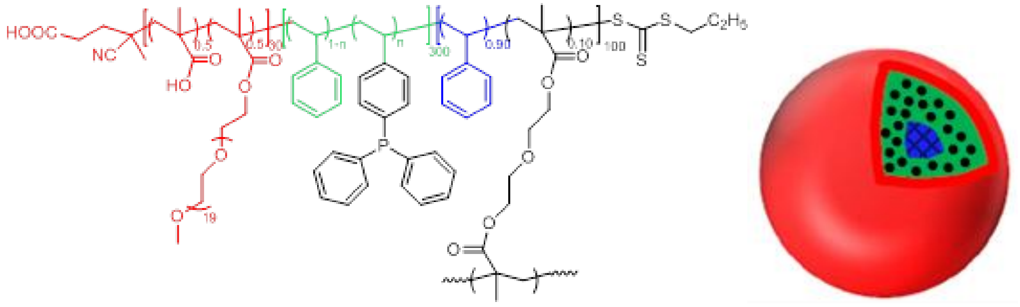

Figure 1: structure of nanosized core-shell polymers.

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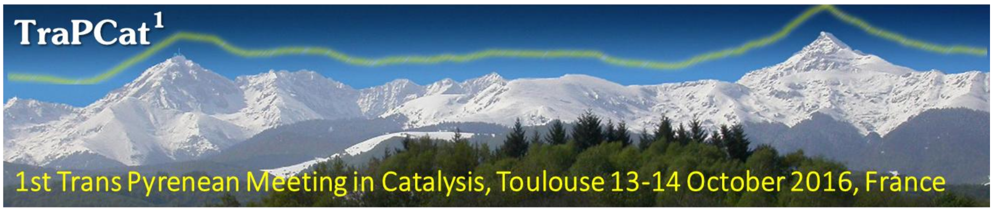

Selective catalytic polymerization ofdifunctionalmonomers

Marta E. G. Mosquera,[1]M. Teresa Muñoz, María Fernández-Millán, Tomás Cuenca

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Aluminium organometallic derivatives containing Al-O bonds are very attractive species because of their remarkable properties in catalytic polymerization. As such, aluminium alkoxides have proven to be very efficient catalysts in ring opening polymerization and copolymerization processes.[1] Also, aluminium heterometallic compounds are appealing catalytic species, as the joint effect of two different metals in the same compound frequently leads to improved catalytic properties, especially when connected by an oxygen atom.[2]

Our research is centered in the preparation of new aluminium homo and heterometallic compounds active in polymerization processes.[3] We have synthesized new aryloxide derivatives bearing functionalized aryl moieties. The presence of the additional functional group in the aromatic ring offers extra coordination points that not only can affect the catalytic behaviour of the complexes, but also can provide them with new structural features. We have achieved a good control of the nuclearity of the compounds prepared by varying the precursors and the reaction conditions. The species synthesized are active in ROP and the influence of their structure in their catalytic activity has been analysed.

Also, well defined heterometallic derivatives bearing aluminium and alkaline metals, as shown in figure 1, have been prepared in our group. These species are active catalysts in acrylate polymerization processes, generating syndiotactic PMMA.

When we performed the studies with a monomer containingtwo different functional groups, we observed that the homometallic and heterometallicspecies are both active in the polymerization process but*via*two different paths. Hence, depending on the catalyst used,the selectivepolymerizationof only one functional group is achieved.

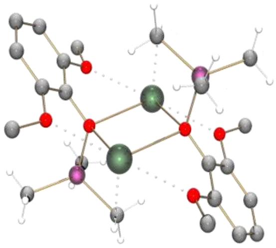

Figure 1.

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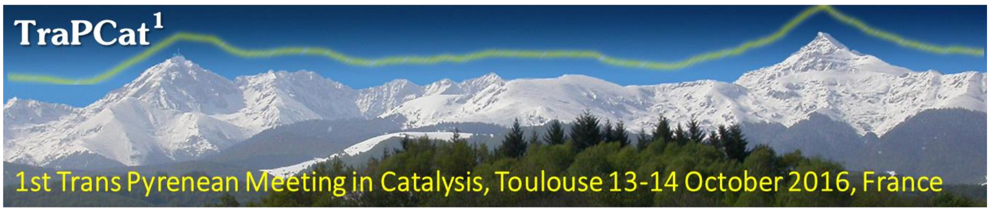

Activation of CO_2 with bidentate nickel complexes

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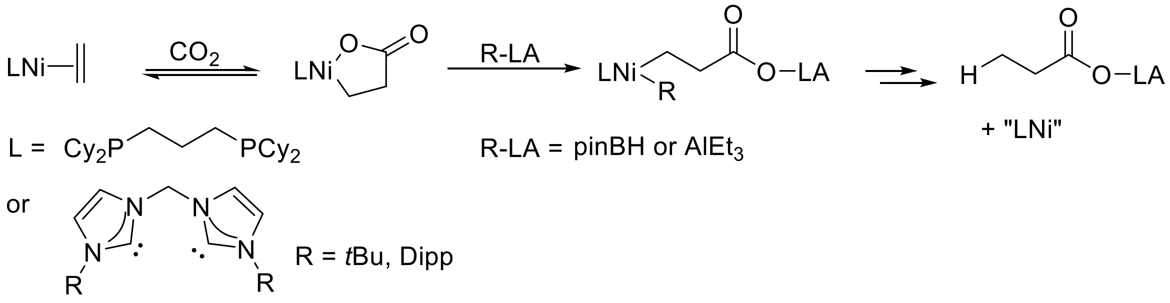
The conversion of carbon dioxide CO_2 into valuable chemicals helps reducing greenhouse gas emissions and developing alternatives to the fossil fuel based energy and chemical production. Despite its thermodynamic stability, CO_2 can be used as a cheap, non-toxic homologation reagent. [1]

Among the various strategies for CO_2 functionalization, CO_2 can be coupled with alkenes or alkynes in the coordination sphere of metals to form metallacycles. The first reactions were discovered in the 1980s by Hoberg [2] and Walther using nickel complexes and Carmona [3] using molybdenum complexes. Unfortunately, difficult β-H elimination on late transition metal complexes and strong oxophilicity of early transition metal complexes hampered the development of catalytic processes. Nickel complexes have mostly been studied and the metallacycles being stable, they require strong electrophiles as methyl iodide [4] or strong Lewis acids as $B(C_6F_5)_3$ [5] to promote the formation of acrylate derivatives. Most interestingly, the development of catalytic processes with nickel complexes has been achieved recently, relying on the use of strong bases such as alcoholates. [6]

In this context, we have been investigating alternative pathways for the reactivity of bisphosphine and biscarbene nickelalactones using boron and aluminum transmetallating reagents. The experimental results are further supported by DFT calculations.



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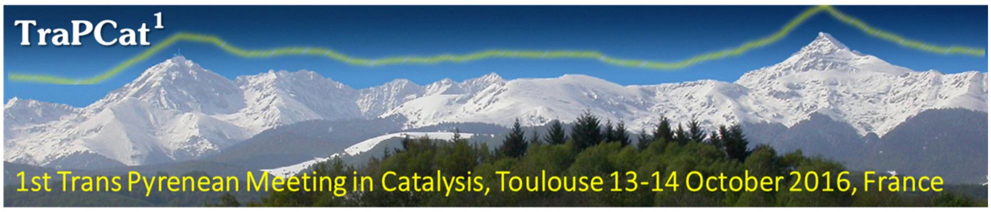

Isoprene polymerization mediated by Vanadium-[ONNO] complexes

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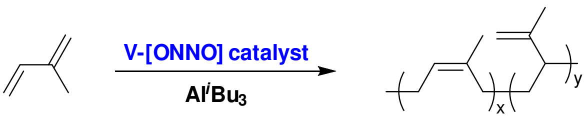
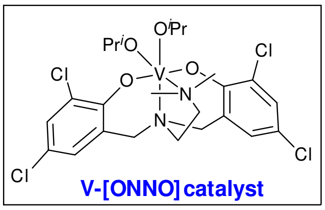
Polyolefins produced by coordination polymerization are important synthetic polymers in our daily life. Vanadium based catalysts for olefin polymerization were discovered in the 1950s as one of the first homogeneous Ziegler–Natta catalysts. These classical Ziegler-type vanadium catalyst systems typically consist of a vanadium compound (e.g. $VOCl_3$) and an organometallic reagent (e.g. Et_2AlCl) and are known to display unique characteristics in olefin polymerization.[1] Indeed, such vanadium-based catalyst systems are known to produce: (i) high molecular weight linear polyethylene with narrow molecular weight distribution, (ii) high molecular weight amorphous polymers applied to the synthesis of ethylene/propylene/diene copolymers used for the manufacture of synthetic rubber and elastomers (EPDM)) as well as ethylene/α-olefin and ethylene/cyclic olefin copolymers with high comonomer incorporations, and (iii) syndiotactic ''living'' polypropylene with narrow molecular weight distribution or diblock copolymers of propylene and methyl methacrylate (MMA).

However, catalyst deactivation is a chronic issue in polymerization mediated by V-based catalysts, and is generally explained by the ease of reduction of catalytically active vanadium species to low-valent, less active, or inactive V(II) species during the catalytic cycle.[1,2] One way to overcome this problem is by designing new ancillary ligands, especially polydentate chelating ligands, to stabilize active vanadium(V) species. This approach has been shown to keep vanadium in high-oxidation state, which subsequently prolongs the catalyst life-time, and had led to a number of more thermally robust, highly active systems.[1,2]

A few years ago, we introduced the dianionic amine bis(phenolate) [ONNO] ligand into vanadium chemistry in order to stabilize vanadium complexes in different oxidation states (+V, +IV, +III and +II). We reported that, upon treatment with chlorinated aluminium alkyls reagents some of these V-[ONNO] complexes served as active catalysts towards ethylene polymerization, and also exhibited favorable capability for ethylene-α-olefin or –cycloolefin copolymerization, affording copolymers with high 1-hexene or norbornene content.[3]

The objective of this study was to assess the aforementioned V-[ONNO] complexes for the polymerization of isoprene and their capability for isoprene coordinative chain transfer polymerization (CCTP).





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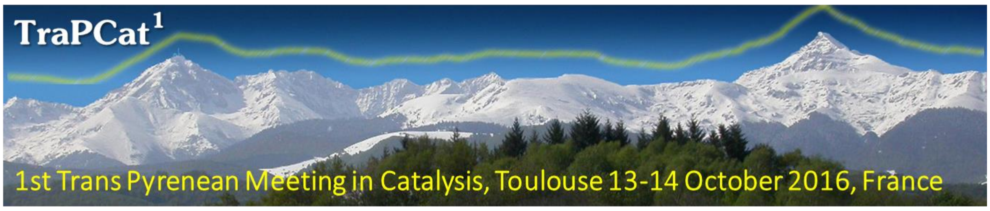

Palladium-catalyzed C(sp^3)–H γ-carbonylation of aminoalcohols

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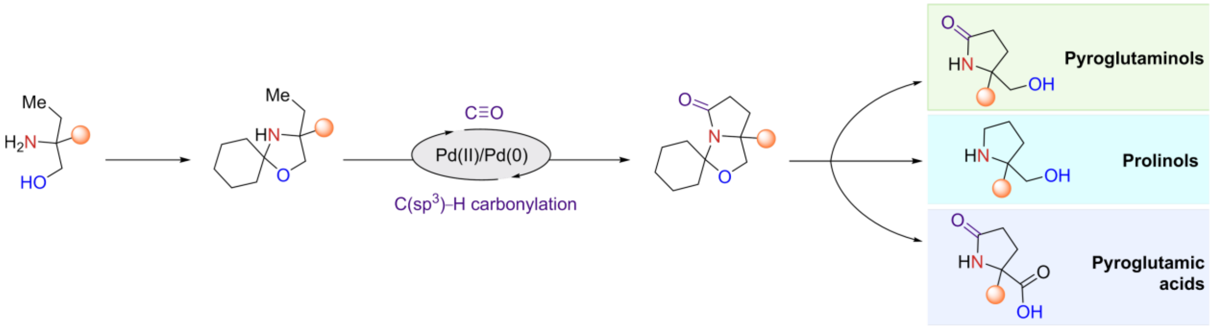
We have recently discovered an amine directed Pd(II)-catalyzed carbonylation of γ C(sp^3)–H bonds of secondary amines via a 5-membered palladacycle intermediate species that allows CO insertion and cyclization for the synthesis of pyrrolidinone moieties. To exploit the inherent affinity of aliphatic amines for electrophilic Pd(II) catalysts represents the most straightforward and atom economical manner to effect remote C(sp^3)–H bond activation. Thus, this strategy spans the inherent directing ability of an amine functional group present in the substrates without the need of any external directing group. This new reaction works for a variety of substrates incorporating quaternary groups α to the amine showing enhanced reactivity for the terminal C(sp^3)–H bond of methyl groups, good functional group tolerance and asymmetric induction. Herein, we report the direct synthesis of γ-substituted pyroglutaminols *via* a Pd(II)/Pd(0)-catalyzed C(sp^3)–H activation/carbonylative cyclization in excellent yield and regioselectivity, thus providing valuable scaffolds that can undergo a variety of downstream transformations. This catalytic method directly transforms simple, easily accessible amines into highly substituted and structurally diverse products and can streamline the synthesis of biologically important amine-containing molecules.[1]



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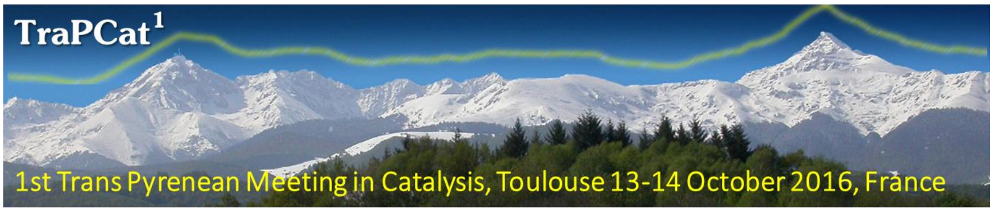

Title: Zn complexes with N_4-donor ligands as catalysts for the cycloaddition of CO_2 to epoxides

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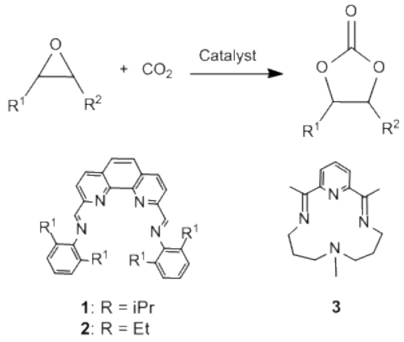
Cyclic carbonates are valuable synthetic targets that are widely used as raw materials for the synthesis of small molecules, polymers, electrolytes and media in lithium-ion secondary batteries, and excellent polar aprotic solvents [1]. They can be obtained by the catalyzedcycloaddition of CO_2 to epoxides. Zinc complexes are good candidates as catalysts for this transformation due to their low toxicity [2] and high stability towards oxidation [3]. A series of zinc salen complexes combined with a nucleophilic ammonium halide salt [4], were active for the synthesis of cyclic carbonates with terminal epoxides under mild conditions [5].Here we report the efficient utilization of robust transition metal complexes based on easy-to-handle 2,9-bis(imino)-1,10-phenanthronyl [6] and macrocyclic [7] ligands (1-3) as catalyst for the coupling of epoxides with carbon dioxide. The complex Zn(**1**)Cl_2 in the presence of tetrabutylamonium bromide produced a 77 % of epoxide conversion in the cycloadition of CO_2 and 1,2-epoxihexane at 30 bars, 80˚C in 20 h (0.2 mol % catalyst loading). This complex is stable under catalytic conditions and could be recycled by simple filtration maintaining the conversion in a second run.



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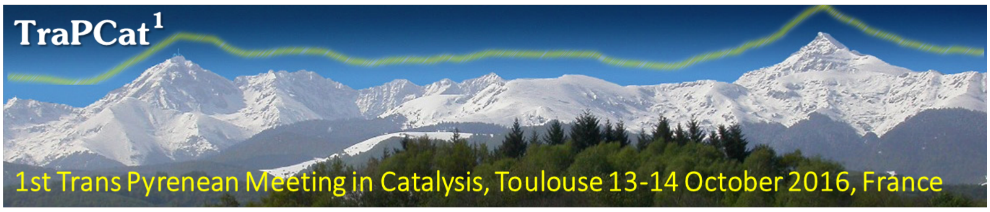
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1st Trans Pyrenean Meeting in Catalysis, Toulouse 13-14 October 2016, France

The Nickel-Catalyzed Heck Reaction: Mechanistic Studies using Hybrid Phosphine-Imine Ligands.

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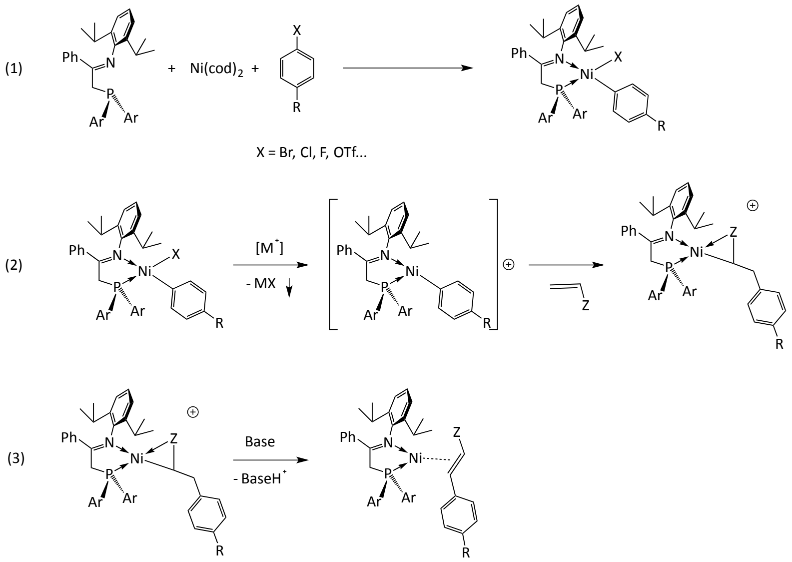
Palladium compounds are extremely efficient catalysts for the Heck reaction, one of the most widely used tools for selective C-C bond.[1] However, in recent years there is a growing interest in replacing costly noble metal catalysts for more abundant first-row transition elements. Nickel is the most obvious replacement for Palladium in the Heck reaction, since both elements share many similar chemical features that are critical for the process.[2] Furthermore, Ni can activate certain substrates (e. g., unreactive aryl sulfonates or chlorides) much more readily than Pd, which suggests that Ni Heck catalysts could represent much more than a cheaper replacement for Pd. In spite of this, very few examples of Ni-catalyzed Heck reactions have been reported. The reasons behind the apparently lower catalytic capacity of Ni complexes in this specific reaction are poorly understood.[3]

Hybrid phosphine-imine ligands provide an ideal background for the study of the basic processes involved in the Heck reaction. It is known that both Ni or Pd complexes with hybrid P-N ligands are robust catalysts olefin oligomerization or polymerization reactions.[4] This implies ability to undergo migratory olefin insertion, and relatively stable catalytic intermediates. Thus, we have investigated the following key steps of the Heck catalytic cycle using P-N stabilized Ni complexes (See Scheme): 1) Oxidative addition of several types of aryl halides; 2) Migratory insertion of several olefins, such as methyl acrylate and 3) base-induced β-hydrogen elimination. The relative ability to undergo each of these steps, and their relative importance in a hypothetical catalytic cycle will be discussed.



Scheme 1.

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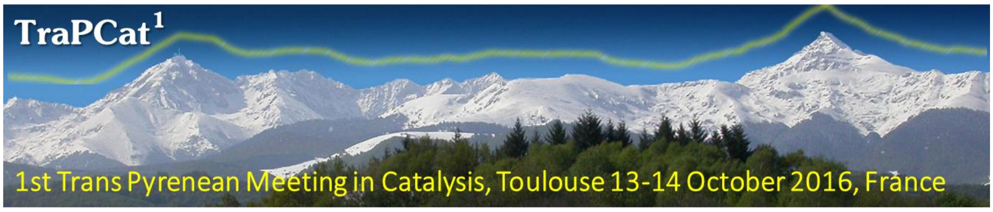

Metal-oxo catalyzed epoxidation of olefins under organic-solvent-free conditions : experimental and theoretical considerations

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M. Loubidi,[1,2,5]N. Uyttebroeck,[1,2] B. Guérin,[1,2] D. Mesquita Fernandes, [1,2]
V. Vrdoljak, [3]R. Santillan,[5] N. Farfan,[4,5]A. Benharref,[6]R. Poli[2,7]

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“Greener” catalytic olefin epoxidation under homogeneous conditions **without organic solvents** were investigated using Mo[1-9], W[9-10] and V[11-12] coordination compounds with extremely low metal loading (metal/substrate ratio from 1/100 down to 2 ppm in the case of polyoxometalates[13]) and good selectivity (>90% in the best cases). Natural products have also been tested as substrates. [4]Investigations of the catalytic mechanism by DFT calculations have revealed the preference for a “Bartlett-like” oxygen atom transfer from the activated catalyst-oxidant complexfor a specific molecular molybdenum system[3] and a new pathway for vanadium.[12] The effect of ligand substituent(s) on the catalyst activity with molybdenum complexes will also be presented and discussed.[7-9]

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Simple and versatile approach for Pd immobilized nanocatalysts Application in alkynes semi-hydrogenation

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Polymer and fine chemicals companies show interest in the selective hydrogenation of alkynes since the alkenes produced by steam reforming contain some alkynes impurities that poisoned the subsequent processes. The preferred option to overcome this issue is the catalytic selective conversion of these impurities into alkene useful product.[1]Several transition metals have been reported for this process in which the main issues are the alkene over-hydrogenation and alkyne oligomerisation.[2] Among these metals, Pd has been identified as the most effective metal in terms of activity and selectivity. In this context, the application of PdNPs as catalysts enables a maximization of the available metal surface area and consequently enhance the catalyst productivity. To date, most heterogeneous catalysts are used in fine powders forms, which make them difficult to handle.[3] Alternative supports such as textile, paper and cotton were contemplated. Among them, conventional filter paper is of interest for catalyst immobilization since it is cost-effective, biodegradable, accessible and flexible.

In the present work, we describe the preparation and characterization of a novel low cost and reusable heterogeneous catalyst by painting a commercial filter paper with a Pd@CNT ink. This catalyst provided excellent results in the selective hydrogenation of alkynes and alkynols and could be recycled at least 5 times without loss of activity and selectivity.

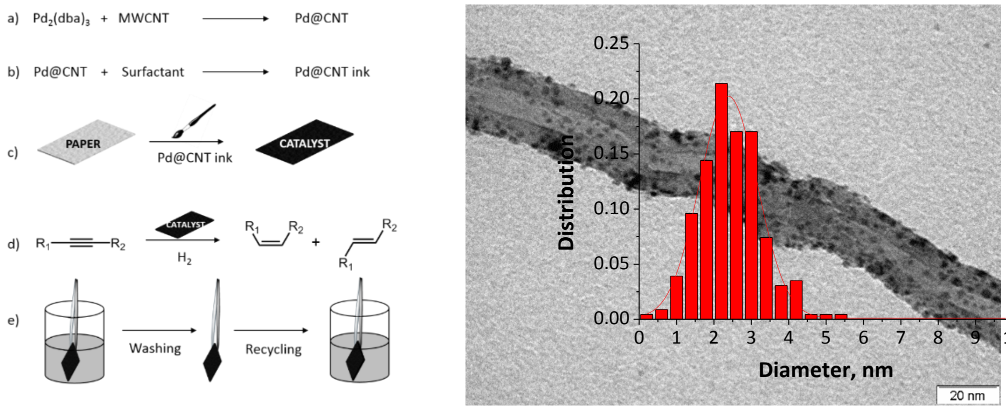

Figure 1. General approach for the preparation of the paper based nanocatalyst and TEM micrograph of Pd@CNT

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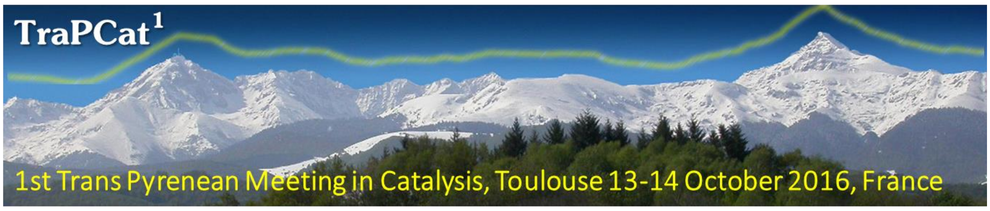

Eco-friendly catalyst based on copper nanoparticles in glycerol

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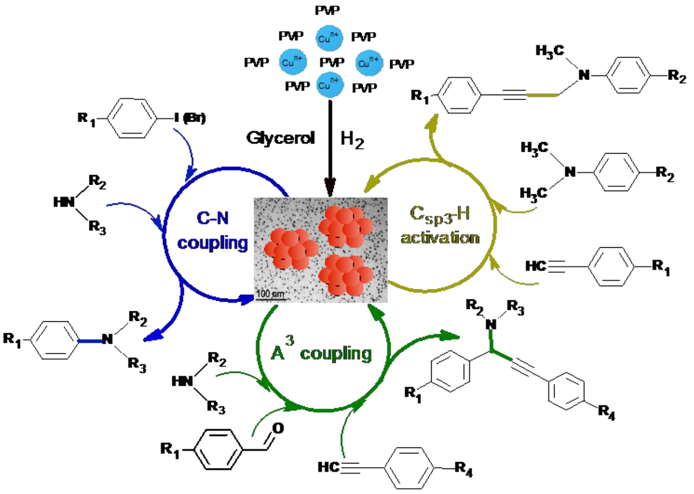
The use of metal nanoparticles (NPs) in catalysis has become more and more attractive for industrial applications [1]. "Nanocatalysis", combining colloidal catalysis and catalysis based on engineered nano-objects, reveals the ability to modify the pathway and selectivity of organic transformations [2]. Concerning solvents, glycerol is considered as an environmentally friendly medium which also permits to immobilise the catalyst, to easily extract the organic products and to recycle the catalytic phase [3]. Based on our previous researches [4], in this communication we report the synthesis of well-defined Cu(0)NPs and their applications in direct C-N bond formation processes, C_{sp3}-H bond alkynylation and three-component A^3 (aldehydes, amines and alkynes) coupling via C-H activation.

CuNPs in neat glycerol and in the presence of poly(vinylpyrrolidone) (PVP) were synthesised under H_2 atmosphere. The effect of the nature of the starting Cu precursors was in particular evaluated. Direct TEM analyses of the resulting colloidal suspensions in glycerol showed the formation of spherical, small (ca. 2 nm) and well-dispersed nanoparticles starting from [Cu(κ^2-*N*,*N*-TMEDA)(μ-OH)]$_2$Cl$_2$, Cu^I/mesityl or CuOAc, but only agglomerates were observed using Cu(OAc)$_2$. The as-prepared copper materials were fully characterised both in colloidal and solid state, by UV-Vis, XRD, HR-TEM, XPS and cyclic voltammetry analyses.



These nanocatalysts were successfully applied in C-N bond formation reactions between aryl halides and amines (including aqueous ammonia), leading to the expected products in high isolated yields. In addition, propargylamines have been selectively synthesised by two different ways: i) oxidative C-C cross coupling of tertiary amines with terminal alkynes using t-BuOOH as oxidant; and ii) a one-pot three-component A^3 process using aldehydes, amines and alkynes. Furthermore, CuNPs-based catalysts in glycerol permit an easy catalyst preparation and handling, together with a convenient recycling.

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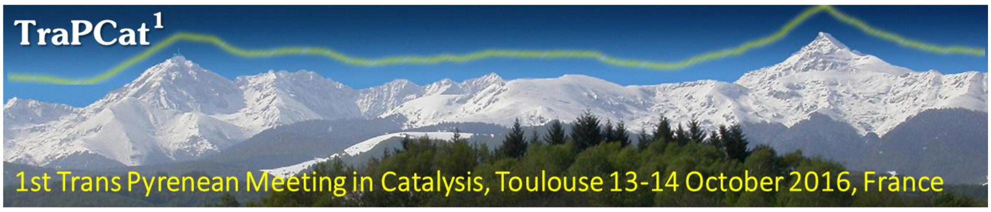

The PDF technique for a better structural characterization of nanocatalysts

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The metallic nanoparticles of catalytic interest have in common with all other nanomaterials to be quite challenging from the the structural characterization point of view, which is however of prime interest to better define the synthesis process, control their adequacy before use or even follow degradation with time. Use of classic X-ray diffraction (XRD) becomes impossible or at least quite ambiguous for very small particles or strongly disordered ones, which is however common for low temperature solution synthesis. But transmission electron microscopy (TEM) also presents limitations and pitfalls making its exclusive use sometimes dangerous (non statistic probe, disorder sensitivity, eventual evolution of sensitive samples).

The use, in association with TEM, of XRD in conditions allowing for Fourier Transform in order to get pair distribution functions (PDF) restores the classic combination local probe / statistic probe. Results of such combined study will of course be often in good agreement but often and more interestingly (from a strictly structural point of view) in disagreement, which should ultimately lead to a better understanding of the material and of the elaboration process.

In the very area of nanocatalysis, such approach contributed to evidence an unexpected structure for Rh, metastable and evolving through a non reversible transition when exposed to H_2[1], to decide the alloyed or segregated character of bimetallic nanoparticles through a simple and objective procedure[2], better understand the real effect of annealing in the optimization process of Pt/Ru alloys[3] and recently to better evaluate the real organization inside very small Fe/Ru nanoparticles[4].

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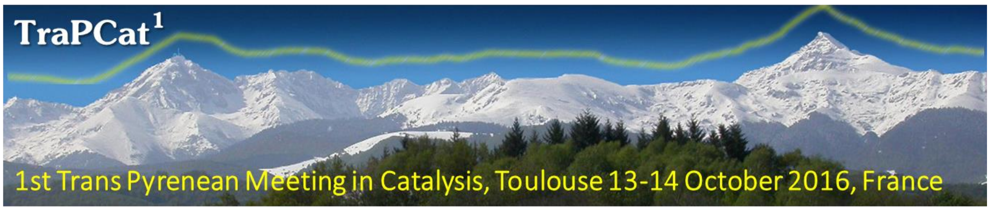

Synthesis of bimetallic catalysts supported on carbon nanotubes for fuel cell application

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Proton exchange membrane fuel cell (PEMFC) is a device that allows converting chemical into electricity. PEMFCs remain expensive compare to fossil energy equipment. The catalyst, platinum particles, represent near to 50% of the stack total cost, that's why most of research nowadays are concentrated on its optimization. Most of the time this catalyst is composed of platinum nanoparticles (~3nm) supported on carbon support[1,2]. It was shown that addition of a transition metal, like cobalt or nickel, to platinum is a good way to increase the catalytic activity[3,4], reducing the platinum content. It is well-known that the efficiency and the resistance of the catalyst are directly influenced by the nature of the support: carbon nanotubes (CNTs), and more precisely nitrogen doped CNTs facilitates the dispersion of nanoparticles and improves the long-term stability of the catalyst[5].

In this study, different kinds of doped CNTs have been synthetized by C-CVD: for which nitrogen doped and undoped sections on the same CNT are present[6]. The prepared material combined the properties of both. Then, these CNTs have been used to support PtCo (Figure 1) and PtNi bimetallic nanoparticles with good dispersion in spite of high metal loading (~45%wt.). Activity for Oxygen Reduction Reaction (ORR) has been studied by Rotating Ring Disk Electrode and half-cell experiments: these catalysts have shown excellent activity and resistance compare to commercial reference (Figure 2).

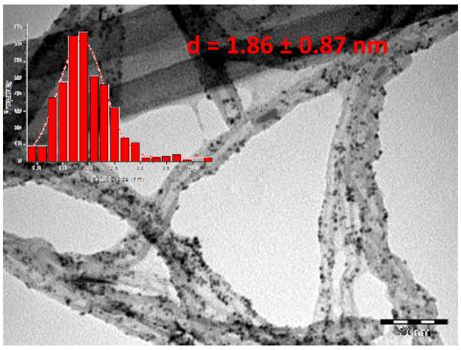

Figure 1

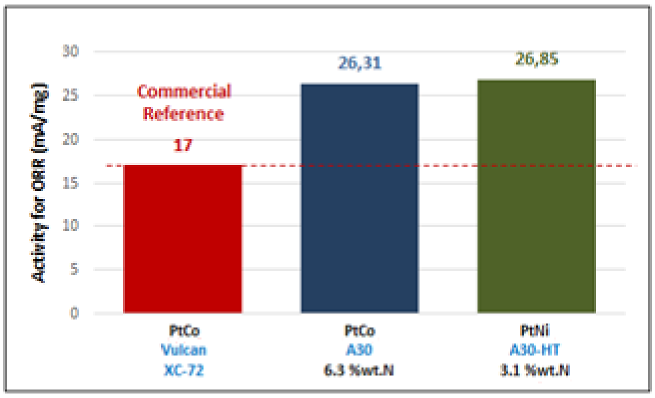

Figure 2

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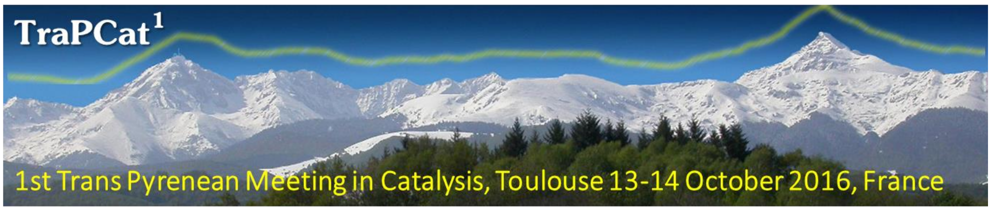

Design, preparation and applications of recyclable nano-catalysts

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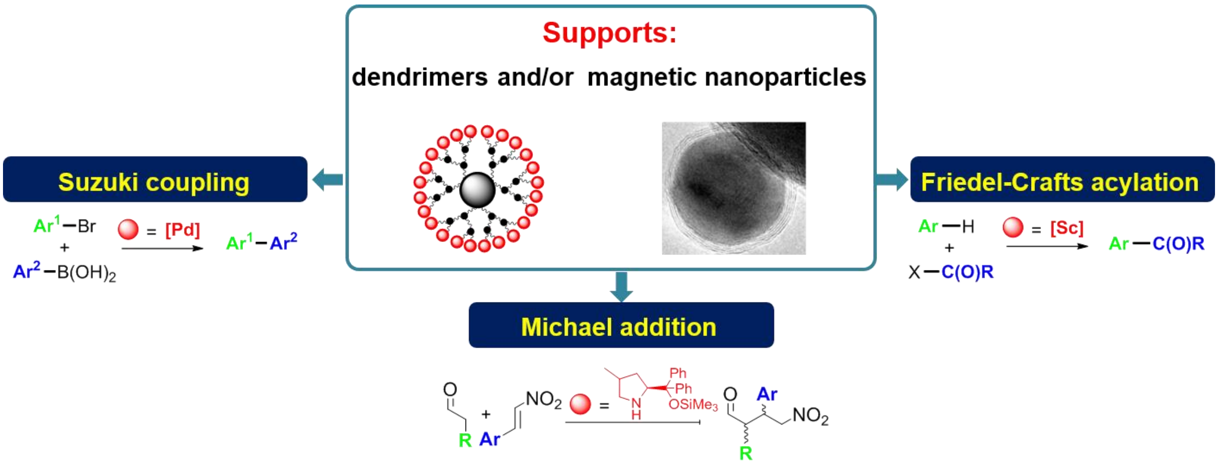
The development of efficient and eco-compatible catalytic systems enabling the preparation of organic compounds is of great concern.

One possible approach to reach this objective consists in rendering the catalysts recyclable by grafting them onto nanometric supports. Here we report the preparation of several supported nano-catalysts[1-4] involving either dendrimers[5] or magnetic nanoparticles as the supports, as well as their applications in various reactions (Figure 1). Besides their high activity and recyclability, some of the reported systems are moreover able to avoid metal leaching contrary to their corresponding molecular counterparts, thus allowing to prepare organic products free from metal traces.



For all examples: until 12 consecutive uses - recycling by precipitation or with a magnet

Figure 1 Some applications of nano-sized metal-based or organo-catalysts

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Platinum nanoparticle shape control to tune the selectivity in catalytic hydrogenation of α,β unsaturated aldehydes

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Since two decades, it is known that in heterogeneous catalysis, size reduction of metallic particles to a nanometric size can increase yields of catalytic reactions [1]. With the improvement of nanoparticles (NPs) synthesis, a better size and shape control of metallic NPs has been achieved. It is even possible to tune the specific crystallographic orientation of a metallic NP, which allows to evaluate the performances of specific crystallographic facets in model catalytic reactions [2, 3].

The cinnamaldehyde hydrogenation is an interesting test reaction to study chemoselectivity because of the simultaneous presence of an aromatic ring, a C=C and a C=O bond. For fine chemical industry, it is a challenge to develop selective catalysts for C=O bond hydrogenation to obtain the unsaturated alcohol. Indeed, the corresponding unsaturated alcohols found applications as intermediates in flavor, fragrance or pharmaceutical [4, 5].

In that frame, we develop the synthesis of platinum NPs showing specific crystallographic orientations. Two characteristic shapes have been produced: multipods (Figure 1), showing (111) specific orientation, and highly concave cubes (Figure 2) showing (hk0) high energy facets.

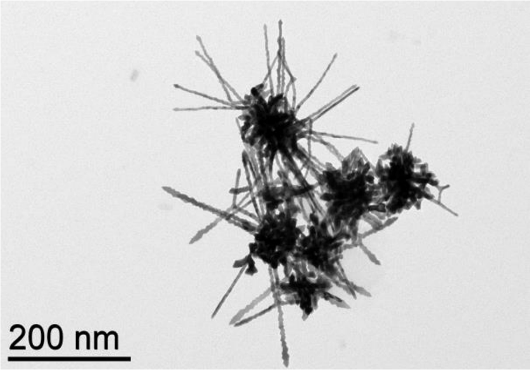

Figure 1 : Platinum multipods

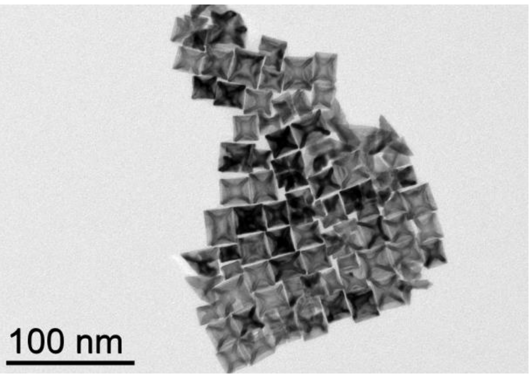

Figure 2 : Platinum concave cubes

Our results show that different orientations of crystallographic Pt NPs facets induce a very different selectivity in the hydrogenation of cinnamaldehyde.

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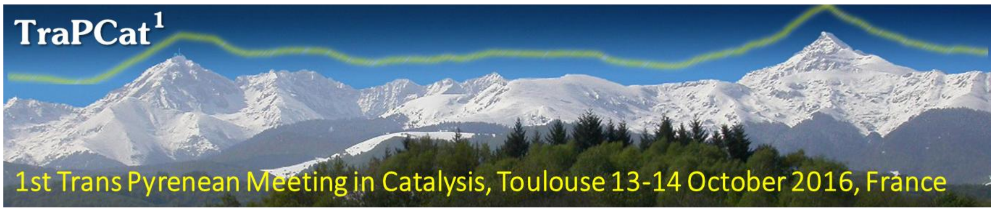

Copper and nickel nanoparticles supported on carbon nanotubes for CO_2 hydrogenation

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The CO_2 hydrogenation is a promising alternative for CO_2conversion into fuels and useful chemicals, such as methanol, formic acid or methane. Homogeneous Ir, Rh or Ru complexes have been extensively used for promoting the CO_2 activation and its further reduction [1, 2]. Although satisfactory activity and selectivity have been reported, the stability of the catalyst and its recovery remains a key challenge. In order to address these issues, the use of supported catalysts has been investigated using a great number of metals (Ru, Rh, Pd, Pt, Ni and Cu) supported on different oxide solids (Al_2O_3, SiO_2, TiO_2, ZrO_2) or carbon materials [3-7]. Among the different supports, multi-walled carbon nanotubes have raised much interest in recent years due to their exceptional features, such as high electrical conductivity, large specific surface area and unique tubular structure, which may efficiently improve the dispersion of the active phase [6,7]. In addition, carbon nanotubes present an excellent hydrogen adsorption-activation capacity, which leads to an enhancement of the performance for CO_2 hydrogenation.

This work deals with the synthesis and characterization of Ni and Cu catalysts supported on CNTs (10 wt.%) and their application in CO_2 hydrogenation. Catalysts were prepared by decomposition of an organometallic precursor, bis(1,5-cyclooctadiene nickel(0) or mesityl copper(I), in THF under hydrogen atmosphere [8,9]. AN-heterocyclic carbene ligand was used as stabilizer. Variation of temperature, metal precursor concentration and molar carbene/metal ratio were performed in order to study their influences on the activity for CO_2 hydrogenation. For the purpose of comparison, unsupported Ni and Cu nanoparticles were also obtained following the same methodology.

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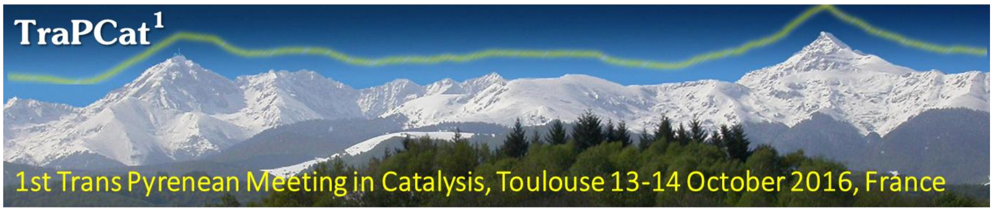

Palladium nanoparticles in glycerol stabilised by alkaloids: design of green-catalysts

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For the last three decades, metallic nanoparticles (MNP) have been largely studied due to their interesting properties,relevant for several applications in different fields (microelectronics, materials and catalysis).[1] “Nanocatalysis” has appeared as a new concept which combines both colloidal catalysis and catalysis based on engineered nano-objects, showing defined structures and composition.In contrast with common organic solvents, glycerol, mainly coming from the biodiesel production generated as a waste, is an innovative solvent for MNP stabilisation, mainly due to its negligible vapour pressure, high solubilising ability, low miscibility with other solvents and low cost.[2] Our team proved the glycerol ability for MNP immobilisation and for the catalytic phase recycling using mostly phosphorous-based ligands.[3] In order to use biomass-based stabilisers offering the possibility to interact with the metallic surface through the aromatic moiety, we have prepared a family of catalysts stabilised by optically pure cinchona type alkaloids. The synthesis of PdNPs in neat glycerol result in small, spherical and well-dispersed nanoparticles, which were fully characterized ((HR)TEM, EDX, XDR, XPS, NMR) and applied in catalysis, leading to a large variety of products thanks to their ability to catalyse different processes. Moreover the catalytic phase could be recycled without any activity lost.

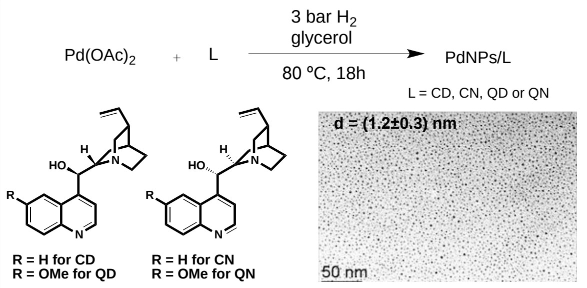

Fig. 1 Synthesis of PdNPs in neat glycerol (top), structure of the cinchona type alkaloids (bottom left) and TEM image of PdNPs stabilsed by QD (bottom right)

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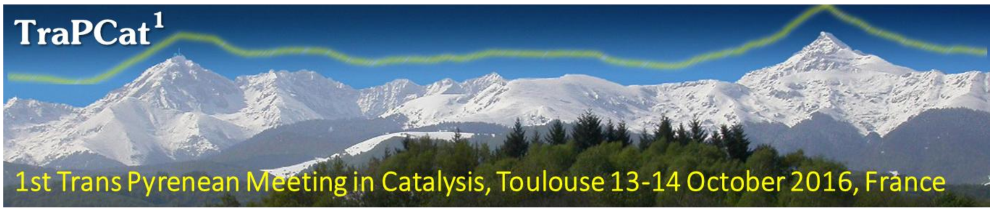

Molecular and Metal Oxide (Nano)catalysts for the Oxidation of Water to Dioxygen

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1. Introduction -Molecular hydrogen is a promising candidate for replacing fossil fuels as energy sources. However, its renewable and clean generation is still a great challenge. A particularly attractive solution is the production of this gas from water splitting (WS) by sunlight (Eq. 1), that is, sunlight is used to promote a thermodynamically uphill reaction where water is transformed into molecular oxygen and hydrogen[1]. Therefore, an enormous progress has been recently made on the development of catalysts to speed up the set of redox half-reactions involved (Eq. (2) and (3)).

$$2H_2O \rightarrow 2\,H_2 + O_2 \quad (1)$$

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \quad (2)$$

$$2\,H^+ + 2e^- \rightarrow H_2 (3)$$

Water oxidation (Eq. (2)) is still nowadays the bottleneck reaction hampering the development of commercial devices for the photo-production of hydrogen.

2. Results and Discussion – both molecular species and metal oxides are plausible candidates for efficiently catalyze this challenging reaction. In general terms, despite high turnover frequencies (TOFs) are obtained with molecular catalysts, the generation of rugged catalysts achieving large turnover numbers (TONs) with no decomposition is still a challenge. However, if durability is the main challenge for molecular WOCs, slow reaction rates are common when their heterogeneous or colloidal counterparts are employed. The lack of both mechanistic and surface chemistry information prevents the rational development of faster nanomaterials for this transformation. This contribution will deal with the work carried out in our laboratories to unravel the key factors that can change these general trends, finally obtaining fast and robust molecular-based anodes[2,3] and extremely fast metal oxides nanocatalysts[4,5] for the oxidation of water.

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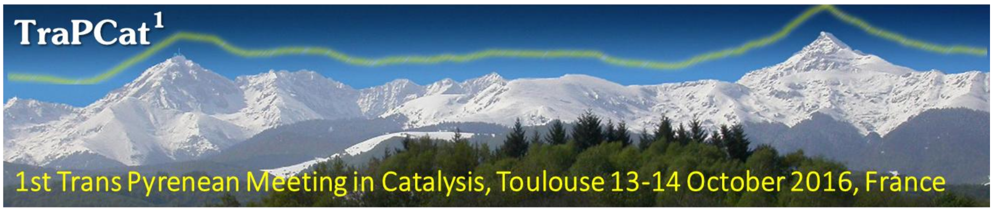

Bio-sourced ionic solvents and supercritical CO_2: design of catalytic systems for sustainable processes

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Developing new green processes is a key driver of chemistry. One of the main challenges is the use of green solvents and avoiding fastidious separation steps or solubility problems.[1] In this context, solvent engineering is a very promising process. This would allow to trigger changes in solubility and in the physicochemical properties of the solvent. Thus, solvent engineering would enable to couple two or more steps of a chemical process, increasing efficiency and decreasing energy and raw materials wastage. Within this project, we are developing new bi-phasic and tunable medium for the synthesis of metal nano-catalysts and target molecules composed of bio-compatible and tunable Deep Eutectic Solvents (DESs) combined with supercritical CO_2 (Fig. 1). Indeed, the DESs will allow the immobilization of the catalyst and avoid the contamination of the desired product.[2,3] However, practical applications of DESs have been hindered by their high viscosities that handicap mass transfer. [4] The addition of supercritical CO_2 can act as an effective, low cost and reversible switch to decrease viscosity and promote transport properties in DESs.

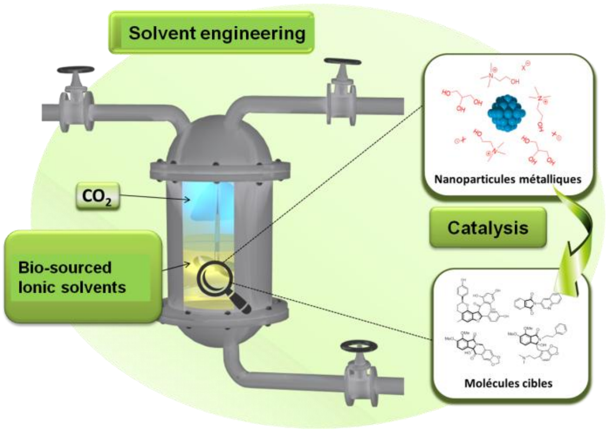

Figure 1: Biphasic systems coupling DES and $scCO_2$ as a bio-compatible and tunable reaction medium for the synthesis of target molecules

Herein, the synthesis of deep eutectic solvents using cholinium based ionic liquids as hydrogen bond acceptor and glycerol as hydrogen bond donor is presented. Their properties in supercritical CO_2 such as their solubility and their viscosity are being determined. Particularly, the viscosity of these systems in supercritical CO_2 is investigated using an original technique based on the detection of the fluorescence emission intensity of molecular rotors.

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Towards New Auto-assembling Artificial Metalloenzymes

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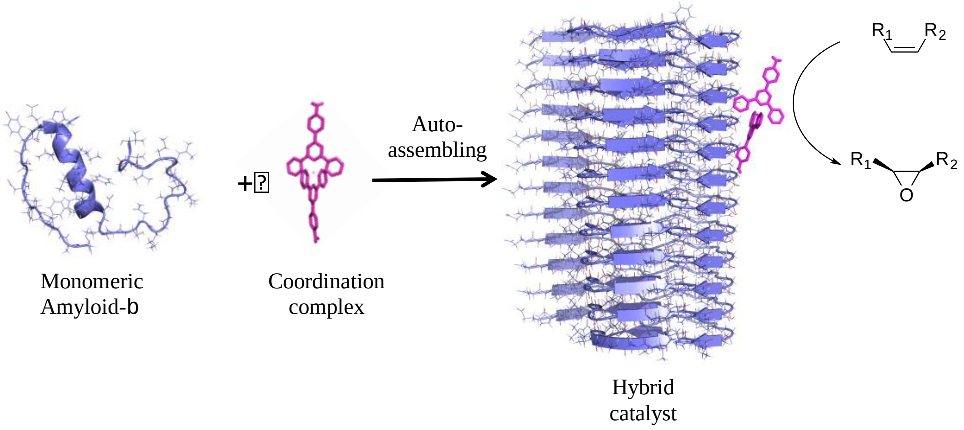
With their unequaled rates, selectivity and specificity, metalloenzymes remain champions of catalysis. These unique properties are the combination of precise fine-tuning of the metal centre together with remote effect of the protein chain. If chemists excel at controlling the catalytic properties of a metal centre, controlling long-distance effects remains difficult. This raised the idea of inserting coordination catalysts into biomolecules (proteins, nucleic acids,…) aiming at enriching their catalytic ability with outer sphere effects. In this context, systems have been developed using many different biomolecules.[1]

We propose to use amyloid peptides to create new self-assembling hybrid catalysts. These peptides have the ability to form stiff and robust fibres in physiological conditions. Incorporating coordination complexes into these fibres would afford a new type of bio-supported catalysts.

In this goal, amyloid-β peptides were recombinantly produced in *Escherichia coli*, and an improved purification procedure was developped.[2] A library of aromatic coordination complexes was synthesized and fully characterized, showing activity in catalytic oxidations. Their interaction with amyloid fibres was assessed using different physicochemical techniques. The resulting scaffolds were tested in catalysis, showing promising properties as hybrid catalysts.



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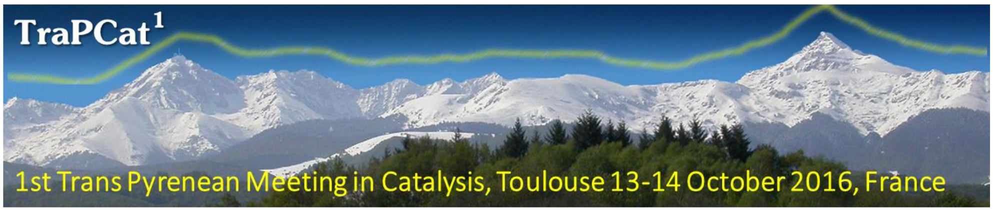

Dry reforming of methane over transition metals-based catalysts

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Methane and carbon dioxide are the two main greenhouse gases which cause the climate changes [1][2]. Dry reforming of methane (Eq. 1) allows converting these gases into the synthesis gas. In this reaction, CO_2 reacts with methane to form syngas, from which many other chemicals, such as methanol, dimethyl ether, hydrogen and liquid hydrocarbons can be produced [3]. In reality, DRM is an interesting option for the valorization of natural gas, biogas, and carbon dioxide recovered from carbon dioxide capture processes. The economic aspect is also propitious. Natural gas reserves, for example, are larger than petroleum reserves [1]. Biogas, formed by anaerobic digestion of organic biomass and wastes, is largely produced at different scales. DRM reaction and its side reactions are expressed in equations (1-5):

Dry reforming of methane:

$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$ (1)

Side reactions:

Water-gas shift reaction: $CO_2 + H_2 \leftrightarrow H_2O + CO$ (2)

Boudouard reaction: $2CO \leftrightarrow C_{(s)} + CO_2$ (3)

Methane cracking reaction: $CH_4 \leftrightarrow C_{(s)} + 2H_2$ (4)

Carbongasification: $H_2O + C_{(s)} \leftrightarrow CO + H_2$(5)

Despite the economic and environmental benefits, no technical solution for DRM has emerged at industrial scale yet. The main reason is the catalytic deactivation by carbon deposition (Equations 3-5) and the sintering of both support and metal particles. So the main challenge of this process is the design of a performant catalyst, which is active and stable under severe operational conditions of DRM. The aim of this work was focused on the investigation of transition-based catalysts using hydroxyapatite as catalytic support. Nickel seemed to be the most performant metal among various metals investigated (Ni, Co, Cu, Zn, Fe). Nickel particle size and the metal-support interaction played the important role for the stability of nickel catalysts prepared. For example, 5 wt.% Ni supported on hydroxyapatite support containing Ni particles around 25-50 nm was found to be active and stable for 300 h of time-on-stream at 700°C. The results obtained were promising for an eventual utilization at industrial scale.

The next work will be focused on the minimization of the nickel particle size (smaller than 10 nm).

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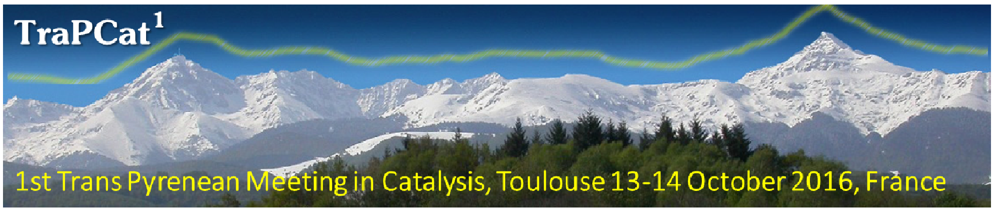

Cobalt aluminate nanoparticles synthesized by nanocasting: Effect of Co/Al ratio on glycerol APR

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Hydrogen can be sustainably produced from biomass-derived oxygenates by aqueous-phase reforming (APR), a low energy cost process. Glycerol is a particularly attractive biomass feed due to its availability.

Transition metals and their oxides are potential candidates for replacing noble metal catalysts due to their high cost-effectiveness and outstanding behaviour. Cobalt containing nanostructured spinel-type oxides ($CoAl_2O_4$), with aluminium in octahedral sites and cobalt in tetrahedral ones, is regarded as an important heterogeneous catalyst for application such as CO oxidation, ethanol steam reforming and water-gas shift [1].

In view of their high specific surface areas, high pore volumes and narrow pore size distributions, ordered mesoporous silica still attracts intensive attention. SBA-15, with its hexagonally packed unidimensional mesopore system and its high thermal and mechanical stability, is considered an excellent functional template for nanocasting [2].

In this work cobalt aluminate nanoparticles have been synthesized by nanocasting using SBA-15 silica as template, and then evaluated their catalytic performance in glycerol APR.

SBA-15 silica mesoporous and nanosized cobalt aluminate spinel with high specific surface area were prepared and characterized by wide variety of methods including thermal analysis, SEM, XRD, N_2 adsorption, spectroscopic analysis (Raman and FTIR) and temperature programmed techniques.

SBA-15 was synthetized by hydrothermal treatment [3] at 383 K for 24 h using non-ionic triblock copolymer Pluronic P123 ($PEO_{20}PPO_{70}PEO_{20}$) as a surfactant, 2M HCl solution and as silica source tetraethyl orthosilicate (TEOS). Finally, the organic-free SBA-15 pore structure was obtained by calcination under air at 1123 K for 6 h in a muffle oven heating in air at 1 K min^{-1}.

Cobalt aluminium oxide catalysts were prepared by incipient wetness impregnation method. Right amounts of cobalt nitrate and aluminium nitrate in order to obtain Co/Al molar ratio between 0.25 and 0.625 were dissolved in water and added to SBA-15 utilizing a rotary evaporator. The samples were calcined by heating in air at 5 K min^{-1}, until 1073 K for 5 h. SBA-15 template was removed by washing with 2M NaOH solution at 333 K. This material is referred to as $SCoAl_2O_4$.

SBA-15 show isotherms type IV with a sharp capillary condensation step at intermediate p/p_0 classification and a H1 hysteresis loop typical for mesoporous materials with uniform pores. FT-IR spectrum for pure SBA-15 reveals four peaks, occurring respectively at 465, 803, 967, 1090 cm^{-1}, that are attributed to Si-O bond stretching of silica compounds. The X-ray diffraction profiles at low angle obtained for SBA-15 detect three characteristic peaks, corresponding to the (1 0 0), (1 1 0) and (2 0 0) reflections, which verifies the structural ordered hexagonal symmetry (*P6mm*) of the pore arrays of these materials [3]. The d-distance for (1 0 0) SBA-15 is about 8.5 nm.

N_2 physisorption isotherm of $SCoAl_2O_4$ exhibits slightly double hysteresis loop demonstrating the existence of the bimodal pore system. According to the XRD registered at high 2θ angle, the observed reflections are attributed to $CoAl_2O_4$ crystalline phase (PDF 44-0160). This is confirmed by FTIR that manifest bands at about 670 and 560 cm^{-1}, characteristics of the cobalt loaded materials.

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Sponsor Index

NEXT (Nano, mesures EXtrêmes and Théorie)

The Nano, EXtreme measurements and Theory (NEXT) project implicates six laboratories on the Toulouse campus (within a 1.5 kilometer radius), working at the frontier of knowledge in the domains of nanophysics and nanochemistry, condensed and soft matter physics, optics, and atomic/cluster physics. It involves on the same site the main French research organism (CNRS), a leading scientific university (Université Paul Sabatier UPS), and a "Grande École"/engineering school hosting a strong research department (INSA Toulouse). NEXT comprise 186 permanent scientists (a good balance between CNRS and UPS/INSA researchers), 89 engineers/technicians, and 160 PhD students/postdocs, and encompasses the entire community of fundamental physics in Toulouse. An original aspect of the NEXT project should be noted: almost one quarter of NEXT staff consists of chemists, who are perfectly integrated in their respective laboratories and work hand-in-hand with physicists. Another specificity of NEXT is the strong interplay between experimental and theoretical teams (3 out of the 4 experimental laboratories include theorists, 2 are well-recognized theoretical laboratories in physics and chemistry). NEXT is involved in different scientific fields of physics:

- Advanced nanomaterials and nanodevices
- Nano optical quantum physics
- Quantum coherence and Information
- Transverse technical platforms

Most of the operations undertaken by NEXT aim to develop new scientific axes, to exploit complementary expertise and to connect different domains of research within ambitious, original, but consistent and realistic scientific projects. In addition, the six laboratories of NEXT are associated with a doctoral school (Sciences de la Matière), and NEXT scientists are strongly involved at the Master and doctoral level. NEXT plans to offer Master scholarships for foreign students, and to develop the Training Center in Nanosciences and online Master training. At the PhD level, NEXT will promote the interactions with the private sector, by giving access to PhD students to the "Doctoriales" (a week-long seminar to facilitate the integration in the private sector), and by promoting a two-months internships in high-tech companies and funding exchange programs during PhD thesis. Scientific achievements of NEXT are also exploited through a strong interaction with the private sector, patent filings, conference organization, and publications in high quality journals.

Institut de Recherche sur les Systèmes Atomiques et Moléculaires Complexes

The Institut de Recherches sur les Systèmes Atomiques et Moléculaires Complexes ou IRSAMC is a federation of chemistry and physics laboratories involved mainly in fundamental research on domains with an applicative interest such as nano-objects, biology, astro-physics, astrochemistry, or laser technologies. A strong participation of theoretical Chemists and Physicists costitutes the originality of this federation. The institute is comprised of four laboratories:
- Laboratoire Collisions Agrégats Réactivité (LCAR) UMR 5589,
- Laboratoire de Chimie et Physique Quantique (LCPQ) UMR 5626,
- Laboratoire de Physique et Chimie des Nano-Objets (LPCNO) UMR 5215,
- Laboratoire de Physique Théorique (LPT) UMR 5152,

All of them are located on the campus of the Paul Sabatier University apart from the LPCNO which is located at the INSA. The institute plays an important scientific animation role through the organization of seminars. It also organizes large public communication events.

Institut National des Sciences Appliquées

With 14,000 alumni present in all economic sectors, the "Institut National des Sciences Appliqu" of Toulouse, an international, pluridisciplinary, state engineering school, is recognised for the excellence of its five-year education which attracts students of a high academic level and who have obtained excellent results at the Baccalaureat. 10 INSA key points Degree courses, widely known and recognized Awell-established network of graduates working all over the world. Every year more than 10 percent of the engineering graduates in France graduate from the INSA Group. International, a prime focus: International programs, multicultural campuses, double degrees, More than 3,600 international students and over 1,100 international agreements Research, cutting edge: Over 50 research units. Scientific and technological developments for application in business and industry. Values, unifying: Based on equality, diversity, inclusiveness and excellence, developing socially-aware engineers. Teaching, differently: Versatility, entrepreneurship High-level engineers with open minds, excellent culture and a taste for sport. Degree opportunities, innovative: Individually tailored, personalized guidance and theme-based courses Innovative and carte projects. High achieving students: Admission open to all degree levels, based on academic record, grades and motivation. Business, partners: Internships, guest lecturers, research contracts, job-dating, expertise Job prospects, exceptional: 1.5 months to find the first job. Campuses, lively: Sport, culture, arts, clubs An education supported by top level research INSA-Toulouse provides a range of 8 engineering specialisations , including computer sciences, civil engineering, mathematical engineering and biochemical engineering. Its courses, linked to the latest scientific advances, are supported by the activity of leading-edge research laboratories , backed by large industrial groups, for example in the fields of new materials for aeronautics, environmental protection techniques and nano-objects. Innovative pedagogy for long-lasting learning Throughout the course, the students are confronted with concrete, complex projects and problems on which they work in groups, with the help of teachers when requested. No questions, no lectures is the principle behind this active learning approach, experimented by renowned universities in America and Northern Europe, and now advocated by UNESCO. Engineers open to the world The international dimension has been a priority for INSA since it opened and international sections have gradually been set up. On campus, one in five students is an international student. INSA welcomes students with a range of profiles: students with a technological baccalaureat, students opting for a cooperative education alternating periods of academic study and industrial experience and continuing education students. Being open to the world also involves the students commitment to the community which is highly valued and credited as part of the course.

Institut National Polytechnique de Toulouse (INPT)

The INP Toulouse includes 7 Grandes Ecoles and nearly 7,000 students. Agronomy , Chemistry , Electronics , Hydraulics, Computer , Telecommunication, Mechanical, Veterinary Science , Meteorology ... are all areas where the INP Toulouse excellence of training is recognized nationally and internationally. Besides the force of his teaching , the INP Toulouse is based on a potential of over 500 faculty members from 17 laboratories anchored at the heart of its schools. Working in collaboration with the CNRS , the INRA and the Toulouse universities, the power of this research allows maintaining and developping relationships with industry , particularly in the context of partnerships.

Institut de Chimie de Toulouse (ICT)

The Institut de Chimie de Toulouse (ICT – FR CNRS 2599) is a Federation that brings together all the lifeblood of molecular chemistry in Toulouse. The ICT has the ambition to be the representative of this community at the national and international levels. The scientific activity of the groups that make up the ICT covers all areas of molecular chemistry ranging from very basic studies to the most applied aspects , and the actions at the interface with other disciplines such as physics and biology . Often the results obtained are valorized in partnership with the major industrial groups or regional SMEs.

Laboratoire de Physique et Chimie des Nano-Objets

Studying the exciting properties of nano-objects is a thriving research field at the crossroads of solid-state physics, chemistry and material science. This research has greatly evolved during the past decades for two main reasons. First, a large variety of growth techniques allow precise control of the physical properties (such as material, size and shape) and therefore the future applications of the nano-objects. Second, advances in nano-electronics and microscopy allow addressing and controlling the properties of individual nano-objects. The goal of this ultimate miniaturization of solid-state devices is to create objects with new properties that cannot be achieved in their macroscopic counterparts. These nano-devices find application in many branches of industry such as telecommunication and information processing, transport, safety, health and environment. They also open up exciting avenues for fundamental research based on controlling individual quantum states optically or electrically. Our research aims to study individual, self-assembled nano-objects with optimized structural quality. The systems studied include semiconductor quantum dots, magnetic nano-particles, nano-tubes, biomolecules and DNA strands. The samples are grown at the LPCNO and by our numerous national and international collaborators. The expertise of the LPCNO covers:

- Optical spectroscopy and semiconductor spin physics
- Nanostructuring
- Nanomagnetism
- Transport measurements
- Synthesis of nanoparticles
- Molecular modeling

Laboratoire de Chimie de Coordination

Research at LCC focuses on fundamental and applied aspects of molecular transition-metal chemistry and hetero-elements chemistry in the context of sustainable growth. Its objectives are targeted on life sciences, atom economy, nanosciences and materials for the future.

Laboratoire Hétérochimie Fondamentale et Appliquée

The “Laboratoire Hétérochimie Fondamentale et Appliquée” (LHFA, UMR CNRS 5069) is one of the components of the “Institut de Chimie de Toulouse”. It is composed of an average of 60 people (including 23 permanent) and its activity occurs mainly in three areas.

1 - Basic research

Through its history and its activities, the LHFA is positioned as one of the leading laboratories in the chemistry of the heteroelements at the national and international level. Its core business is the synthesis and study of original molecules, highly reactive species. This axis represents a common denominator of the activities of the different teams and gives a good thematic coherence to the laboratory. However, the developed research themes go beyond study highly reactive species derived from the p-block elements. Thus, activity and expertise of the LHFA have been greatly enriched and important projects related to the chemistry of the heteroelements were gradually initiated. In particular may be reported significant contributions in coordination chemistry and Organometallic chemistry, in the field of nanoparticles (in base metals or heteroelements), in the chemistry of polymers. Interest increasingly harder for Catalysis also grew, as well for the fine chemicals for the controlled polymer synthesis. The title even laboratory, Heterochimie basic and applied, reflects perfectly its positioning and its thematic priorities. The guideline is to combine fundamental cutting-edge research (unusual chemical structures, original link modes, new chemical transformations) with aspects more applied areas strong stakes (catalysis, materials and nanochemistry).

2 - Valuation

Industrial contracts account for nearly 2/3 of the resources of the unit (excluding salaries). The LHFA collaborates with large industrial groups such as Arkema, Ifpen, Sanofi, Solvay, and SMEs (paintings Maestría).

3 - Education

The LHFA is actively involved in training and research in hosting students from 1st to 3rd cycle courses: IUT, BTS, high schools (ENS, École Polytechnique), Masters, universities. The laboratory is also attached to the Graduate School of Sciences of the matter of Toulouse (ED 482). The LHFA consists of 4 research teams which have focused their activities around six main themes (not usual multiple bonds - cash electron deficiency - organometallic complexes - fine chemicals - Catalysis - materials) and two accompanying services.

Laboratoire de Génie Chimique

A joint research unit The LGC is a chemical engineering research centre located in Toulouse It is a joint research unit (UMR5503) bringing together: The National Centre of Scientific Research (CNRS), The Institut National Polytechnique (INP) and the Universitul Sabatier (UPS) ...linked to ... Industry Research in association with more than 50 industrial partners Technology Transfer Regional centre for innovation and technology transfer (CRITT) TTT (Toulouse Tech Transfer) Training : Schools and University UPS INP (ENSIACET / ENSAT) Intra-University Working group in process engineering Midi-Pyres Region International: numerous universities abroad and organised into 6 research departments. The aim of research at LGC through these 6 research departments is to design, optimize and scale-up new products, materials or transformation processes to respond to industrial demand for development and product adaptation. aided by the service for technical support for research within the LGC. - The main function of the Service for Process Analysis (SAP) is to ensure high quality services to the research teams, but also to any company that requires technical or intellectual assistance in the field of process engineering which concern the feasibility, the improvement and the control of a process. - The SAP is based on the scientific environment and the expertise of the laboratory. It can implement about twenty analytical apparatuses to produce ”Process data”. - The LGC also benefits from an on-campus mechanical workshop that enables the design and construction of experimental rigs and pilot plants for research purposes. A research activity In process industries including the chemical, pharmaceutical, biochemical, food and wastewater treatment industries a number of physical, chemical and/or biological operations are performed in order to transform raw materials into a final product. Multidisciplinary research conducted at LGC focuses on the understanding and the implementation of these diverse process operations combining experimental, modelling and numerical approaches. The scale of interest ranges from molecules and multiphase interfaces to micro-reaction engineering and industrial pilot plants. which targets the industrial processes... Research conducted at the LGC impacts numerous industries and sectors including biotechnology, and the medical and environment sectors. situated on 3 Campuses The LGC employs more than 300 staff in 7 000m located on 3 different campuses around Toulouse : at Paul Sabatier University : 1 500m at the Facults Sciences et Ingerie 300m at the Facult Pharmacie at INP - ENSIACET : 4 500m at lEcole Nationale Supeure des Ingeurs en Arts Chimiques et Technologiques (ENSIACET) At INP - ENSAT : 500m at lEcole Nationale Supeure Agronomique de Toulouse (ENSAT)

Interuniversity Center for Materials Research and Engineering

The CIRIMAT Carnot Institute gathers more than 200 people working in the field of Materials Science and engineering, Physico-chemists, materials scientists, pharmacists, polymer physicians unite their expertise in this future-oriented institute aiming at providing new answers to nowadays challenges. Divided into 7 research groups, dedicated to complementary aspects of materials science and engineering, CIRIMATs research concerns all families of materials : metals/alloys, ceramics, polymers... and composites ; and in link with a wide range of applications. The CIRIMAT develops research on the conception, elaboration, characterization, and evaluation of in use properties, for metallic, ceramic, or polymer materials. It is largely involved in technology transfer concerning the innovative materials that are being investigated. It is equipped with specific tools dedicated to the study of materials durability as well as relating to scale-up aspects. Competences: Core business: Materials Mechanics and processes Hight competences: Micro and nano technologies / systems Energy Transport Technologies for health

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