

SCF2021 Congress

June 29th & 30th, 2021

Catalysis web-session

DivCAt  

BOOK OF ABSTRACTS

Welcome to SCF21-Catalysis web conference.

This event is organized place in replacement on the Catalysis session of the 2021 Congress of the French Chemical Society which should have taken place during in Nantes.

The conference is organized by the Catalysis Division (DivCat) of the French Chemical Society.

The organizers are grateful to the University of Lille for providing the technical resources.

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PROGRAM



Tuesday, June 29th 2021 – MORNING

9h15 – 9h30 **Welcome** - Françoise MAUGÉ & Axel LÖFBERG

SESSION 1 – Chairs: Françoise MAUGÉ & Franck LAUNAY

S1 9h30 10h45	9h30	KN1	Reaction-induced changes in structure and activity of supported platinum catalysts investigated in situ: from single atoms to clusters	DESSAL Caroline, LEN Thomas, AFANASIEV Pavel, MORFIN Franck, ROUSSET Jean-Luc, AOUIINE Mimoun, CHIZALLET Céline, SOLER Lluís, LLORCA Jordi, PICCOLO Laurent	IRCELYON, UNIV. LYON - CNRS	
	10h00	#154	O1	Oxidation catalysis at isolated sites modeled by polyoxometalates	<u>GUILLEMOT Geoffroy</u> , ZHANG Teng, SOLÉ-DAURA Albert, POBLET Josep-Maria, PROUST Anna, CARBO Jorge J	IPCM, SORBONNE UNIVERSITE
	10h15	#118	O2	Hydrogenation in water of mono- and disaccharides to polyols using Ni-Fe/SiO ₂ catalysts: optimization of the reaction conditions and beneficial effects of Fe	<u>SADIER Achraf</u> , ROBERT François, AMIENS Catherine, PHILIPPOT Karine, WOJCIESZAK Robert, MARCEAU Eric	UCCS-UNIVERSITÉ DE LILLE- CNRS
	10h30	#13	O3	Metal-metal synergy in silica-supported early/late heterobimetallic catalysts	<u>CAMP Clément</u> , LASSALLE Sébastien, VEYRE Laurent, JABBOUR Ribal, GAJAN David, LESAGE Anne, DEL ROSAL Iker, MARON Laurent, THIEULEUX Chloé	CP2M, UNIV. LYON - CNRS

10h45 – 11h00 **Pause**

SESSION 2 – Chairs: Dorothée LAURENTI & Clément GUIBERT

S2 11h 12h	11h00	#277	O4	Magnetically induced CO ₂ methanation in continuous flow over supported nickel catalyst and the role of supports	<u>GHOSH Sourav</u> , OURLIN Thibault, CHAUDRET Bruno	LPCNO, INSA, CNRS, TOULOUSE
	11h15	#301	O5	Abatement of toluene through “storage-catalytic regeneration” cycling	<u>SONAR Shilpa</u> , GIRAUDON Jean-Marc, JEAN-FRANÇOIS LAMONIER, MORENT Rino, DE GEYTER Nathalie, LÖFBERG Axel	UCCS, UNIVERSITY OF LILLE - CNRS
	11h30	#38	O6	Reactivity of glucose over homogeneous tungsten- and molybdenum-based catalysts	CHIZALLET Céline, <u>EL MOHAMMAD Sabah</u> , LARMIER Kim	IFPEN
	11h45	#28	O7	Improved activity and enantioselectivity of heterogenized molecular catalysts	<u>CANIVET Jérôme</u>	IRCELYON, UNIV. LYON - CNRS

Tuesday, June 29th 2021 - AFTERNOON

SESSION 3 – Chairs: H     OLIVIER-BOURBIGOU & Eric MARCEAU

S3 14h 15h30	14h00	KN2	Biodiversity as an amazing source of enzymes for electrocatalysis	LOJOU Elisabeth	BIP-CNRS-MARSEILLE UNIVERSITY
	14h30 #103	O8	Synthesis of bio-inspired electrode materials for hydrogen evolution	ZAMADER Afridi	CEA GRENOBLE
	14h45 #152	O9	Exploratory study of new hybrid catalysis systems based on enzymes and gold catalysts supported on layered double hydroxydes	GASTALDI Cedric , HELAINE Christine, FORANO Claude, GAUTIER Arnaud	Universit�� Clermont Auvergne CNRS
	15h00 #60	O10	Photodecolourization of methylene blue by TiO ₂ supported zeolite clinoptilolite	BASER Emre , SONMEZ Buse	HISAR SCHOOL
	15h15 #224	P1	Hydrogenation of furfural and nitrobenzene with nickel carbide (Ni ₃ C) and phosphides (Ni ₂ P, Ni ₁₂ P ₅) in mild conditions	ANDRE R��mi , MEYNIEL L��na, CARENCO Sophie	LCMCP, SORBONNE UNIVERSITE - CNRS
	15h20 #236	P2	Heterogeneous second-sphere coordination modified iron porphyrin for carbon dioxide reduction	ZHANG Chanjuan , BOITREL Bernard, HALIME ZAKARIA, AUKAULOO Ally	IC2M, UNIVERSITE PARIS SACLAY
	15h25 #272	P3	Hydrodeoxygenation and hydrogenolysis of biomass-derived products magnetic induction	MUSTIELES MARIN Irene	LPCNO, INSA TOULOUSE-CNRS
	15h30 #276	P4	Zero-valent nickel nanoparticles on halloysite-based supports: synthesis, characterization and applications	PEREZ ALONSO Alejandro	IMT MINES ALBI

15h35 – 15h50 Pause

SESSION 4 – Chairs: Karine VIGIER & Malika BOUALLEG

S4 15h50 17h05	15h50 #279	O11	Electrocatalysis promoted by non-covalent halogen bonding	SCH��LLHORN Bernd , FAVE CLAIRE, GRONI SIHEM, G��RARD H����, ROBERT MARC	LEM, UNIVERSIT�� DE PARIS
	16h05 #92	O12	Nickel catalyzed allylation reaction with allylic alcohol	MOUHSINE Bouchaib , KARIM Abdallah, DUMONT Cl��ment, SUISSSE Isabelle, SAUTHIER Mathieu	UCCS, UNIVERSITY OF LILLE - CNRS
	16h20 #96	O13	Asymmetric transfer hydrogenation of ketones promoted by a well-defined manganese pre-catalyst supported by chiral aminophosphines	AZOUZI Karim	LCC-CNRS-TOULOUSE
	16h35 #162	O14	Borinic acids as catalysts in organic synthesis	ALMETWALI Fatima	LCMT, ENSICAEN
	16h50 #271	O15	Selective formation of nitroso-sulfapyridine by new catalytic system: decatungstate/magnetite/H ₂ O ₂	CHENG Peng , SARAHA Mohamed, BONNET Pierre, MOUSTY Christine, MAILHOT Gilles	UNIVERSITE CLERMONT AUVERGNE, CNRS

Wednesday, June 30th 2021 - MORNING

9h15 – 9h30 **Welcome**

SESSION 5 – Chairs: Nathalie TANCHOUX & Céline CHIZALLET

S5 9h30 10h45	9h30	KN3	Nanochemistry inspired by molecular chemistry for catalysis	<u>PHILIPPOT Karine</u>	LCC-CNRS-TOULOUSE
	10h00	#51	O16 Gold nanoelectrocatalysts for glycerol oxidation towards hydrogen production	HOLADE Yaovi, REMITA Hynd, TINGRY Sophie, <u>TULEUSHOVA Nazym</u> , ABDELLAH Ibrahim, CORNU David	IEM, UNIVERSITY OF MONTPELLIER
	10h15	#159	O17 Influence of copper precursor on the catalytic transformation of oleylamine during Cu nanoparticles synthesis	<u>PESESSE Antoine</u> , CARENCO Sophie	LCMCP-SORBONNE UNIVERSITE
	10h30	#193	O18 Upgrading biomass by bimetallic catalysts	<u>CARDONA Miquel</u> , LECANTE Pierre, DINOI Chiara, DEL ROSAL Iker, POTEAU Romuald, PHILIPPOT Karine, AXET M. Rosa	LCC-CNRS-TOULOUSE

10h45 – 11h00 **Pause**

SESSION 6 – Chairs: Pascal FONGARLAND & Benoît LOUIS

S6 11h 12h	11h00	#201	O19 CO ₂ reduction in the liquid phase from immobilized CNC-pincer nickel(II) complexes	<u>DE TOVAR Jonathan</u> , REUILLARD Bertrand, KOEPF Matthieu, ARTERO Vincent	CBM, CEA Grenoble
	11h15	#239	O20 In situ/operando x-ray absorption spectroelectrochemistry: new insights in the catalytic reduction of CO ₂ by Fe porphyrins	<u>MENDOZA Daniela</u> , ANXOLABEHRE-MALLART Elodie, ROBERT Marc, LASSALLE-KAISER Benedikt	SYNCHROTRON SOLEIL
	11h30	#296	O21 Effective homogeneous catalysis of electrochemical reduction of nitrous oxide to dinitrogen at transition metal complexes.	<u>DEEBA Rana</u> , CHARDON-NOBLAT Sylvie, COSTENTIN Cyrille	DCM UGA CNRS
	11h45	#105	O22 Amphiphilic polymeric nanoreactors containing Rh(I)-NHC complexes for aqueous biphasic hydrogenation catalysis	<u>LABANDE Agnès</u> , SAMBOU Salomon Sasaline, HROMOV Roman, RUZHLYLO Illia, WANG Hui, ALLANDRIEU Audrey, SABATIER Cassandra, COPPEL Yannick, DARAN Jean-Claude, GAYET Florence, MANOURY Eric, POLI Rinaldo	LCC-CNRS-TOULOUSE

KEYNOTE LECTURES

REACTION-INDUCED CHANGES IN STRUCTURE AND ACTIVITY OF SUPPORTED PLATINUM CATALYSTS INVESTIGATED *IN SITU*: FROM SINGLE ATOMS TO CLUSTERS

C. Dessal,¹ T. Len,¹ P. Afanasiev,¹ F. Morfin, J.L. Rousset,¹ M. Aouine,¹ C. Chizallet,² L. Soler,³ J. Llorca,³ L. Piccolo¹

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Keywords: Heterogeneous catalysis; single-atom catalysts; *in situ/operando* characterization

Summary: Stimulated by recent advances in scanning transmission electron microscopy (STEM), single-atom catalysts (SACs) have become prominent materials in heterogeneous catalysis.^[1] In spite of the numerous reports on promising catalytic performance and noble-metal saving, single-atom stabilization remains a challenge – in particular for noble metals on oxides.^[2] In addition, single atoms are not necessarily more efficient than their cluster or nanoparticle counterparts.^[3] In this presentation, the previous issues will be illustrated for two prototypical catalytic systems: CO oxidation on Pt/Al₂O₃ and photocatalytic hydrogen evolution reaction over Pt/TiO₂. The combined use of catalytic testing, STEM, *operando* X-ray and infrared absorption spectroscopies, and DFT calculations, reveal the influence of the reactive environment on Pt nuclearity and oxidation state (generally consisting in clustering and reduction, as shown in Fig. 1), which in turn correlate to changes in catalytic activity.^[4–7] From this knowledge, strategies can be suggested to stabilize the metals in an ultradispersed state.

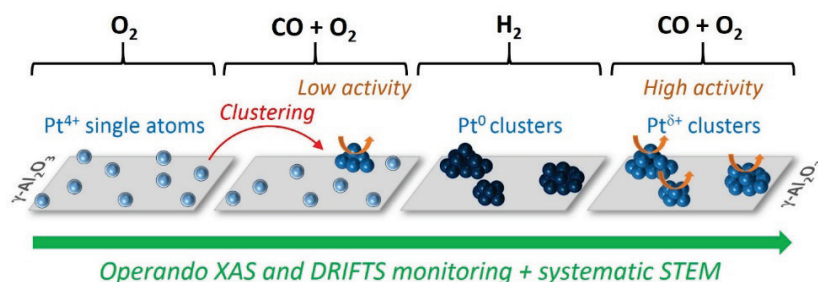


Fig. 1 Illustration of clustering and activation phenomena in alumina-supported single Pt atoms during CO oxidation or after exposure to hydrogen.^[5]

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BIODIVERSITY AS AN AMAZING SOURCE OF ENZYMES FOR ELECTROCATALYSIS **KN 2**Elisabeth LOJOU¹

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Keywords: Metalloenzymes, Electrocatalyse, Extremophilic bacteria, Copper homeostasis

Summary:

Extreme environments host bacteria adapted to withstand conditions that are a priori harmful to any living organism. The metalloenzymes which catalyze within these microorganisms numerous chemical reactions necessary for their metabolism, exhibit themselves outstanding properties. They thus appear as attractive catalysts for developing sustainable biotechnologies. Resistance to high salt concentrations, high temperatures, presence of metals, activity in conditions of low pH and substrate concentration ... these are the factors whose impact on the electrocatalysis of the reduction of oxygen and the oxidation of hydrogen have been studied. Thanks to the knowledge of the molecular basis which ensure an optimal electron transfer to electrodes, the interest of the use of these extremozymes in a high temperature enzymatic fuel cell is demonstrated.

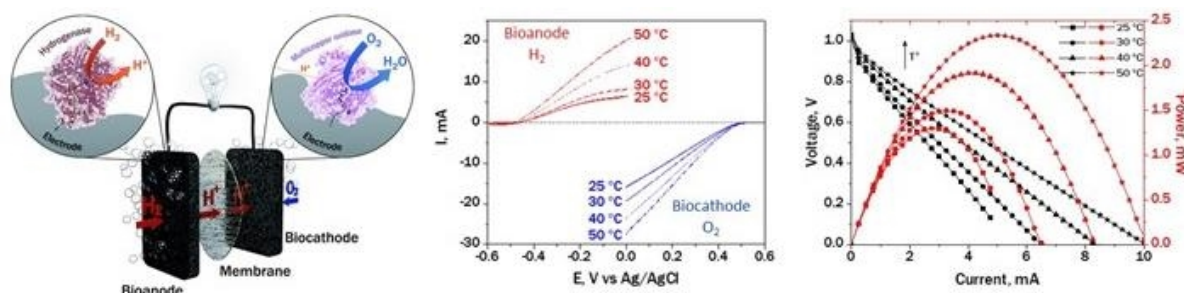


Fig. 1 Performance of the enzymatic fuel cell based on the hyperthermophilic hydrogenase from *A. aeolicus* and on the thermostable bilirubin oxidase from *B. pumilus*.

References:

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Nanochemistry inspired by molecular chemistry for catalysis

Karine PHILIPPOT ^{1,2}

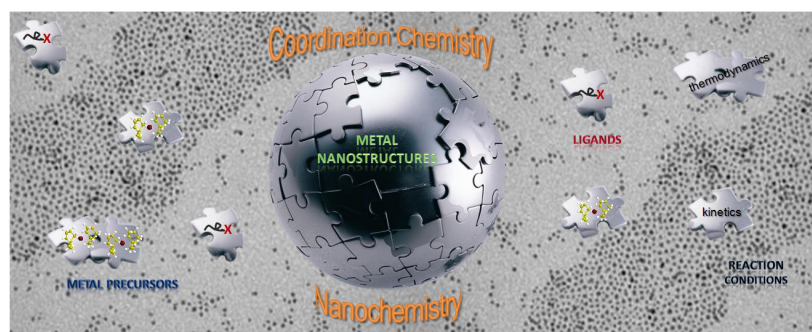
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Keywords: molecular and coordination chemistry; nanochemistry; metal nanoparticles; nanomaterials; catalysis

Summary: Many efforts are devoted to get well-defined metal-based nanomaterials given their attractive properties in catalysis.¹ The team Engineering of Metal Nanoparticles at LCC-CNRS (Toulouse, France), develops efficient tools for the synthesis of controlled metal nanoparticles by using the concepts of molecular chemistry, i.e. by hydrogenation of organometallic/metal organic complexes in mild conditions (r.t.; 3 bar H₂).² This approach can lead to ultrasmall nanoparticles of controlled size dispersion and composition, either monometallic or bimetallic (alloy, core-shell, surface-decorated) and also supported (on silica or carbon supports). The obtained nanomaterials present interesting properties in catalysis³⁻⁵ or energy.⁶⁻⁸ This will be exemplified through recent results.



References

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- 8 Fu X.-P., Peres L., Esvan J., Amiens C., Philippot K., Yan N., *Nanoscale* **2021**, in press (DOI: 10.1039/d1nr01054a).

ORAL COMMUNICATIONS

OXIDATION CATALYSIS AT ISOLATED SITES MODELED BY POLYOXOMETALATES

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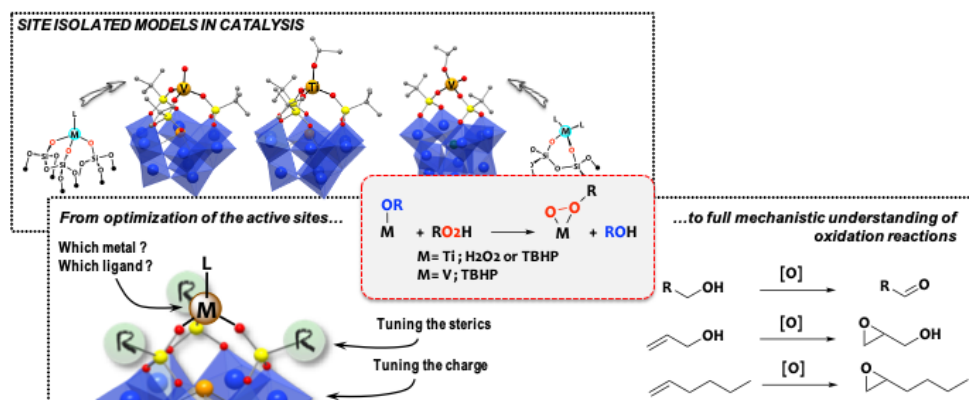
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Keywords: Site-isolated model; polyoxotungstate; titanium; vanadium; oxidation; mechanistic study.

Summary: Reliable structure-activity relationship assignment in heterogeneous catalysis is a difficult task because of the complexity of the surface and to the fact that only a small fraction of the sites is actually involved in the catalytic reaction. Whereas major progresses in the conception of single-site heterogeneous catalysts are possible through a rational molecular approach,^[1] the use of discrete molecular models can still provide valuable clues to improve our understanding of the intermediates and mechanisms occurring in heterogeneous systems. The silanol-decorated polyoxometalates (SiloxPOMs) that are depicted in the figure below provide preorganized coordination environments that model site-isolation in heterogeneous systems.^[2] In this presentation, we want to stress their analogy with silica-supported catalysts and highlight how their use as catalysts allow us (i) to assess a reliable structure-activity relationship relevant to liquid phase heterogeneous oxidation catalysis,^[2-3] and (ii) to understand mechanistic aspects and to unveil the nature of the sites that are effectively active in oxidation catalysis by titanium-silicalite TS-1^[4-5] and by vanadium oxides.^[6]



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HYDROGENATION IN WATER OF MONO- AND DISACCHARIDES TO POLYOLS USING NI-FE/SIO₂ CATALYSTS: OPTIMIZATION OF THE REACTION CONDITIONS AND BENEFICIAL EFFECTS OF FE

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Keywords: xylose, maltose, hydrogenation, bimetallic catalysts, leaching

Summary: Sugars issued from lignocellulosic biomass can be used as platform molecules for the manufacturing of polyols by catalytic hydrogenation. Apart from costly noble metals, pure or metal-promoted Ni has been used to catalyze these reactions, but concerns exist about the catalyst stability and metal leaching. Furthermore, compared with the hydrogenation of glucose or fructose, the literature is scarce for the hydrogenation of xylose and maltose to, respectively, xylitol and maltitol, two molecules of interest for the food and pharmaceutical industries. Supported Ni-Fe alloyed nanoparticles were reported to present high conversion and selectivity in the hydrogenation of xylose at 150°C,^[1] and, indeed, Ni-Fe catalysts are known to outperform Ni systems in a series of hydrogenation reactions in the gas phase or in non-aqueous media.^[2] Investigating to what extent this benefit also exists for the hydrogenation of mono- and disaccharides in water is the purpose of the present work.

The hydrogenation of xylose (4-11 wt% in water) was tested in batch conditions under 20 bar H₂ using two 50 wt_{metal}% catalysts, Ni/SiO₂ and bimetallic Ni₇₀Fe₃₀/SiO₂, prepared by deposition-precipitation with urea (same metal particle size Ø = 5-7 nm).^[3] The selectivity to xylitol was 100% and the carbon balance > 98% in the temperature range 80-150°C. The Ni-Fe catalyst turned out to be the more active, more significantly at 80°C, showing a 40% higher initial reaction rate compared with the Ni catalyst, and a 100% conversion after 4h at that temperature (110 mg catalyst). Moreover, Ni/SiO₂ reverted to an inactive Ni²⁺-phyllosilicate phase upon two recycles, while the structure and activity of the Ni-Fe nanoparticles were conserved. Performing the reaction at 80°C limited the leaching of each metal below 15 ppm; at 50°C the leaching was 5 ppm Fe and 8 ppm Ni only, but the reaction took 15h to complete. Maltose hydrogenation was carried out in similar conditions (4-19 wt% in water, 20 bar H₂), with a carbon balance > 98%. Setting the reaction temperature to 80°C not only limited the metal leaching on the two catalysts, but also allowed cancelling side-reactions of maltose hydrolysis to glucose, and subsequent hydrogenation to sorbitol. Here as well, the Ni-Fe catalyst was more active and more stable than the Ni catalyst (initial reaction rate higher by 70%), but the hydrogenation of maltose was slower than that of xylose, as 24h were needed to complete the reaction with Ni-Fe at 80°C (selectivity to maltitol: 100%). A lower reaction order with respect to xylose or maltose suggests a stronger adsorption of the substrates onto the surface of bimetallic Ni-Fe particles. A comparison with SiO₂-supported Ni-Fe nanoparticles tailored *via* an organometallic route (hydrogenation of [Ni(COD)₂] and {Fe[N(SiMe₃)₂]₂}; Ø = 3-4 nm) emphasizes the importance of keeping the two metals in their reduced form for an optimum activity, the beneficial role of Fe-enriched surfaces, and the higher activity of the Ni₇₀Fe₃₀ formulation.

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METAL-METAL SYNERGY IN SILICA-SUPPORTED EARLY/LATE HETEROBIMETALLIC CATALYSTS O 3

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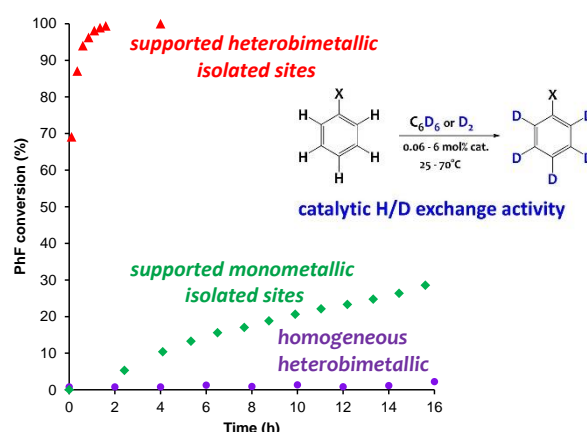
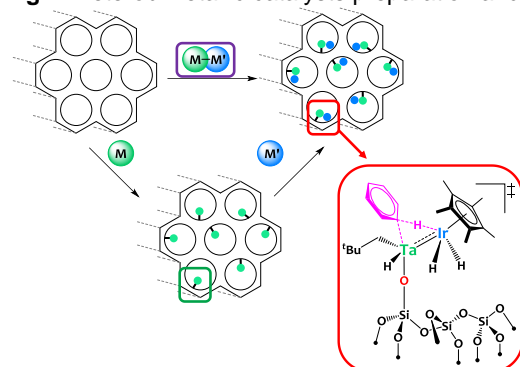
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Keywords: Dual-Atom Catalysis; Surface Organometallic Chemistry, Hydrogen Isotope Exchange

Summary: A current frontier area in organometallic catalysis is cooperative activity between two distinct metal centers in order to promote original chemistry.^[1] Most systems associating early and late transition metals developed to date feature bulky ligands in order to stabilize such heterobimetallic edifices, but most of the time prevent substrates to bind across the two metals, which could explain why catalytic applications of these heterobimetallic complexes are limited at the moment.^[2] Surface Organometallic Chemistry (SOMC) allows the isolation of highly unsaturated early metal (eg. Ta, Hf) species featuring unique reactivity, and is an attractive approach to overcome this limitation. In this presentation we will describe our latest results focused on the development of new synthetic approaches to yield well-defined Ta/Ir and Hf/Ir heterobimetallic species featuring usual metal-metal bonds in solution and supported at the surface of silica materials.^[3,4] The SOMC methodology prevents undesired dimerization/agglomeration as seen in solution and therefore allows to access unique and stable low-coordinate single-site species not attainable in solution. These original supported M/Ir (M = Hf, Ta) species are stable and exhibit drastically enhanced catalytic performances in H/D exchange reactions with respect to (i) monometallic analogues as well as (ii) homogeneous systems. In particular, deuteration of arenes is achieved with excellent productivity under mild conditions (25°C, low D₂ pressure) without any additives. Mechanistic studies suggest a rare heterobimetallic oxidative addition of C–H bonds across the two metals mostly driven by the accessibility of the early metal site.^[5]

Fig. 1 Heterobimetallic catalysts preparation and HIE activity.



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MAGNETICALLY INDUCED CO₂ METHANATION IN CONTINUOUS FLOW OVER SUPPORTED NICKEL CATALYST AND THE ROLE OF SUPPORTS O 4

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Keywords: Heterogeneous Catalysis; Magnetic Induction; Supported Catalyst; Magnetic Hyperthermia; Sabatier Reaction; Power-to-Gas

Summary: The rising issues related to carbon dioxide (CO₂) have been recently debated in Intergovernmental Panel on Climate Change (IPCC) and Conference of the Parties (COP), and global guideline has been established for sustainable development toward “zero emission”. These issues reinforce the quest for more secure and diversified strategies for controlling the carbon neutrality. Inspired by the photosynthetic process in nature, the chemical activation and transformation of CO₂ with the aid of heterogeneous catalysis is likely the best way to regenerate fuels and value-added chemicals. Although CO₂ hydrogenation is challenging because of the high thermal stability of CO₂, resulting in low reaction conversions, significant progress has been made toward transforming CO₂ to single carbon products (methane, methanol, formaldehyde, formic acid, and notably, carbon monoxide) via direct hydrogen reduction process in gas and solution phase.^[1] In this context, Sabatier reaction (CO₂ to methane conversion) is an efficient process for generating renewable energy and integration into local power-to-gas (P2G) units.

Traditionally, supported first-row transition metal (Ni) and noble metals (Ru or Rh) are being used as a heterogeneous catalyst under continuous flow condition at the mid-temperature range for the Sabatier reaction under conventional thermal heating. Recently, the magnetically induced heating process has been utilized to carry out the Sabatier reaction using magnetic nanoparticles which play the dual role of heating agent and catalyst.^[2] It has been suggested that the heating of the catalytic system using magnetic induction effect gives major benefits in terms of activation rate, which is quite fast (~100 ms), and the system temperature can reach the desired reaction temperature (200-400°C) in a few minutes with respect to the hours for traditional heating. But the conventional magnetic nanoparticles suffers from agglomeration at high temperature under dynamic reaction operating condition. The objective of the current study is to utilize the magnetic induced heating effect of commercially available heating agents to carry out the Sabatier reaction under magnetic induction using a supported nickel catalyst. Herein supported nickel catalyst has been prepared using an organometallic decomposition route. The characterizations of the structure of supported nickel catalysts by TEM microscopies and of the electronic properties by XPS spectroscopy will be presented and put into perspective of the activities of these catalysts on Sabatier reaction. Also, the energy efficiency of the magnetically induced heating condition will be discussed.

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ABATEMENT OF TOLUENE THROUGH “STORAGE-CATALYTIC REGENERATION” CYCLING O 5

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Keywords: Adsorption, catalytic oxidation, sequential process, Toluene abatement, Hopcalite, Silver.

Summary:

Volatile organic compounds (VOCs) such as toluene are emitted from industrial activities, wastewater and so on. Due to the increased concern about human health and air quality the research of efficient technologies is needed in order to meet the increasingly stringent environmental legislations. Among them “storage-regeneration” cycling is proposed as an effective and promising way to eliminate low-concentrations of VOC. ^[1] Toluene is, first, adsorbed on the catalyst followed by regeneration of the material through thermal oxidation into CO₂ and H₂O. For this purpose, Hopcalite is chosen due to its strong combination of adsorption and redox properties. The catalytic properties of Hopcalite were enhanced by impregnating it with Silver (Ag = 0-10 wt%), which is known for the formation of lattice defect, oxygen vacancies and oxygen mobilities and reduction abilities, all of which aid in the oxidation of VOCs at low reaction temperature. ^[2] We performed the adsorption of toluene (100 ppm) for 35 min, resulting in a valuable adsorption capacity. During thermal regeneration good selectivity toward CO₂ (~100 %) and overall CO₂ yield (70-100 %) were obtained. Hopcalite without Silver and Hopcalite-1 Ag have been subjected to a cyclic process for four times without significant evolution of performances. This indicates good stability of materials which was further confirmed by analysing fresh and used material (XPS, XRD and Raman). This work opens the path for the development of low energy demanding processes for the abatement of low concentration VOCs from air streams.

Table 1 Comparison of materials during toluene (100 ppm) adsorption followed by temperature programmed desorption in oxidizing atmosphere.

Materials	Toluene ADS at RT (μmol g ⁻¹)	Toluene DES at RT (μmol g ⁻¹)	Toluene DES During TPR (μmol g ⁻¹)	T _{max} CO ₂	CO ₂ Formed During TPR (μmol g ⁻¹)	CO ₂ Yield (%)
Hopcalite	35.3	0.1	0.8	200	241.0	97.5
Hopcalite-0.5 Ag	35.8	0.2	0.2	140	247.9	98.9
Hopcalite-1 Ag	40.1	1.0	11.4	195	193.9	69.1
Hopcalite-2 Ag	40.5	0.9	10.7	200	202	71.2
Hopcalite-10 Ag	51.7	1.3	1.8	190	340.5	94.1

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REACTIVITY OF GLUCOSE OVER HOMOGENOUS TUNGSTEN- AND MOLYBDENUM-BASED CATALYSTS

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Keywords: Glucose, Retro-aldol condensation (RAC), Isomerization, Epimerization, Molybdenum and Tungsten Homopolyanions.

Summary: The production of ethylene glycol from biomass-based glucose is possible through Retro-aldol Condensation reaction (RAC) towards the glycolaldehyde key intermediate.^[1] Undesired C₃ species (dihydroxyacetone, glyceraldehyde) are likely to be formed due to the formation of fructose,^[1] via isomerization of glucose.^[2] The epimerization of glucose to mannose forms another secondary transformation. However, the RAC of mannose leads to the formation of C₂ intermediates. Homogenous tungsten and molybdenum salts [tungstic and molybdic acids or homopolyanions such as ammonium metatungstate (AMT) and ammonium heptamolybdate (HMA)] are active catalysts for the RAC of sugars, but are less active in glucose interconversion to fructose.^[1,3] These species are also catalytically active for epimerization.^[1] A clear understanding of the reaction mechanism and of the nature of the active species at a molecular scale has not been yet reached. Herein, we provide a combined spectroscopic study including XAS, NMR and Raman techniques, together with density functional theory (DFT) calculations to investigate this problematic. A first study aimed at detecting the possible metal-carbohydrate complexes by means of NMR measurements. Various molybdate and tungstate complexes with glucose, mannose and fructose were modeled and optimized using Gaussian 09 and their ¹H and ¹³C chemical shifts were computed. DFT calculations provide markedly good correlation with experiments. All the detected species are complexes involving a sugar ligand chelated to a ditungstate or dimolybdate ion. Based on the ex-situ NMR analysis, confirmed by DFT calculations, the carbonyl group is not implicated in any of the complexes and either linear hydrate or furanose forms of the sugars are favored (Fig. 1, a, b). We also studied the catalytic behavior of such complexes by conducting kinetic analysis with various homogenous W- and Mo-based species to evaluate the effect of changing the initial form of the metal precursor. In addition, various operating conditions (pH, temperature, reaction atmosphere, metal/sugar ratio, ...) were changed in order to determine the most relevant parameters affecting the selectivity. In parallel, the optimized complexes were used as starting points for the calculation of reaction pathways for the formation of the different possible products. Activation free energies and formation free energies of the W- active species, in particular mononuclear complexes, (Fig. 1, c) leading to the main product, glycolaldehyde, have explained why little selectivity is observed for isomerization.

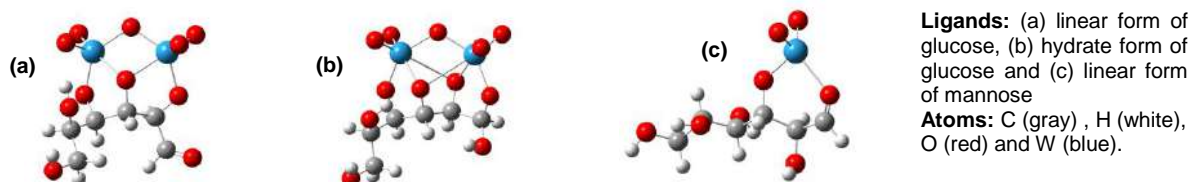


Fig. 1: DFT optimized models for tungstate complexes of glucose and mannose.

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IMPROVED ACTIVITY AND ENANTIOSELECTIVITY OF HETEROGENIZED MOLECULAR CATALYSTS

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Keywords: Porous Organic Polymers, Metal-Organic Frameworks, Molecular Catalyst, Heterogenization

Summary: Heterogeneous catalysis allows to circumvent the problem of separation of the catalyst from the products and to simplify its recyclability. The integration of the catalytically active centers into a solid support without loss of performance compared to the homogeneous analog is still a major challenge.

To change the paradigm of molecular catalytic processes for fine chemical synthesis and green fuel production, we introduced recently the concept of solid porous macroligand for heterogenized molecular catalysis.^[1] Having molecularly-defined active sites, porous macroligands have been found to drive the activity and the selectivity of heterogenized catalytic processes on a similar way as molecular ligands but with the advantage of the structuration in a three-dimensional framework^[2] and the confinement within a porous nanospace.^[3]

We first demonstrated that the design of highly efficient heterogeneous catalyst based on porous organic polymer (POP) and metal-organic frameworks (MOF) is driven by the Hammett parameter of bipyridine-chelating macroligand as demonstrated for the photoreduction of carbon dioxide, with turnover frequencies among the highest reported for heterogeneous photocatalytic formate production.^[2,4] More recently, we showed that the heterogenization of a chiral benzene ruthenium molecular complex within the MIL-101-NH-Gly-Pro cavity allows a threefold enhancement of the selectivity in the catalyzed asymmetric transfer hydrogenation of ketone compared to homogenous analogue system.^[3] The DFT-level computations supported by experimental data highlight the crucial role of the MOF as a macroligand for the ruthenium catalyst to direct the enantioselectivity of the reaction. In these two cases, accurate descriptor at the molecular level can be used to predict activity and selectivity of confined molecular catalysts within macroligands.

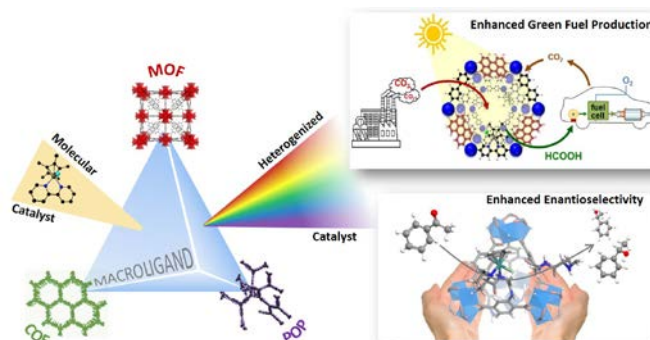


Fig. 1 Concept of Porous Macroligands for Improved Catalytic Efficiency

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SYNTHESIS OF BIO-INSPIRED ELECTRODE MATERIALS FOR HYDROGEN EVOLUTION

O 8

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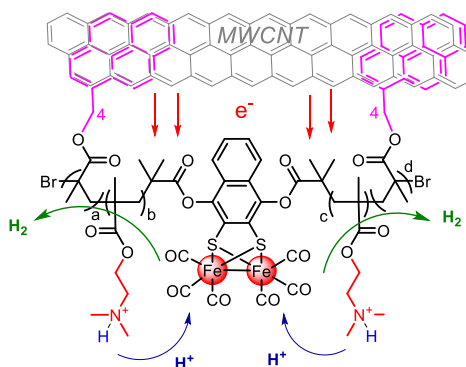
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Keywords: [FeFe] hydrogenase, hydrogen production, oxygen stable, functional polymers, MWNTs

Summary: [FeFe] hydrogenase enzymes have attracted tremendous attention for their reversible hydrogen production with remarkable catalytic rate (6000–9000 molecules H₂ s⁻¹ per site) operating close to thermodynamic equilibrium under physiological condition (pH 6-8) using only earth-abundant metals.^[1] Industrial usage of such enzymes is challenging due to their oxygen sensitivity and fragility.^[2] However, they are also valuable blueprints in the development of synthetic catalysts for hydrogen production.^[3] Hence, during the last few decades, structural and functional mimics of these enzymes have become of interest for large-scale hydrogen production as a promising alternative to carbon-based economy.^[4]

Our recent work focuses on the preparation of oxygen stable hydrogen evolution catalyst (HEC) by embedding a [FeS(CO)₃]₂ core, a mimic of native enzyme, within functional polymers structures, based on recently reported metallopolymers.^[5] Specifically, we are developing a methodology to anchor these metallopolymers onto nanostructured electrode substrates such as multiwalled carbon nanotubes (MWNTs) in a stable manner. This has allowed thorough assessment of the catalytic performance of the cathode materials for hydrogen production at neutral pH using electrochemical methods coupled to gas chromatography and spectroscopic techniques.

Fig .1 Schematic representation of metallopolymers immobilised on MWNTs for H₂ production.



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EXPLORATORY STUDY OF NEW HYBRID CATALYSIS SYSTEMS BASED ON ENZYMES AND GOLD CATALYSTS SUPPORTED ON LAYERED DOUBLE HYDROXIDES

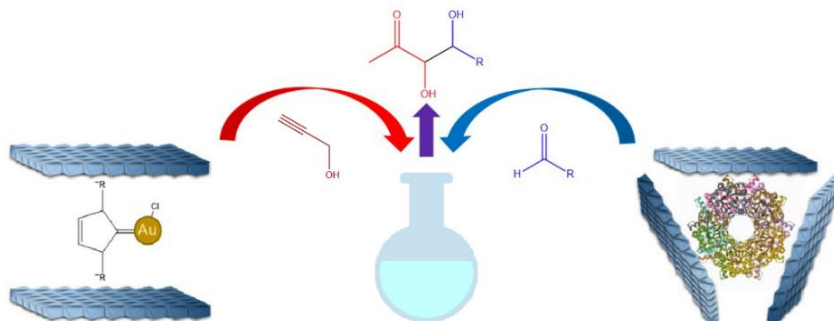
O 9

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Keywords: Hybrid catalysis; Biocatalysis; Immobilization; Layered Double Hydroxide

Summary: Hybrid catalysis or chemo-enzymatic catalysis is a very hot and challenging topic that aims at realize a scientific breakthrough in the concepts and experimental approaches of chemical synthesis, under the goal of Green Chemistry. Indeed, hybrid catalysis combines enzyme catalysts and chemical catalyst systems to lead to highly efficient one-pot reaction cascades ^[1] (yield, selectivity, atom economy, minimization of side reactions, reuse of catalysts). This allows access to complex organic molecules in a limited number of steps. This reaction concept is still little explored ^[2] because of important scientific obstacles concerning i) the choice of catalysts and ii) the compatibility of the conditions of association between enzymatic processes and metal-catalyzed reactions. The challenge is therefore to succeed in the compatible association between enzymes and organometallic catalysts.



Scheme 1 One pot/one step catalysis model

The model catalytic chemo-enzymatic reaction (Scheme. 1) that we explore aims at the one pot one step synthesis of chiral monosaccharides. The first step deals with the formation of hydroxyacetone from propargylic alcohol catalyzed by gold complexes ^[3]. The second step consists of an aldolisation reaction using an aldolase as catalyst, Fructose-6-phosphate aldolase (FSA) ^[4]. The main scientific hurdle to be overcome concerns the compatibility of the conditions of the two catalytic reactions, acid pH and high temperature for the first reaction, neutral pH for the optimum activity of the biocatalysis. To overcome this difficulty, the immobilization of the two catalysts, enzyme and gold organocatalyst, in Layered Double Hydroxide (LDH) structures is implemented by optimizing LDH composition, morphology and confinement methods selectively adapted to both catalysts ^[5].

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PHOTODECOLOURIZATION OF METHYLENE BLUE BY TiO₂ SUPPORTED ZEOLITE CLINOPTILOLITE

O 10

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Keywords: methylene blue, titanium dioxide, zeolite clinoptilolite, photodecolourization

Summary: Titanium dioxide (TiO₂) is one of the most studied photocatalysts due to its cost-effective, highly efficient and environmentally friendly properties [1]. Zeolite clinoptilolite (ZC) is a natural zeolite used for the adsorption of various wastewater contaminants attributable to its large surface area and thermal, chemical and structural stability [2]. Zeolites have been used to assist TiO₂ particles by enhancing the absorption potential of TiO₂ particles, the stability of intermediates (such as hydroxyl radicals) and the preconcentration near photoactive sites [3-4].

Dyes are recalcitrant molecules that are difficult to degrade biologically [5], and thus chemical degradation is a simple, cost-effective and efficient way to degrade them. The presence of harmful organic dyes in industrial wastewater has risen with the growth of the economy, which threatens the health of humans alongside many animals [6]. Methylene blue (MB) is a cationic azo dye and research has shown that MB causes multiple health problems such as skin irritation, nausea, diarrhea, asthma and even cancer in living organisms [7-8]. Hence, the removal of MB from aqueous solutions and cleaning industrial wastes from textile dyes have received substantial attention as a means to treat wastewater [9].

This study aims to increase the photodecolourization efficiency of TiO₂ on MB by preparing TiO₂ supported Zeolite Clinoptilolite catalysts. The photocatalytic performances of these prepared catalysts were examined for the photodecolourization of MB solution under UV irradiation, LED irradiation and no irradiation (dark). The effect of titania concentration on decolourization efficiency was observed by performing a comparative analysis between TiO₂, ZC, 20% TiO₂-ZC, 33% TiO₂-ZC and 50% TiO₂-ZC.

X-ray diffraction (XRD), surface area measurements (BET), Scanning Electron Microscopy (SEM) and energy dispersive X-ray analysis (EDX) were used to determine the characterization of the prepared catalysts. Additionally, Ultraviolet-Visible Spectroscopy was used to investigate the degraded dye amounts. The results show promising results for the removal of methylene blue from wastewater by the TiO₂ supported Zeolite clinoptilolite catalysts.

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ELECTROCATALYSIS PROMOTED BY NON-COVALENT HALOGEN BONDING

O 11

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Keywords: halogen bonding, redox catalysis, electrochemistry, supramolecular chemistry,

Redox-catalysis is an important and still challenging domain. The use of electrochemical methods to assist or to drive such catalytic electron-transfer reactions is not only an elegant approach but it can also be the solution for the development of novel analytic and synthetic applications. Only recently non-covalent σ -hole bonding interactions such as halogen bonding (XB) have been explored in organo-catalytic reactions.^[1] In the past years we have explored the electrochemical activation and control of non-covalent XB in solution^[2] and on SAM modified electrodes.^[3] We have demonstrated that the XB-acceptor strength of quinones can be controlled by the modulation of their oxidation state ("redox switching").^[4]

Recently, we examined the potential of *p*-quinones as redox mediators for the dissociative reduction^[5] of covalent carbon-halogen bonds. The possible formation of an intermediate halogen bond (XB) complex between the anionic form of the mediator and the organo halide, prior to its reduction, was assumed and the role of XB in the involved electron-transfer was investigated by electrochemical experiments and computational studies. Experimental and theoretical evidence strongly supports an inner-sphere ET mechanism involving an intermediate XB complex (Fig. 1). Computational studies confirm the decisive role of XB facilitating the electron transfer during this redox catalysis.

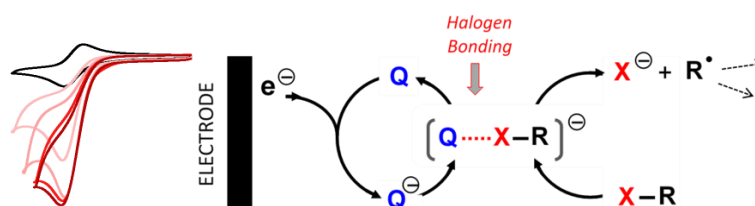


Fig. 1 Electro-catalytic reduction of the C-I bond involving an intermediate XB complex.

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NICKEL CATALYZED ALLYLATION REACTION WITH ALLYLIC ALCOHOLS O 12

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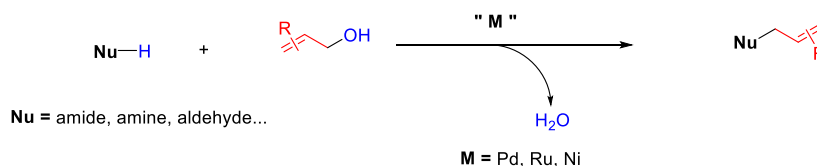
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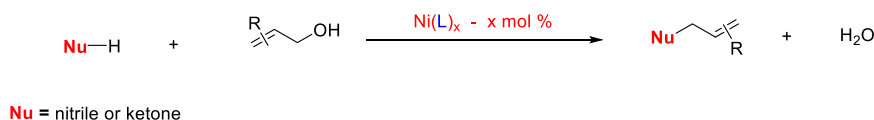
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Keywords: allylation; nickel; allylic alcohol; nitriles; ketones; terpenes.

Summary: The use of allylic alcohols instead of halogenated derivatives is an attractive and green synthetic approach to carry out allylation reactions as water is formed as sole by-product. Transition metal catalysts have been shown to efficiently activate allyl alcohol and nucleophiles but it is noteworthy that, in many cases, precious metals and additional stoichiometric activating reagents or bases are used. ^[1] The use of nickel based catalysts has been found to be particularly effective for the allylation of activated N- and C-nucleophiles under neutral conditions (no added base). ^[2] Recently, less activated aldehydes have been involved in alpha-allylation reactions under perfectly neutral conditions as well as tandem aldolization / allylation reactions. ^[3]



The main aim of our study is to extend this nickel-catalyzed reaction with different nucleophiles under perfectly clean conditions and to apply the reaction on natural compounds such as terpenes. In this study, we were able until now to perform this reaction on less activated nucleophiles such as ketones ^[4] and nitriles, ^[5] other studies on nickel-catalyzed allylation reaction are also in progress. The presentation gives details on these reactions: the optimization of reaction conditions and the study of the substrates scope.



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ASYMMETRIC TRANSFER HYDROGENATION OF KETONES PROMOTED BY A WELL-DEFINED MANGANESE PRE-CATALYST SUPPORTED BY CHIRAL AMINOPHOSPHINES

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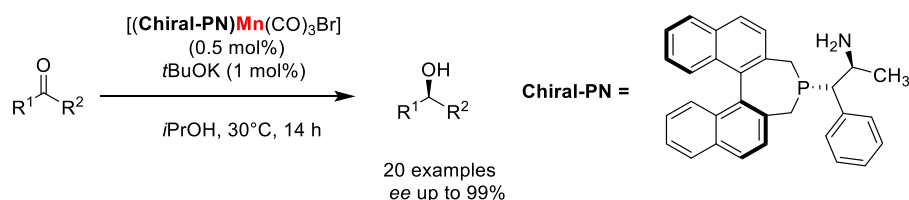
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Keywords : Manganese; asymmetric transfer hydrogenation; aminophosphine ligands; reduction

Summary: Chiral alcohols are highly valuable synthetic intermediates for the production of pharmaceutical, agrochemical and fine chemical products. As a result, asymmetric reduction of ketones by direct hydrogenation (ADH) or hydrogen transfer (ATH) catalyzed by organometallic complexes has been intensively investigated. ATH represents an efficient and appealing approach since it uses alcohols, or an azeotropic mixture of formic acid and triethylamine, as solvent and reducing agent, and avoids therefore the use of pressurized hydrogen gas. Although noble metals have proven their efficiency for this class of transformation, and for this reason are still widely used, this field of research has recently met a significant shift towards the use of earth-abundant, inexpensive and more environmentally friendly first row transition metals such as Fe, Co and Mn.^[1,2,3] In this context, we have developed a catalytic system based on commercially available chiral amino-phosphines, in combination with Mn(CO)₅Br for the asymmetric reduction of ketones, using isopropanol as hydrogen source.^[4] With the most selective ligand, the corresponding manganese complex was synthesized, fully characterized and implemented in ATH. A series of ketones (20 examples) was hydrogenated in the presence of 0.5 mol% of the manganese pre-catalyst at 30 °C. All the results will be detailed in the present communication.



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BORINIC ACIDS AS CATALYSTS IN ORGANIC SYNTHESIS

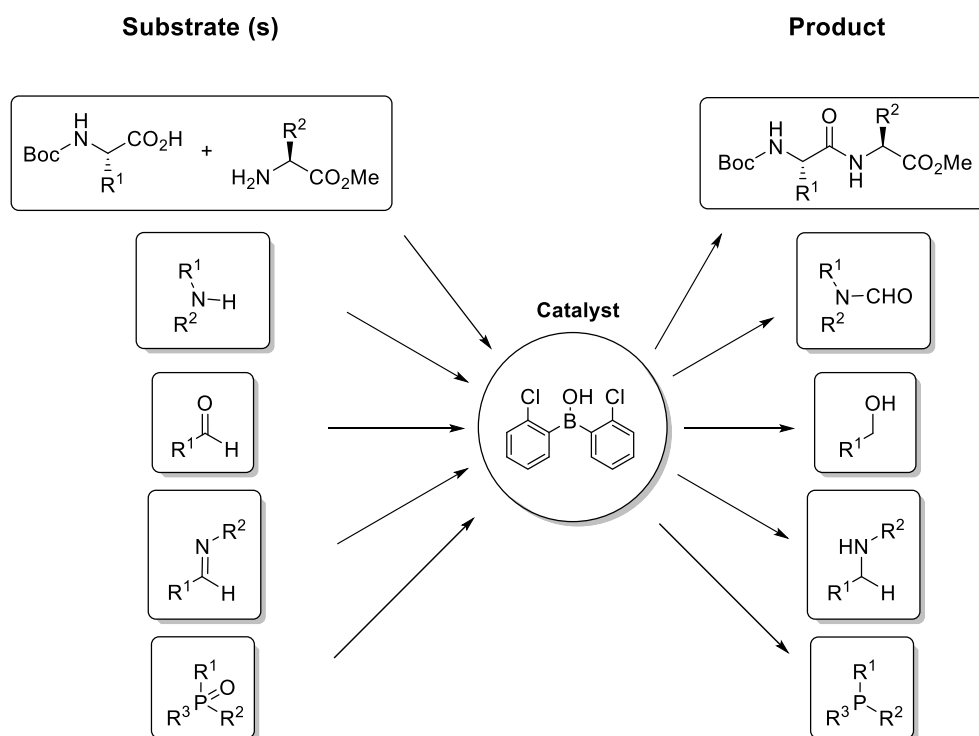
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Keywords: Green chemistry; organoboron catalysis; borinic acid; Lewis acidity

Summary: From a green chemistry perspective, organoboron catalysts provide several advantages as a catalyst group, including their low cost and toxicity, as well as their high functional group tolerance. Namely, borinic acids, which possess a simple structure and intermediate Lewis acidity between that of boronic acids and boranes, have proven to be efficient organocatalysts for challenging reactions. Previous work in our group has demonstrated the applicability and effectiveness of borinic acids as catalysts for a) dipeptide synthesis,^[1] b) formamide synthesis,^[2] c) reduction of amides, ketones, aldehydes, phosphine oxides, sulfoxides, and imines with hydrosilanes.^[3]

**Fig.1** Catalytic activity of bis(2-chlorophenyl)borinic acid**References:**

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SELECTIVE FORMATION OF NITROSO-SULFAPYRIDINE BY NEW CATALYTIC SYSTEM: DECATUNGSTATE/MAGNETITE/H₂O₂

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Keywords: decatungstate; magnetite; Hydrogen peroxide; oxidation; nitroso derivative

Summary:

Decatungstate as a polyoxometalates catalyst has been largely used in original synthesis and wastewater depollution [1]. With a combination of hydrogen peroxide, this “green” method of organic synthesis has gained significant impact over the past decades. Moreover, nitroso compounds are highly valuable chemical intermediates, which were observed in the process of human metabolism and widely used as powerful synthetic reagents in variety of synthetic chemical transformations [1].

In the present study, we prepared nano-magnetite as a support for sodium decatungstate (SW) and used H₂O₂ as oxidant in order to form a new SW/magnetite/H₂O₂ ternary system which will induce selective oxidation of amino compounds into nitroso compounds.

As clearly seen in Fig. 1, in the presence of H₂O₂ alone, a negligible conversion was obtained representing roughly 1.5 % within 120 min. In the presence of SW/H₂O₂ and Magnetite/H₂O₂, the sulfapyridine conversion reached 1.7 % and 4.5 % respectively within 120 min. In contrast, in SW/magnetite/H₂O₂ ternary system, the conversion percentage reached rapidly 75.4 % which clearly demonstrates the oxidation ability of the SW/magnetite/H₂O₂ system. The conversion follows a first order kinetic process and the rate constant was estimated to $1.13 \times 10^{-2} \text{ min}^{-1}$. This result indicates that the SW/magnetite/H₂O₂ ternary system is very efficient for the oxidation of amine groups to nitroso groups.

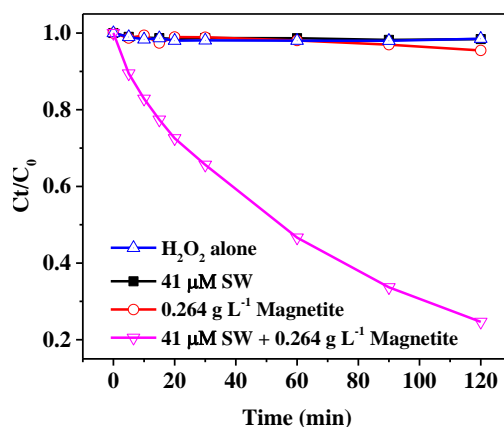


Fig. 1 Conversion kinetics of SPD in the different systems
[SPD] = 30.0 μM; [H₂O₂] = 5.0 mM; pH = 3.0

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GOLD NANOELECTROCATALYSTS FOR GLYCEROL OXIDATION TOWARDS HYDROGEN PRODUCTION

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Keywords: Gold nanoparticles; glycerol electrooxidation; gamma radiation;

Summary: The electrocatalytic oxidation of organic molecules is emerging as an effective method for low-energy input hydrogen production in membrane reactors. Glycerol is a promising hydrogen source due to a given low thermodynamic barrier of its electrooxidation^[1] in alkaline medium, the possibility to co-generate valuable C₃-compounds^[2] and low overall cost.^[3] Our research project thus aims to develop electrocatalysts based on monometallic Au and bimetallic Au-Ag nanoparticles for the electrooxidation of glycerol.

We have developed a gamma irradiation method to deposit gold nanoparticles by reducing Au (III) salts. Using this radiolytic method, fine spherical nanoparticles as well as unusual flower-shaped particles were obtained directly on a carbon electrode (Figure 1a). This type of the electrode allowed performing electro-oxidation of glycerol that can be modulated by varying the concentration and nature of the reducing agent. Also, gamma functionalization led to 2-3-fold higher performance than that of AuNPs obtained by simple electrodeposition. Gamma irradiation of aqueous solutions with mixed Au(III) and Ag(I) salts allowed the deposition of Au-Ag bimetallic nanoparticles (Figure 1b) with improved catalytic activity for glycerol oxidation, as observed by cyclic voltammetry in Figure 1c. We studied the best Au:Ag molar ratio to improve the electrocatalytic activity of the electro-catalysts, with the perspective of determining their selectivity in an H₂ electrolyzer.

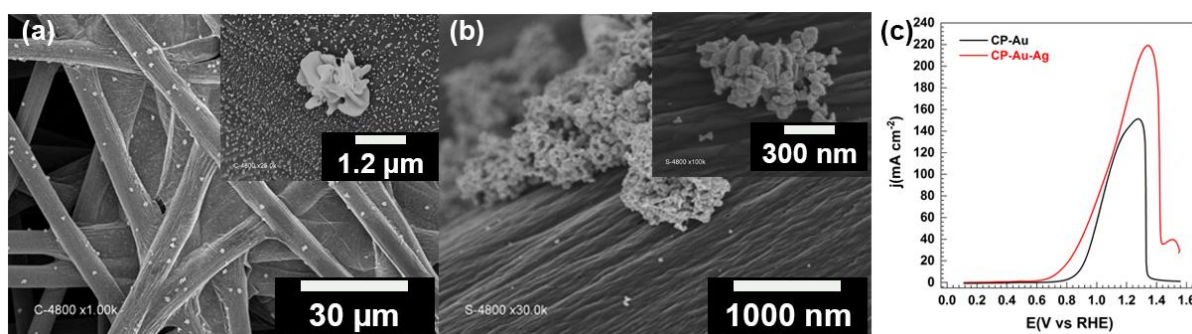


Figure 1. SEM images of Au (a) and Au-Ag (b) nanostructures directly grown at the surface of a fiber of carbon paper electrode by gamma radiation; c) Cyclic voltammogram of Au and Au-Ag nanoparticles deposited on the carbon paper electrode in the presence of glycerol (1 M KOH + 0.5 M glycerol, 25 °C, 50 mV s⁻¹)

The authors gratefully acknowledge CNRS GdR Or-Nano for funding.

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INFLUENCE OF COPPER PRECURSOR ON THE CATALYTIC TRANSFORMATION OF OLEYLAMINE DURING CU NANOPARTICLES SYNTHESIS

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Keywords: copper nanoparticles synthesis, oleylamine, organic transformation, catalysis

Summary: For the improvement of nanoparticles synthesis, in-depth understanding of the reaction mechanisms and fine characterization of the final product are equally relevant. However, most insights are coming from characterization techniques focusing on the inorganic component, e.g. the nanoparticle core. Molecular techniques are often overlooked, making the description of the synthesis incomplete with a lack of information regarding the organic shell of ligands and the molecular process governing the inorganic core nature. This is detrimental to fine interpretation of the nanoparticles behavior, in particular regarding catalytic processes.

In this study, we showed that the nature of the copper precursor has a strong influence on the inorganic surface of the nanoparticles by thoroughly characterizing the molecular reactions happening during the synthesis. Organic transformations were studied quantitatively using ¹H Nuclear Magnetic Resonance and qualitatively by Infra-red spectroscopy and Electrospray Ionisation-Mass spectrometry.

Syntheses from Cu(OAc)₂ resulted in high amount of water and few byproducts while synthesis with Cu(acac)₂ resulted in low amount of water and many products. The resulting nanoparticles showed a different ability to further dehydrogenate and transaminate oleylamine in the synthesis reaction pot. This was explained by the presence of a slight amount of copper oxide at the surface of nanoparticles from Cu(OAc)₂. This study underlines the relevance of side-reaction of examining the organic species involved in nanoparticles synthesis to design nanoparticles with controlled features and catalytic properties.

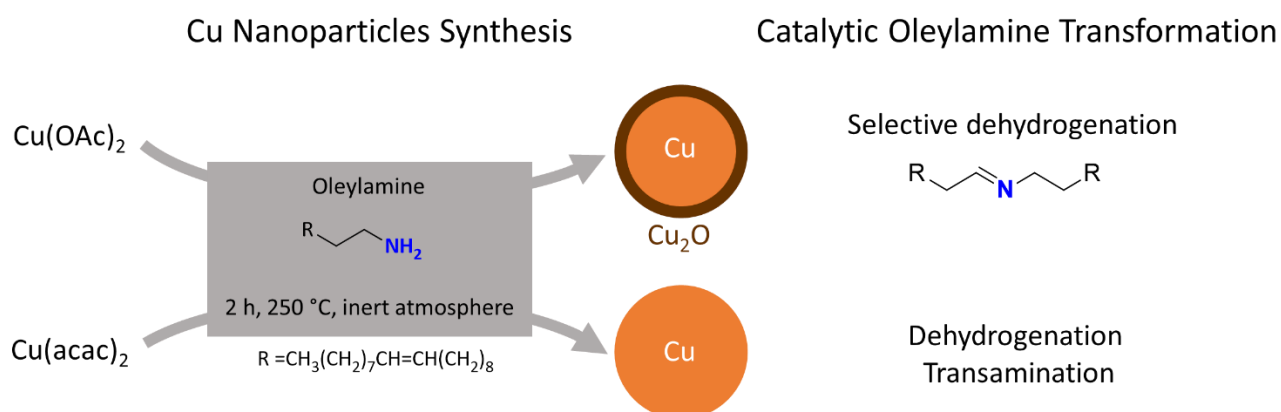


Fig. 1 : Graphical summary of the influence of the copper precursor on the nature of nanoparticles obtained and their catalytic properties for oleylamine transformation



UPGRADING BIOMASS BY BIMETALLIC CATALYSTS

O 18

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Keywords: biomass; furfural; 5-hydroxymethyl furfural; bimetallic nanoparticles; catalysis; theoretical calculations

Summary: Converting lignocellulosic biomass into sustainable chemicals and fuels is of major interest to reduce dependence on fossil fuel sources. Ideally, liquid fuels would be made from second generation feedstocks compatible with current combustion engines, and chemically identical to those obtained from petroleum. A promising feedstock is lignocellulosic biomass, which contains cellulose, hemicellulose, and lignin, and is abundant in the form of agricultural

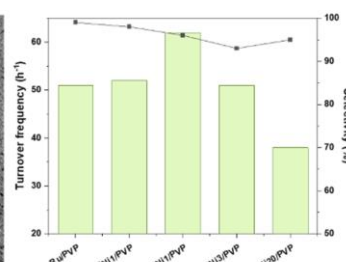
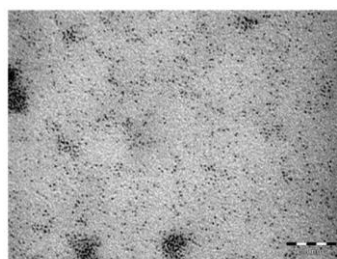


Fig. 1 Left, TEM image of Ru₇Ni₁; Right, Turnover frequency (bars) and selectivity towards 2-(hydroxymethyl)furan (dots) as function of catalysts in the selective hydrogenation of furfural

residues, waste streams, wood, and energy crops. It is also of interest to replace petroleum derived chemicals with similar products derived from biomass, as chemicals from renewable sources can reduce the environmental impact.^[1] From lignocellulosic biomass, furfural and 5-hydroxymethylfurfural (HMF), two platform molecules, can be produced. In turn, both of them, by selective hydrogenation, can produce a plethora of interesting compounds, among them methylfuran or 2,5-dimethylfuran, respectively, that are potential biofuels.^{[2][3]} Selective and efficient bimetallic nanocatalysts based on earth-abundant metals applied to upgrade biomass can contribute to a more sustainable chemistry. With this aim, we have developed a family of bimetallic materials constituted by Ni and Cu nanoalloyed with Ru for their application as catalysts for furfural and 5-hydroxymethylfurfural selective hydrogenations. Ultra-small (<2nm) RuNi and RuCu nanoparticles have been successfully prepared on which the ratio of both metals is controlled straightforwardly. RuNi based catalysts efficiently catalysed the selective reduction of furfural and 5-hydroxymethylfurfural, showing a synergetic effect between both metals. We have relied in DFT calculations to get insights on the coordination mode and strength of the species present during catalysis towards hydrogenated Ru nanoparticle models. The theoretical results are in line with the experimental ones, well supporting the activity and selectivity trends found in catalysis. To our knowledge, this is the first time that these systems have been studied.

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CO₂ REDUCTION IN THE LIQUID PHASE FROM IMMOBILIZED CNC-PINCER NICKEL(II) COMPLEXES

O 19

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Keywords: Carbon dioxide reduction; Proton reduction; Nickel complexes, Carbon nanotubes

Well-defined nickel complexes bearing CNC pincer ligands were prepared and evaluated as catalysts for the electrodriven CO₂ reduction reaction in acetonitrile in the presence of a suitable proton source. Results showed that the catalytic behavior of the complexes depends on the nature of the N-heterocyclic carbene ligand. For instance, **C1a** exhibited higher current densities than **C1b**.

Next to these studies involving soluble molecular Ni-complexes, the catalysts were modified by incorporating pyrene-anchoring moieties (Fig. 1). π -stacking grafting of these modified complexes onto the surface of carbon nanotubes^[1] afforded new hybrid materials that were systematically tested for the electro-driven CO₂ reduction. The catalytic performance of grafted and non-grafted Ni-catalysts will be presented and discussed in this communication.

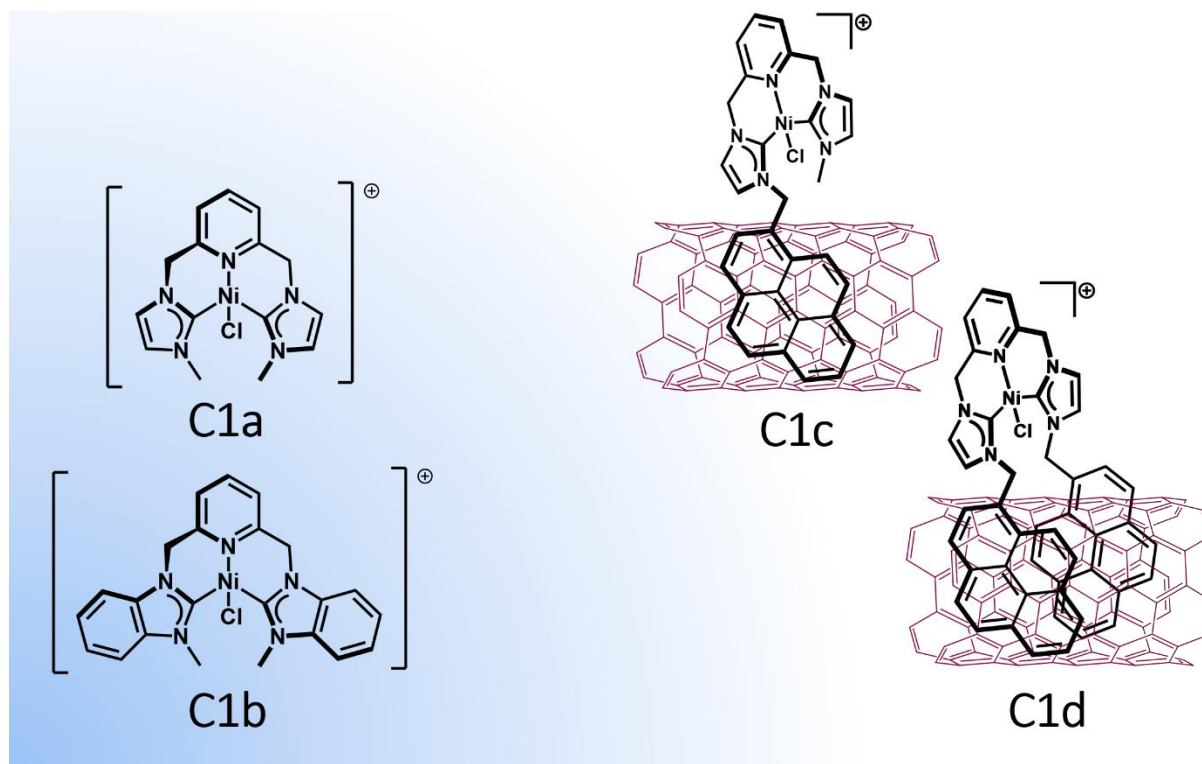


Fig. 1 C1a-d catalysts prepared and used in this work.

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IN SITU/OPERANDO X-RAY ABSORPTION SPECTROELECTROCHEMISTRY: NEW INSIGHTS IN THE CATALYTIC REDUCTION OF CO₂ BY FE PORPHYRINS

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Keywords: CO₂ reduction, spectroelectrochemistry, X-Ray absorption spectroscopy, iron porphyrins

Summary: Greenhouse gases have kept the required climate to make the conditions in Earth habitable. Nevertheless, the atmospheric level of these gases are nowadays increasing drastically, threatening life on our planet. The most prevalent and longer-lived gas is CO₂, which its emissions are expected to increase global temperatures up to 1.5 degrees in the coming years^[1]. One way to cope with this increase is by electrochemically reduce CO₂ into other building blocks or fuels such as CO, CH₄, CH₃OH₂, etc. However, the kinetic inertness and thermodynamic stability of CO₂ makes its activation rather difficult, requiring the use of catalyst for an efficient conversion. Molecular catalyst, such as iron porphyrins, has shown one of the highest activity, durability and selectivity, being an optimal catalyst both in organic and aqueous solutions towards the CO₂ reduction process^{[2],[3]}.

Even if kinetic parameters have already been elucidated in organic media, a complete picture of the mechanism (Figure 1) is still missing mostly because of the lack of spectroscopic data. Fundamental knowledge is necessary to better understand the reaction and to use this knowledge to better control selectivity and improve activity. X-Ray absorption spectroscopy (XAS) is an element specific technique that allows the determination of structural and electronic changes. We have recently developed spectroelectrochemical cells leading to a unique set-up for *in situ/operando* studies. These tools have been used to better understand the structural-activity relationship of the iron tetraphenyl porphyrin (FeTPP) catalyst in organic media. Spectral changes in the pre-edge and XANES region has been followed, making possible the identification of intermediate species under both inert and catalytic conditions. We will present how this powerful technique has helped understanding changes occurring in the course of the reaction.

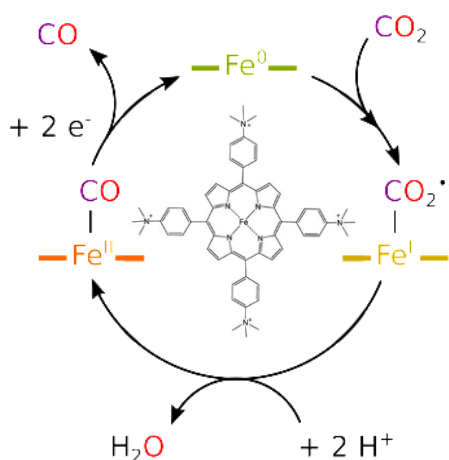


Fig. 1 Simplified mechanism for the electrochemical reduction of CO₂ by iron porphyrins

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EFFECTIVE HOMOGENEOUS CATALYSIS OF ELECTROCHEMICAL REDUCTION OF NITROUS OXIDE TO DINITROGEN AT TRANSITION METAL COMPLEXES.

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Keywords: Catalysis; Molecular Electrochemistry, N₂O, Mechanism, Small molecule activation

Summary: Due to increasing concerns regarding global warming, an interest in N₂O reduction is gradually increasing in the recent days. N₂O has been categorized as the greatest contributor to stratospheric ozone depletion, and is regarded as the third most significant anthropogenic greenhouse gas. Because of human activities such as agriculture, waste management, and industrial productions of adipic and nitric acid, its atmospheric concentration has significantly increased in the last centuries raising environmental issues. Reduction of N₂O to N₂ is therefore of interest. N₂O being an inert molecule, the electrochemical activation of N₂O requires the implementation of a catalytic process which can be either an electrocatalysis process (involving the electrode material) or a molecular catalysis process consisting of electrochemically generating a chemical reducing agent capable of reducing N₂O in solution with a low energy barrier. ^[1] In this presentation we will show that reduced rhenium bipyridyl carbonyl complexes are stable and selective catalysts for deoxygenation of nitrous oxide (N₂O) in organic media in the presence of water. Cyclic voltammetry analysis indicates that the Re complex is first reduced to produce the activated species. Then N₂O binds to labile position at the reduced metal and the resulting adduct is further reduced to trigger N-O bond breaking and release of N₂. Proton donors are beneficial to enhance the catalytic rate as well as the electrochemical limiting event. ^[2]

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AMPHIPHILIC POLYMERIC NANOREACTORS CONTAINING RH(I)-NHC COMPLEXES FOR AQUEOUS BIPHASIC HYDROGENATION CATALYSIS

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Keywords: Biphasic catalysis; N-heterocyclic carbene; rhodium; hydrogenation; core-shell polymers

Summary: The recovery and recycling of catalysts have become essential prerequisites, for industrial applications, to improve energetic efficiency, limit the environmental footprint and lower the cost, especially when rare metals and expensive ligands are involved.

The use of polymeric structures with controlled architecture as catalytic supports is an emerging area. Our group has been interested for some time in the synthesis of unimolecular nanoreactors, called core-cross-linked micelles (CCMs), obtained by cross-linking of linear amphiphilic polymers after their self-assembly as micelles.^[1] The main advantages of these objects compared to classical micelles is the absence of an equilibrium with free amphiphilic noncross-linked arms, leading to lower polymer and catalyst losses.

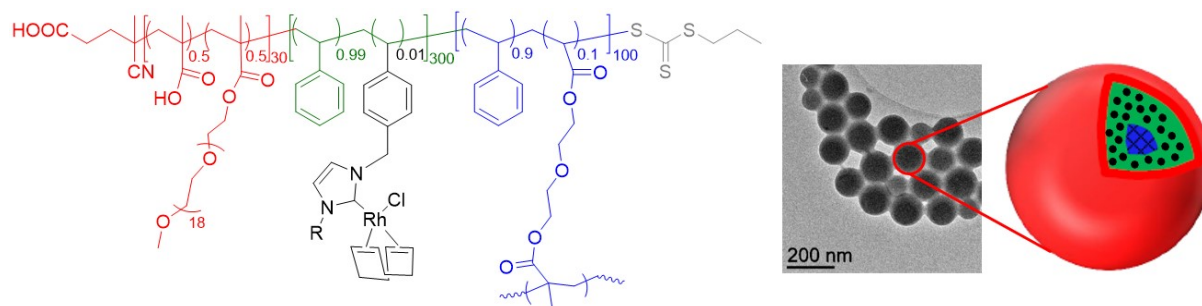


Fig. 1 [NHC-Rh]-containing amphiphilic, polymeric core-cross-linked micelles (CCMs)

We have developed CCMs that incorporate rhodium(I) complexes bearing monodentate N-heterocyclic carbene ligands. The complexes have been covalently bound to the polymeric chains by incorporation of a polymerizable unit on the NHC ligand. The substituent on the NHC has been changed in order to study its influence on the properties of the CCMs and on their activity in catalysis. The CCMs have been characterized by Dynamic Light Scattering, Transition Electron Microscopy and NMR, and evaluated as nanocatalysts for the hydrogenation of styrene under biphasic conditions.

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POSTERS

HYDROGENATION OF FURFURAL AND NITROBENZENE WITH NICKEL CARBIDE (Ni₃C) AND PHOSPHIDES (Ni₂P, Ni₁₂P₅) IN MILD CONDITIONS

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Keywords: nickel phosphide; nickel carbide; nanoparticles; furfural; hydrogenation

Summary:

The ever growing need for biofuel refinery justifies the current research for H₂ activation in the liquid phase under mild conditions (low temperatures and low H₂ pressures). In the recent years, strong interest was devoted to metal derivatives such as carbides, sulfides and phosphides as these materials are more stable and poison-resistant than their metallic counterparts.^[1] We propose here to use nickel phosphide (Ni₂P and Ni₁₂P₅) and nickel carbide (Ni₃C) nanoparticles for the hydrogenation of furfural, a biosourced platform molecule, and nitrobenzene. The catalytic activity of nickel phosphide for this reaction was recently reported but that of nickel carbide is unheard of.^[2,3]

All the catalyst nanoparticles were synthesised by the reduction of nickel acetylacetonate Ni(acac)₂ in solvent mixtures (oleylamine, octadecene, octyl ether) at high temperatures (220-300 °C), and in the presence of trioctylphosphine for phosphides syntheses. A particular effort was made on the catalyst characterization by X-ray Absorption Spectroscopy to identify the chemical environment of the nickel atoms. The hydrogenation of furfural in furfuryl alcohol and of nitrobenzene in aniline was attained at 100 °C with H₂ pressures as low as 7 bar, when conducted in isopropanol or butanol.

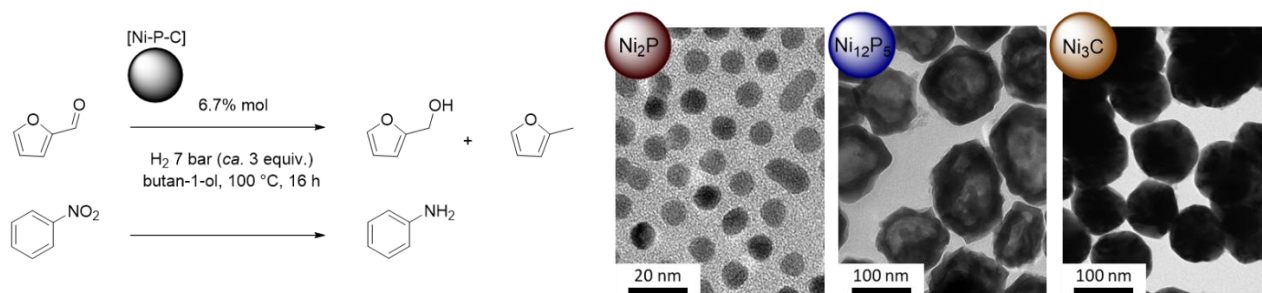


Fig. 1 Hydrogenation reactions of furfural and nitrobenzene (left) and TEM images of Ni₂P, Ni₁₂P₅ and Ni₃C nanoparticles (right)

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HETEROGENEOUS SECOND-SPHERE COORDINATION MODIFIED IRON PORPHYRIN FOR CARBON DIOXIDE REDUCTION

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Keywords: Iron porphyrins; CO₂ reduction; bio-inspired systems, heterogeneous catalysts

Summary: Carbon monoxide dehydrogenase (CODH), an enzyme found in some anaerobic bacteria, is capable of reducing reversibly and selectively CO₂ to CO with a high reaction rate and almost no overpotential.^[1] Inspired by the active site of this enzyme (Figure 1), we had previously developed an iron-porphyrin catalyst (FeUr, Figure 1) for the homogenous electrocatalytic reduction of CO₂.^[2] The urea groups introduced in the second coordination sphere of this biomimetic catalyst were shown to play a similar role to that of amino acid residues found in the second coordination sphere of the CODH active site. This role consists of establishing multiple hydrogen bonds to increase the catalyst affinity for CO₂ bonding and stabilize reactive intermediates. The second coordination sphere brought a significant improvement in the overpotential of the CO₂ electrocatalytic reduction compared to the non-functionalized iron-tetraphenylporphyrin (FeTPP, Figure 1) while keeping a good selectivity and high reaction rate.

Homogenous catalysis has a practical advantage when it comes to performing spectroscopic studies to better understand the reaction mechanism or to introduce structural modifications on the catalyst.^[3] However, the electrocatalytic reaction is generally performed in organic solvents and takes place only in the first diffusion layer of the electrode which limits the scale-up of the reaction. To take our catalyst one step further toward an industrial application for CO₂ reduction, we developed a new modified electrode by immobilizing the FeUr catalyst on carbon paper using multiwall carbon nanotubes (MWCNT) (Figure 1). Our results show that the second coordination sphere effect can be transposed to heterogeneous catalysis for electrocatalytic reduction of CO₂ in water. We also demonstrated that the FeUr-modified electrode displays better selectivity and four times higher current density than that of FeTPP-modified electrode.

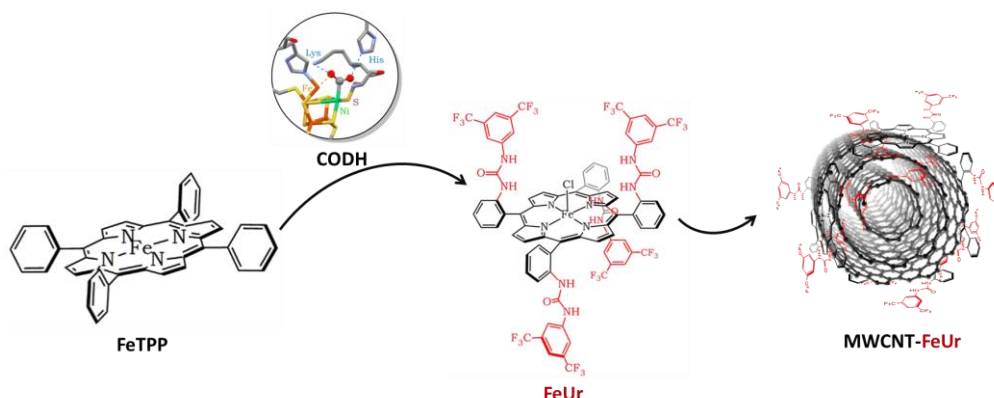


Figure 1. Introduction of urea groups in the second coordination sphere of iron porphyrin and its heterogenization.

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HYDRODEOXYGENATION AND HYDROGENOLYSIS OF BIOMASS-DERIVED PRODUCTS USING MAGNETIC INDUCTION

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Keywords: magnetic nanoparticles; magnetic-induced catalysis, biomass hydrodeoxygenation, biomass hydrogenolysis, C-O bond activation

Summary: Valorization of biomass products is gaining increasing attention due to need to find new fuel resources other than fossil. For example, 2,5-dimethylfuran, deriving from lignocellulose, appears as a promising candidate to be used as biofuel.^[1] The separation of lignin from the cellulosic part leads to the generation of platform molecules, which after a hydrodeoxygenation reaction, can be converted in valuable chemicals. This transformation is generally catalyzed by noble metals at high H₂ pressures and temperatures. Magnetic induction has demonstrated to be very effective in solid-gas catalysis^[2] but also in solution,^[3] rendering the temperature and pressure conditions milder compared to those used with conventional heating.

In this work, we present the catalytic conversion of biomass-derived products by application of magnetic heating and using a non-noble metal catalyst, FeNi₃ nanoparticles (NPs).^[4] FeNi₃ NPs allowed us to activate the C-O bond of different biomass-derived molecules. Hydrodeoxygenation of furfural derivatives and the cleavage of lignin model molecules, such as benzyl phenyl ether or phenyl ether, were successfully achieved employing very low pressures of H₂ (3 bar).^[5]

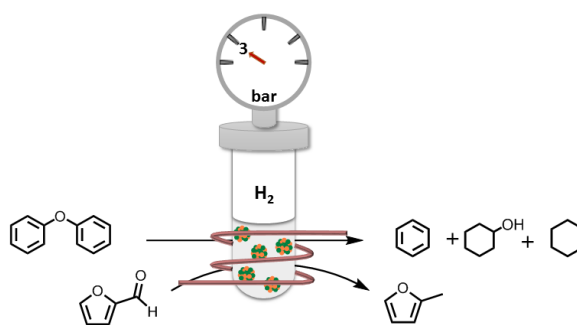


Fig. 1 Schematic representation of the setup and catalytic reactions performed.

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ZERO-VALENT NICKEL NANOPARTICLES ON HALLOYSITE-BASED SUPPORTS: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS IN CATALYTIC HYDROGENATIONS

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Keywords: Nickel Nanoparticles, Nano-structured clays, Heterogeneous Catalysis, Hydrogenations

Summary: Over the past decade, the functionalization of halloysite (HAL), a nano-structured clay, has attracted great attention for the development of metal-based catalysts applied in the designing of sustainable processes.^[1] Herein, we report the synthesis of nickel nanoparticles supported on HAL, both natural and functionalized clays, by one-pot methodology: reduction of $[\text{Ni}(\text{COD})_2]$ to Ni(0) nanoparticles (NiNP) in the presence of the halloysite support under smooth conditions (ethanol, 90 °C under 3 bar of H₂), based on the methodology previously described by our team.^[2] The as-prepared materials were fully characterized (elemental analysis, TGA, DSC, ICP-AES, IR, XPS, PXRD and TEM) (Figure 1).

The NiNP@HAL catalytic materials have been tested in the hydrogenation of different unsaturated functional groups (alkynes, alkenes, aldehydes, ketones, nitrile, nitro), which evidence remarkable differences in their catalytic behavior, depending on the nature of the support and the stabilizer. Actually, NiNP-QUINIDINE@HAL catalyst was highly efficient towards the main part of tested substrates, including fatty acids and squalene. Moreover, a recycling study was done.

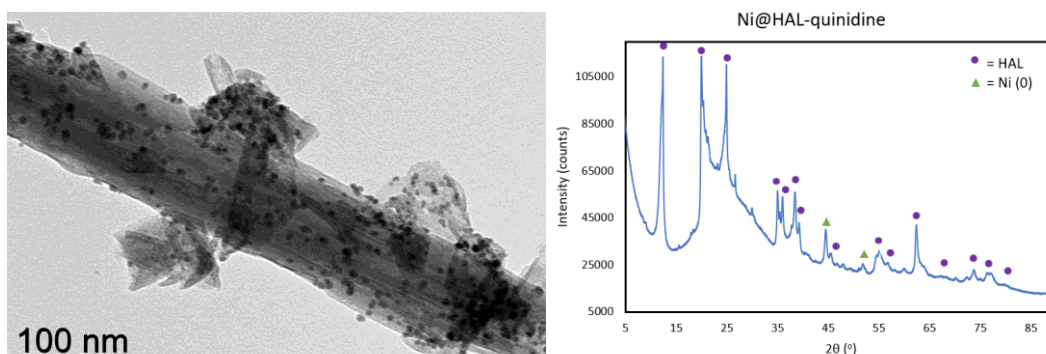


Fig. 1 TEM micrographs of supported Ni(0) nanoparticles halloysites and PXRD

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