

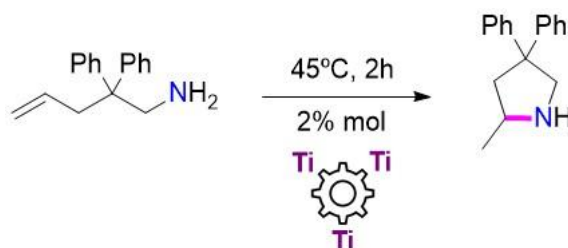
Multinuclear titanium complexes for catalytic transformations

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The increasing demand of more sustainable transformations has risen particular attention in multimetallic complexes. Through cooperation of the metals in close proximity, these species display enhanced catalytic properties in an arrange of organic transformations (e.g.: C-C, C-N bond formation)^[1] over their monometallic counterparts. In contrast to the large number of examples of late transition metals, multimetallic systems formed by abundant and early transition metals are scarce. In specific, titanium is the 9th most abundant of all elements in the earth's crust and offers great potential in catalytic applications,^[2] however the synthesized polymetallic species up to date are mostly bimetallic compounds linked by labile anionic ligands, and their applications are limited to polymerization.^[3]

Herein we report the preparation and characterization of new trinuclear titanium species generated by metalation reaction of preorganized bridging ligands. The isolated compounds were tested in catalytic intramolecular hydroamination of non-activated alkenes. Preliminary mechanistic investigations point a crucial role played by the multimetallic synergy, which enables intramolecular cyclization under relatively mild reaction conditions.



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Performance of Pt catalysts dispersed on modified TiO₂ supports for the water-gas shift reaction

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The water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, $\Delta H = -41,1 \text{ kJ mol}^{-1}$), is one of the most studied reactions due to its applicability in various industrial chemical processes such as ammonia synthesis and petroleum hydro-processing [1]. The WGS reaction can be also used for the purification of PEM fuel cell feeds in order to reduce the CO content of the H₂-rich gas streams resulting from hydrocarbons reforming processes [1,2]. Well established industrial processes typically implement two WGS reactors in sequence, with the first operating at 350 – 450 °C (high-temperature shift, HTS) and the second at 180 – 250 °C (low-temperature shift, LTS) [3]. The HTS accelerates CO conversion, which is favored at elevated temperatures, whereas the LTS reduces the CO content at the desired levels exploiting the endothermic nature of the equilibrium limited WGS reaction [3]. Previous studies in our laboratory showed that Pt exhibits the highest activity toward WGS reaction among a series of noble metals investigated, including Pd, Rh and Ru, whereas the activity is maximized when it is supported on “reducible” supports, such as TiO₂ [4]. It has been also found that the promotion of TiO₂ with alkali and alkaline earth metals [5] as well as the combination of TiO₂ with a second oxide [6] can further improve the WGS activity of dispersed Pt crystallites. The aim of the present work is to study a series of Pt catalysts supported on modified TiO₂ based on the results of our previous studies [1-6]. Specifically, the effects of the combined promotion with alkali (Na, Cs) or alkaline earth metals (Ca, Sr), the addition of CeO₂ in the support, and the use of a second metal (Fe, Cu, Cr, Ru) on the WGS activity of the Pt/TiO₂ catalyst was investigated in detail. Catalytic performance tests were carried out employing an apparatus consisting of a fixed bed microreactor, an HPLC pump and an evaporator to control the H₂O content and a set of mass flow controllers to adjust the flow of the feed gasses (He, CO, CO₂, H₂). Analysis of the reactants and products of the WGS reaction was performed employing gas chromatography. The results showed that the 0.5wt.%Pt/2wt.%CaO/TiO₂ catalytic system exhibited the highest activity for both HTS and LTS reactions. The performance of the optimized catalysts in the form of pellets or coatings on ceramic monoliths was further investigated under realistic reaction conditions and was compared with that of commercial catalysts (SUDCHEMIE and Johnson-Matthey). It was found that the optimized catalyst exhibited activity similar to that of the SUDCHEMIE catalyst under HTS conditions and to the Johnson-Matthey catalyst under LTS conditions.

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Optimisation of a catalytic process for CO₂ purification from oxycombustion

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Anthropogenic CO₂ is one of major contributors towards global greenhouse gas emissions resulting in global warming, a major global concern. According to International Energy Agency Report for 2019, industrial sector contributed 40% of the total global CO₂ emissions followed by the transportation sector that accounted for 27%. One of the promising methods to reduce these CO₂ emissions is by capturing it before being released into the atmosphere and then, either storing it under geological structures or valorising it into other valuable chemicals, fuels, durable materials or to mineral carbonation and construction materials. This technique is collectively known as Carbon Capture, Storage and Utilisation (CCUS). Carbon capture technologies can be divided into three main groups: (i) precombustion (capturing CO₂ from feed gas), (ii) post-combustion (capturing CO₂ from the flue gas after fuel combustion) and (iii) oxy-combustion (capturing CO₂ from the CO₂-rich flue gas obtained after fuel combustion under nearly pure O₂). In this project, the studies are made for oxy-combustion carbon-capture methodology applied specifically to next generation cement units. Moreover, depending on the composition of the combusting fuel and O₂-carrying feed gas, the resulting flue gas can contain components like CO, NO_x, SO_x and H₂O along with huge amount of CO₂ and O₂. NO_x and SO_x are known to be toxic and corrosive when reacted with water thereby damaging the gas transfer pipelines. Therefore, it is important to treat (deNO_x and deSO_x) the flue gas stream before feeding it to the carbon capture unit. In this project, the deNO_x gas treatment is achieved via a catalytic reduction process using CO and inexpensive catalytic materials to make the gas-treatment process economically feasible. However, presence of large amount of O₂, H₂O and CO₂ will challenge the overall catalytic activity and therefore need to be considered while formulating the catalyst. Hence, following objectives are outlined for the doctoral project:

- (1) Research of inexpensive materials and synthesis of the active catalysts
- (2) Testing catalytic performance under the simulated industrial flue gas conditions and comparing these results with different synthesized catalytic materials and performing additional material characterizations to further understand the catalytic behaviour
- (3) Large-scale synthesis (1 kg) of the best performing catalyst followed by shaping of the catalyst.
- (4) Testing the shaped catalyst at semi-pilot plant under simulated industrial flue gas conditions and comparing the performance with that of a commercial catalyst.
- (5) Development of a kinetic model for the observed catalytic activity and incorporating it into a built-in reactor model in Aspen Plus simulation software.

HYDRAZINE SELECTIVE DECOMPOSITION OVER METAL FREE CARBONACEOUS MATERIALS

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Hydrous Hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) can be employed as an efficient hydrogen carrier because it is liquid, can be easily transported,¹ and it is carbon-free fuel, with an intrinsic hydrogen content as high as 12.5 wt%.² The decomposition of hydrous hydrazine can follow two different pathways.³ The first reaction is the *complete reforming pathway*, where only molecular hydrogen and nitrogen are obtained. In the second case, the thermodynamically favoured one, ammonia and nitrogen are produced, also known as *incomplete decomposition*. Noble metal based materials, such as supported Ir⁴ and Rh⁵, are among the most employed catalyst for this reaction due to their excellent results in terms of catalytic activity and selectivity, but presenting high related costs. Herein, combining experimental and computational investigations, we are able to unravel the hydrous hydrazine decomposition on metal-free catalysts. The study focused on commercial graphite and two different carbon nanofibers, Pyrolytically Stripped (CNFs-PS) and High-Heat Treated (CNFs-HHT), presenting a different number of intrinsic defects. Through Raman spectroscopy a correlation between intrinsic defectiveness (I_D/I_G) and the initial catalytic activity was found. The most defective material (CNFs-PS, $I_D/I_G = 1.54$) was recognized as the most performing metal-free material, with a hydrous hydrazine conversion as high as 94% (6 h) and H_2 selectivity of 89%. The role of NaOH was unravelled by comparing the results obtained for the most active material, in presence and absence of NaOH. Through Density Functional Theory (DFT) and Quantum Theory of Atoms in Molecules (QTAIM) simulations, single vacancies (SV) were identified as the only active sites promoting the selective decomposition. Two symmetrical and one asymmetrical dehydrogenation pathways were studied, in addition to the incomplete decomposition pathway. In the initial hydrazine dissociative adsorption, the dehydrogenation pathway is more favourable than the scission of the N-N bond, which lead to NH_3 production (Figure 1). We were able to recognize the first step as the crucial one to determine the reaction. Moreover, we confirmed that the presence of NaOH in the reaction environment can modify the energy gap between the two pathways, leading to an increased reaction rate as well as H_2 selectivity.

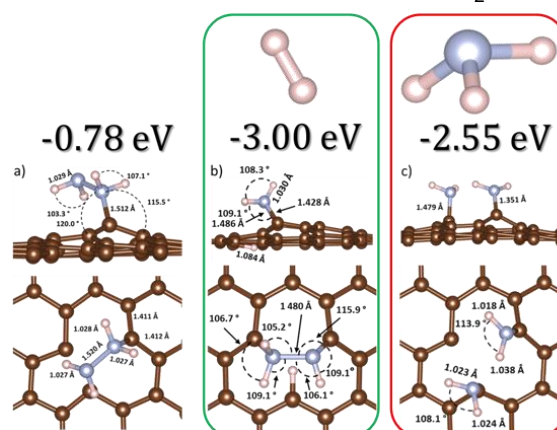


Figure 1 Most favourable Hydrazine configurations and related adsorption energy: a) a-SL b) cB-H c) cB-N.

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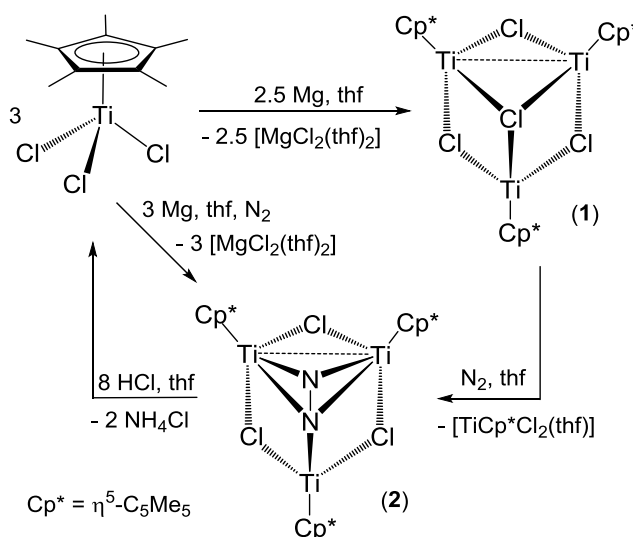
Dinitrogen Activation and Functionalization at Low-Valent Titanium Monocyclopentadienyl Complexes

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The synthesis of ammonia constitutes one of the most important chemical processes at the industrial level as illustrated by the production of about 150 million metric tons of this molecule in 2021.^[1] Today, the industrial synthesis of ammonia relies on the Haber-Bosch process, developed over 100 years ago, and performed in large-scale plants where dinitrogen and dihydrogen gases are combined under harsh conditions (300-500 °C and 200-300 bar) in the presence of a heterogeneous catalyst. However, this extremely energy-intensive process consumes about 2% of the world's total energy and generates ~1% of global CO₂ emissions annually and, unsurprisingly, the development of a sustainable production of ammonia has been identified as one of the IUPAC Top Ten Emerging Technologies in Chemistry 2021.^[2]

Inspired in the natural nitrogen fixation carried out under ambient conditions by certain microorganisms which convert N₂ into ammonia using electrons and protons at nitrogenase enzymes, organometallic and inorganic chemists have long explored homogenous catalysts capable of operating at milder conditions.^[3] The fixation of dinitrogen by titanium species has been known for decades, and nowadays a variety of coordination modes of the N₂ unit to the titanium centers is well-documented.^[4] While the largest families of titanium-dinitrogen complexes are based in bis(cyclopentadienyl)titanium or tri- and tetradentate PN ligand systems, few examples of monocyclopentadienyl compounds are known.^[4,5] Therefore, we have recently begun a research program devoted to the study of dinitrogen activation by low-valent titanium monocyclopentadienyl species. For instance, we have recently reported the reduction of [TiCp*Cl₃] to give a mixed-valence trinuclear complex **1** capable of incorporating N₂ under ambient conditions in solution to give the first example of a stable derivative **2** with a μ₃-η¹:η²:η²-N₂ ligand (see Scheme).^[6] This dinitrogen complex reacts with excess HCl to regenerate [TiCp*Cl₃] with NH₄Cl formation, and several cycles alternating N₂/HCl atmospheres on a [TiCp*Cl₃]/Mg(excess)/thf system can be performed to produce NH₄Cl on a relatively large scale. In this communication, we will present new examples of activation and functionalization of dinitrogen at low-valent titanium complexes under mild conditions.



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Thermocatalytic hydrogenation of CO₂ to methanol using Cu-ZnO bimetallic catalysts supported on metal-organic frameworks

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Abstract

The thermocatalytic hydrogenation of carbon dioxide (CO₂) to methanol is considered as a potential route for green hydrogen storage as well as a mean for utilizing captured CO₂, owing to the many established applications of methanol.¹⁻³ Copper–zinc bimetallic catalysts supported on a zirconium-based UiO-66 metal–organic framework (MOF) were prepared via slurry phase impregnation and benchmarked against the promoted, co-precipitated, conventional ternary CuO/ZnO/Al₂O₃ (CZA) catalyst for the thermocatalytic hydrogenation of CO₂ to methanol. A decrease in crystallinity and specific surface area of the UiO-66 support was observed using X-ray diffraction and N₂-sorption isotherms, whereas hydrogen-temperature-programmed reduction and X-ray photoelectron spectroscopy revealed the presence of copper active sites after impregnation and thermal activation. Other characterisation techniques such as scanning electron microscopy, transmission electron microscopy, and thermogravimetric analysis were employed to assess the physicochemical properties of the resulting catalysts. The UiO-66 (Zr) MOF-supported catalyst exhibited a good CO₂ conversion of 27 and 16% selectivity towards methanol, whereas the magnesium-promoted CZA catalyst had a CO₂ conversion of 31% and methanol selectivity of 24%. The prepared catalysts performed similarly to a CZA commercial catalyst which exhibited a CO₂ conversion and methanol selectivity of 30 and 15%. The study demonstrates the prospective use of Cu-Zn bimetallic catalysts supported on MOFs for direct CO₂ hydrogenation to produce green methanol.

Keywords: CO₂ hydrogenation; bimetallic catalysts; metal–organic frameworks; catalysis; methanol economy

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Design of 2D covalent organic frameworks-incorporated heteropolyacid materials for acid catalysis

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Keggin-type heteropolyacids (HPAs) have diverse molecular structures, strong Brønsted acidity, reversible multi-stage redox activity, high stability and high solubility. Therefore, they were widely used as homogeneous catalysts into acid- and redox-catalyzed reactions[1]. Proton exchange, tethering, grafting and encapsulation methods were commonly used for heterogenization of HPAs to achieve effectively their recycling. Encapsulation method can maintain HPAs in their soluble native form inside insoluble porous materials without loss of active sites and leaching. Therefore, it's a promising method for HPAs heterogenization[2].

Covalent organic frameworks (COF) prepared by covalent bonding are rapidly developing in the field of porous materials. These materials possess high porosity and designable functionality with potential application in gas storage, separation of gases, organic electronics and catalysis[3]. CIN-1 is an imine-based COF, which can be prepared via a Schiff-base condensation reaction between melamine and 1,4-piperazinedicarboxyaldehyde. It has a two-dimensional layered-sheet structure that makes HPAs encapsulation between adjacent CIN-1 layers feasible[4].

In this work, we successfully heterogenized phosphotungstic acid (HPW) via encapsulating it between the adjacent layers of CIN-1. The obtained HPW@CIN-1 material showed catalytic activity in the model reaction of esterification of ethanol with acetic acid (Figure 1a). HPW can be considered as a structure directing agent during synthesis of CIN-1 due to the interaction between HPW and CIN-1. When HPW loading is of 18 wt%, the material possesses a highly crystallinity (Figure 1b,c), which can effectively limits the diffusional limitations, promoting catalytic reactions. Therefore, 18wt%HPW@CIN-1 gave the highest activity. This material provided high stability and no leaching of acid during the reaction.

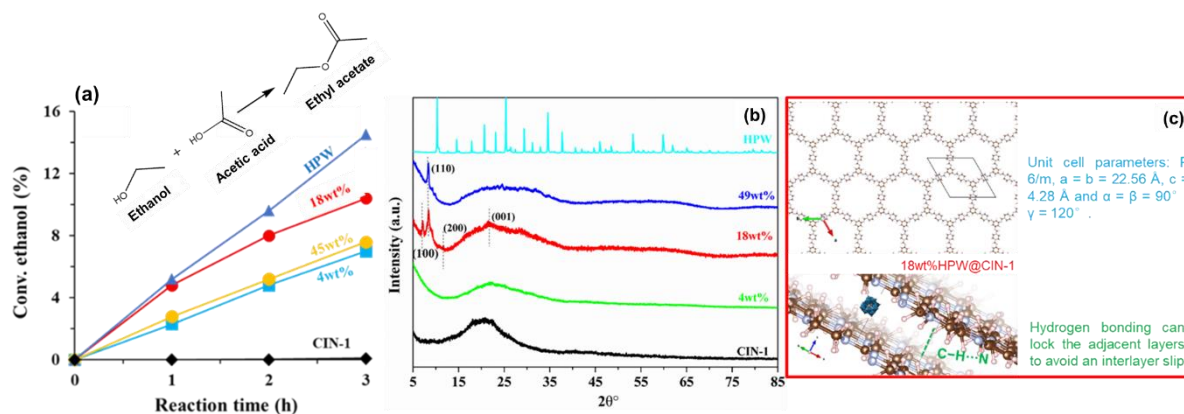


Fig. 1: Catalytic activity of HPW@CIN-1 in esterification of ethanol with acetic acid. Reaction conditions: ethanol, 1 g; acetic acid, 1 g; 0.01 g of HPW; temperature, 60 °C (a). XRD analysis of HPW@CIN-1 with different HPW loadings (b) and model of 18wt%HPW@CIN-1 (c).

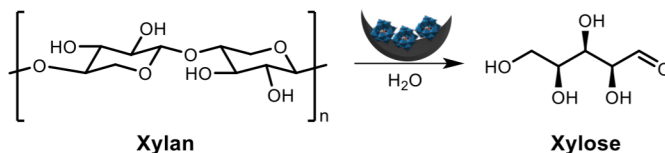
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Carbon Supported Heteropolyacids for the Valorization of Hemicellulose

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Introduction



In times of climate change and diminishing fossil resources, the transition to renewable raw materials such as lignocellulose is indispensable. Still, their transformation into fuels and valuable platform chemicals is challenging. Herein, the acid-catalyzed hydrolysis of hemicellulose to the platform chemical xylose is investigated using the model compound xylan as substrate. For the hydrolytic cleavage of cellulose, heteropolyacids (HPAs) have been established as promising catalysts.^[1] They exhibit a particularly high Brønsted acidity, possess tunable redox activity and are soluble in water and most organic solvents. The latter makes them ideal for homogeneous applications but impedes their recycling and thus industrial application. To meet this challenge, the immobilization of HPAs on suitable heterogeneous supports is of high interest.^[2]

Results and discussion

Initially, commercially available HPAs were tested in the hydrolysis of xylan to xylose whereby phosphotungstic acid (PTA) showed the highest activity (90% conversion) and selectivity to xylose (81%) after optimization of the reaction parameters. Therefore, PTA was chosen for the impregnation on porous activated carbons (AC). Although some studies have been carried out using carbon supports for the immobilization of HPAs^[3], it is not fully clarified yet whether the HPA-carbon interaction is of physical or chemical nature, whereas the latter could take place by an acid-base-interaction of the HPA with oxygen moieties on the carbon surface (Figure 1). In this regard, PTA was impregnated on an oxygen-rich carbon with a high specific surface area of 2023 m²/g.^[3] After the optimization of the impregnation procedure, the prepared solid acid catalyst PTA/AC was thoroughly characterized. N₂-physisorption revealed a significant decrease in the specific surface area to 1219 m²/g. ICP confirms a high PTA-loading of 473 mg/g, which is in accordance with a significant increase of acidic sites found by NH₃-TPD. In the hydrolysis of xylan to xylose, PTA/AC showed a high activity with 91% conversion. The selectivity to xylose was with 98% even higher compared to the homogeneous system. Furthermore, the long-term stability of the catalyst was demonstrated in batch recycling experiments. The observed loss in activity correlates with a moderate PTA-leaching of 2-3%. Nevertheless, a moderate conversion of 44% was still achieved after 20 recycling runs.

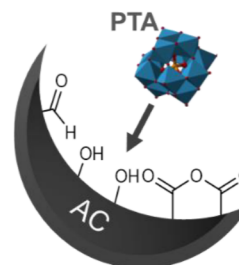


Figure 1: Immobilization of PTA on carbon.

Conclusion

Activated carbon was found to be a promising support material for heteropoly acids. The PTA/AC catalyst was successfully applied in the hydrolysis of xylan to xylose. The long-term-stability of the catalyst was already shown in recycling experiments over 20 runs. Further investigation of the PTA-carbon interaction as well as the implementation of a continuous set-up is currently in progress.

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Full catalytic dehalogenation of brominated flame retardants

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BFRs belong to a large group of organohalogen chemicals, which are highly persistent, bioaccumulative and cause adverse effects in humans and wildlife. These BFRs are used as additives or reactive components in a variety of polymers such as foam, high-impact polystyrene, and epoxy resins, which are then used in commercial products such as computers, electronics and electrical equipment, textiles, and furniture foam [1]. For the BFRs, the best current method is to debrominate them fully via pyrolysis, via hydrothermal treatment or catalytic pyrolysis. However this leads to a very low value fraction which is at best suitable to be used as fuel [2]. Ultimately the compounds are burned or incinerated.

In this context, we are developing a catalytic method to debrominate BFRs with both aromatic and cycloaliphatic structures (e.g. Decabromodiphenyl ether; Hexabromocyclododecane, Tetrabromobisphenol A and 1,2-bis(2,4,6-tribromophenoxy)ethane. For debromination of Decabromodiphenyl ether we use a combination of two reactions such as, catalytic hydrogenolysis using palladium catalyst supported on carbon ($\text{C-Br} + \text{H}_2 \rightarrow \text{C-H} + \text{H-Br}$) in combination with deep dehalogenation in the presence of CO (carbonylation: $\text{C-Br} + \text{CO} + \text{H}_2\text{O} \rightarrow \text{C-COOH} + \text{H-Br}$). The resulting oligocarboxylic acids are easily recovered and revalorized, e.g. in resins. In our reactions we have obtained 100% conversion of Decabromodiphenyl ether to lower brominated diphenyl ethers and diphenyl ether (nonbrominated compound). We have obtained 25% yield of dibromodiphenyl ether which has been used afterwards as a model reactant to carbonylate (using CO) and in the presence of methanol to produce diphenyl esters with 80% yield.

Moreover, for debromination of HBCD (hexabromocyclododecane) we are using the same catalytic hydrogenolysis with Pd/C in mild conditions (50 °C, 4 bar) in order to obtain halogen free compounds (100 % conversion), e.g. cyclododecane, which is a precursor to lauro lactam, a precursor to the polymer Nylon 12 [4].

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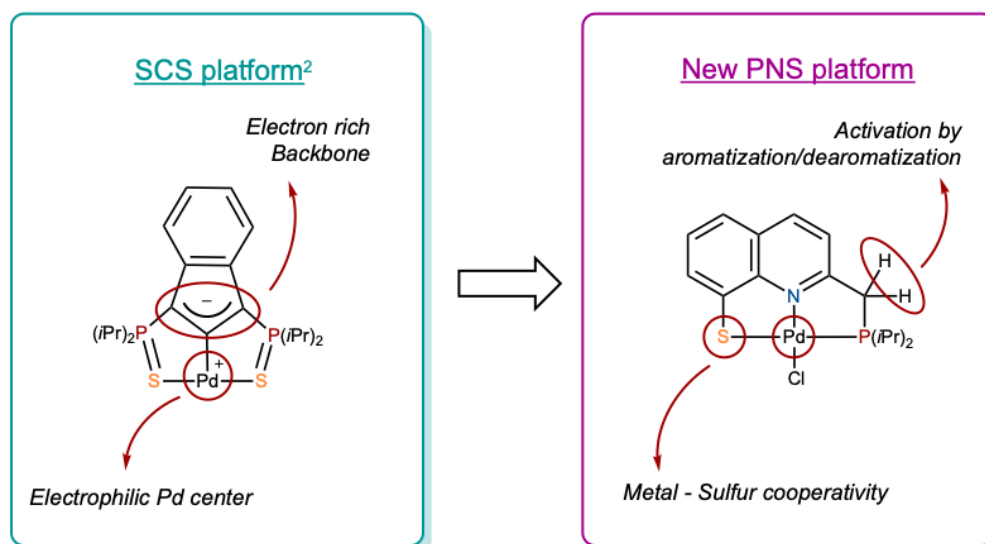
Development of a new non-innocent platform for group 10 metals

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Over the last decade, cooperative effects in transition metal catalysis have attracted increasing interest from the scientific community. Thanks to the synergy between two different catalytic sites, extraordinary improvements in efficiency and selectivity can be achieved. In this context, metal/ligand cooperation (MLC), in which one of the ligands participates actively to the activations of the substrates, can be highlighted.¹ In this domain, pincer complexes of transition metals play an important role. One of the most representative models was reported by Milstein¹, based on an aromatization/dearomatization process of a pyridine based pincer.

Although group 10 metals are widely used in catalysis, they are less studied in MLC than metals of group 8 and 9.² Indeed, the two active sites are further away in the square planar geometry of d^8 complexes of group 10 metals. In this context, our group has reported indenediide Palladium complexes bearing an electron rich backbone.³ Remarkable results have been obtained in catalytic cyclisation processes involving C-O/C-N & C-C bonds formation.

To further develop MLC with group 10 metals, we are now working on a new platform deriving from the quinoline moiety that can combine two types of non-innocent behavior. The activation can either occur via aromatization/dearomatization of the quinoline moiety, or may involve the sulfur atom as described by Ohki & Oestreich⁴. The synthesis of the ligand and its coordination to group 10 metals will be presented. Evidence of the accessibility of both modes of cooperativity will be provided along with emerging catalytic applications.



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Solar light – driven photocatalytic degradation of pharmaceutical compounds by Cu_3P / ZnSnO_3 composites.

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Over the last years, the extensive use of pharmaceuticals in conjunction with the inefficiency of conventional physicochemical and biological water treatment methods, has led not only to the detection but also to the quantification of pharmaceutically active compounds (PhACs) in surface water and groundwater [1] [2]. To address the aforementioned issue, the scientific community has focused on the development of effective water treatment technologies for the removal of residual PhACs. Advanced oxidation processes (AOPs) are considered as one of the most promising techniques for water remediation, enabling the transformation of hazardous organic compounds into smaller, inert molecules such as CO_2 and H_2O [3]. Heterogeneous photocatalysis holds a prominent position among AOPs, since it can utilize solar light in order to face environmental pollution problems [4].

In the present work, the degradation of losartan (LOS), a widely administered medicine for high blood pressure, by ZnSnO_3 (zinc stannate, ZSO) modified with copper phosphide (0 - 1 wt. % Cu_3P) photocatalysts was investigated under simulated solar irradiation. ZSO belongs to the class of ternary oxides and has a reported band gap of 3.22 eV [5]. The physicochemical properties of the samples were determined by means of Brunauer–Emmett–Teller (BET) method, X-Ray diffraction (XRD) and scanning electron microscopy (SEM). Optimal results were obtained in the case of 0.25% $\text{Cu}_3\text{P}/\text{ZnSnO}_3$ where complete degradation of 0.5 mg/L LOS in ultrapure water (UPW) was achieved in 180 min. The markedly enhanced photocatalytic performance of 0.25% $\text{Cu}_3\text{P}/\text{ZnSnO}_3$ was attributed to the efficient separation of the photogenerated species (electron - holes). The effect of some operating parameters of the process (e.g. pH value, LOS initial concentration, catalyst concentration), as well as adsorption and photolysis phenomena were also investigated. Additional experiments were conducted in bottled water (BW) and wastewater (WW) revealing considerably lower efficiency towards LOS degradation. Furthermore, experiments were performed with the addition of humic acid (HA), which simulates the organic fraction naturally occurring in water, NaHCO_3 and NaCl (i.e. the dominant inorganic ions in waters) in UPW. The addition of HCO_3^- decelerated the elimination of LOS while the presence of HA and Cl^- had a minor impact to the process. Subsequently, quenching tests were carried out, revealing the photogenerated holes (h^+) as the main oxidation species in the system.

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Metal-Free Phosphorus-Directed Borylation of aromatic C-H Bonds

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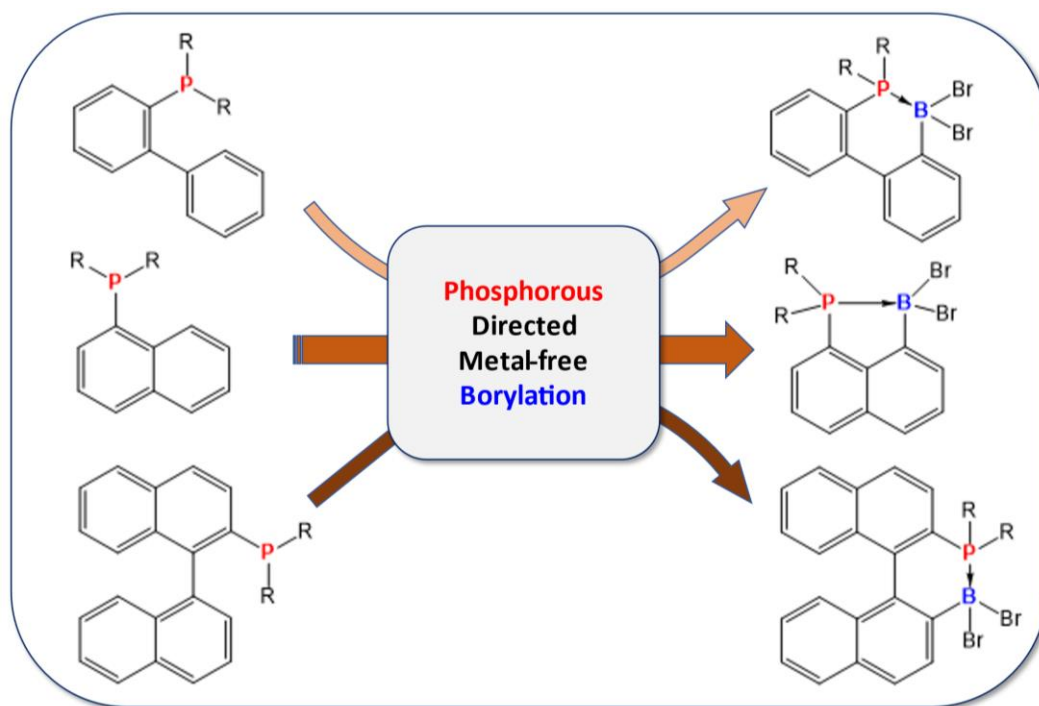
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Phosphines-boranes has recently gathered an increasing interest, regarding their ability to act as ambiphilic ligands^[1] as well as metal-free FLP catalysts.^[2] Borylation of phosphine has the potential to offer an easy and efficient way to synthesize such compounds. Spectacular progress has recently been achieved in transition metal-catalyzed C-H borylation of phosphines^[3] as well as directed electrophilic C-H borylation.^[4] However, to the best of our knowledge, only one example of metal-free phosphorous-directed borylation was reported so far.^[5]

In this context, we reported recently a new synthetic pathway for phosphorous-directed borylation.^[6] Under metal-free conditions, this efficient methodology allowed our team to synthesize a wide range of phosphine-boranes as it is compatible with a large variety of substrates and enables post-functionalization of the borane.



Furthermore, mechanistic studies and DFT calculations brought us a better understanding of the elementary steps of this type of reaction.

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Assessment of DFT calculations across periodic models and finite-size clusters for the conversion of methyl levulinate to γ -valerolactone on UiO-66 MOF

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Conversion of biomass to generate target chemical products to fulfil the feedstock demand is a prominent way to curtail the depletion of petroleum sources and natural gas. Metal-organic frameworks (MOFs) consisting of inorganic nodes and organic linkers are promising porous catalysts due to their large surface area, high activity, selectivity and easily regeneration.¹ Among them, the Zr-based MOF UiO-66 exhibits great performance for the transformation of methyl levulinate (ML) to γ -valerolactone (GVL) by using catalytic transfer hydrogenation (CTH).^{2,3} DFT simulations are indispensable to obtain deeper insights into the mechanism providing useful active sites and energetic details. By means of periodic DFT, our recent work proposed a feasible mechanism of the CTH reaction using UiO-66 with isopropanol as a hydrogen donor.⁴ Although periodic calculations simulate the porous structure and crystalline properties of UiO-66, they are computationally expensive and restricted to local density functionals. Therefore, herein we prepare cluster models to evaluate the molecular interactions with different density functional methods. In comparison with the periodic model, the reaction pathway is similar from a structural point of view, but the Gibbs energy barriers are slightly higher. Next, we evaluate the impact of the density functional employed and their potential role when estimating reaction rates.

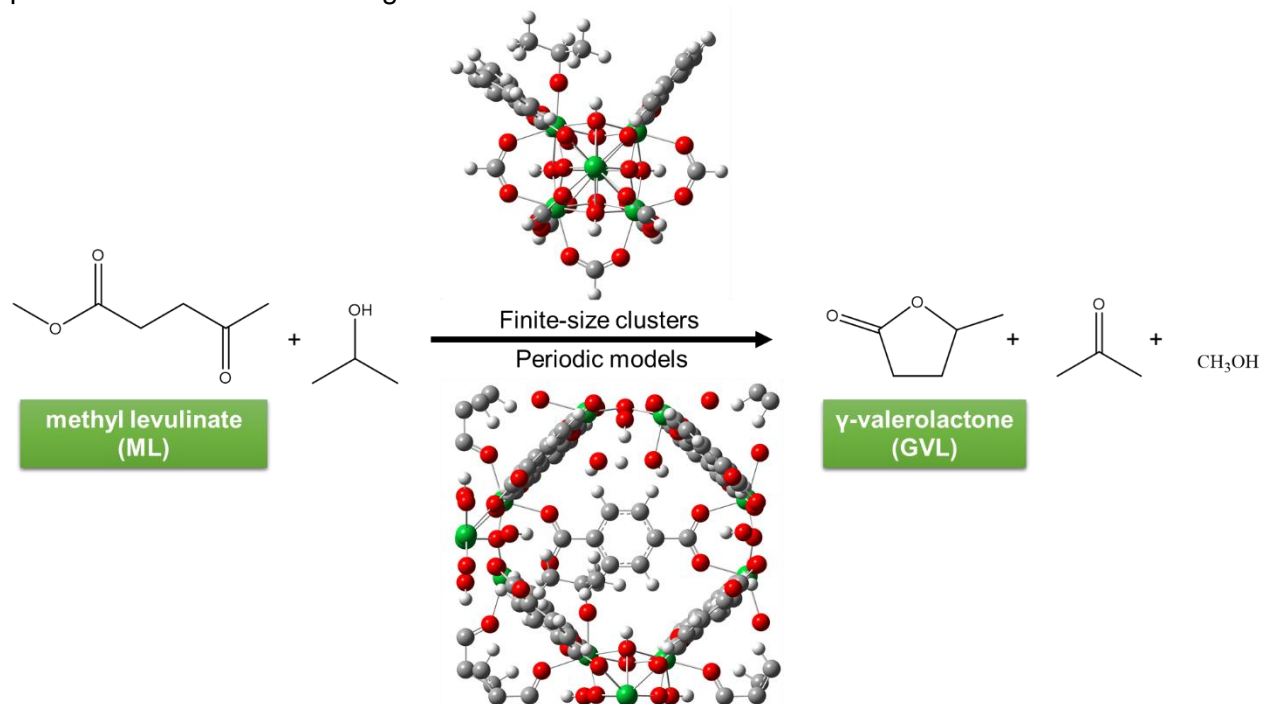


Figure 1. Conversion of methyl levulinate (ML) into γ -valerolactone (GVL) on cluster UiO-66 and on periodic UiO-66 model catalysts.

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Dry reforming of methane for syngas production over Ru catalysts supported on mixed CeO₂ - M₂O₃ oxides (M: La, Pr, Nd, Eu, Gd, Tb, Dy, Er)

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The European Union has pledged to reach carbon neutrality by 2050 harnessing renewable energy sources that have enormous potential as fossil fuel alternatives. Among many, like solar, wind or tidal, biogas is a promising factor in decarbonizing our energy systems. Biogas is composed mainly by CH₄, CO₂, two relatively inert gases that could be utilized to either produce hydrogen or synthetic fuels [1,2]. The Dry Reforming of Methane (DRM) reaction to produce syngas (H₂ and CO) has been gaining increasing popularity over the years in the scientific community compared to the Steam Reforming of Methane (SRM) reaction or the Partial Oxidation of Methane (POM) reaction. This is attributed to the advantages that DRM offers in comparison with the two alternative reforming reactions, namely the valorization of the two most important greenhouse gases (CH₄, CO₂), the production of syngas with a H₂/CO ratio close to unity which renders it ideal for Fischer-Tropsch reactions to produce synthetic fuels, as well as the ability to directly use biogas deriving from anaerobic digestion of biomass from landfills or sewage refining facilities, which is composed of 50-70 % CH₄ and 25-50 % CO₂ [3,4]. Of great importance, when it comes to the yield of the DRM reaction using supported metallic catalysts, is the nature of the support and the promoters employed. The promotion of Cerium oxide (CeO₂) with rare earth elements (e.g. Pr) improves the ability of CeO₂ to store oxygen [5] but also the lability of the lattice oxygen, thereby diminishing the carbon formed on the surface of the catalyst and facilitating the activation of CO₂. Toward this direction a series of 1 wt.% Ru catalysts supported on mixed oxides Ce_{0.8}M_{0.2}O_x (M: La, Pr, Nd, Eu, Gd, Dy and Er) were synthesized by the wet impregnation method in order to be studied as it concerns their DRM activity. The supports were synthesized via the co-precipitation method [6] with a molecular ratio of Ce:M equal to 80:20. The as synthesized catalysts were characterized with respect to their specific surface area and phase composition employing the BET method and X-ray diffraction technique, respectively. The reducibility of the catalysts was investigated with the TPR-H₂ technique. The catalytic performance tests were performed in the temperature range 550-800 °C with a volumetric feed ratio of CH₄: CO₂ equal to 50:50. Ru catalysts supported on Ce_{0.8}Dy_{0.2}O_x and Ce_{0.8}Gd_{0.2}O_x mixed oxide carriers have shown the best results.

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Non-oxidative dehydrogenation of methanol to formaldehyde over bulk β -Ga₂O₃

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Formaldehyde (CH₂O) is one of the most important industrial chemicals, which is conventionally produced in the form of aqueous solution by the selective vapor-phase oxidation of methanol (CH₃OH) over silver or iron-molybdenum catalysts. Although the non-oxidative dehydrogenation of CH₃OH is an attractive alternative route due to direct formation of anhydrous CH₂O and H₂ as a valuable coupled product, the process has still not been developed for large-scale applications. Recent studies^[1] have demonstrated that β -Ga₂O₃ can effectively catalyze the dehydrogenation of primary and secondary alcohols. In our work, we investigate the effect of reaction conditions on the catalytic performance of β -Ga₂O₃ under the conditions of non-oxidative dehydrogenation of CH₃OH with focus on deactivation and possible regeneration of the catalyst.

The catalytic activity of β -Ga₂O₃ is strongly dependent on temperature (Figure 1a), and a high selectivity to CH₂O was observed between 500 °C and 650 °C. In the long-term studies (Figure 1b) an initial selectivity to CH₂O of 77% was obtained at a CH₃OH conversion of 72% at 550 °C and a GHSV of 45500 h⁻¹. The catalyst suffered from deactivation caused by formation of carbon deposits and partial reduction of Ga₂O₃ but it was possible to regenerate its initial activity after at 500 °C and 550 °C completely by an oxidative treatment. In contrast, irreversible deactivation occurred at 650 °C due to partial volatilization of Ga₂O₃.

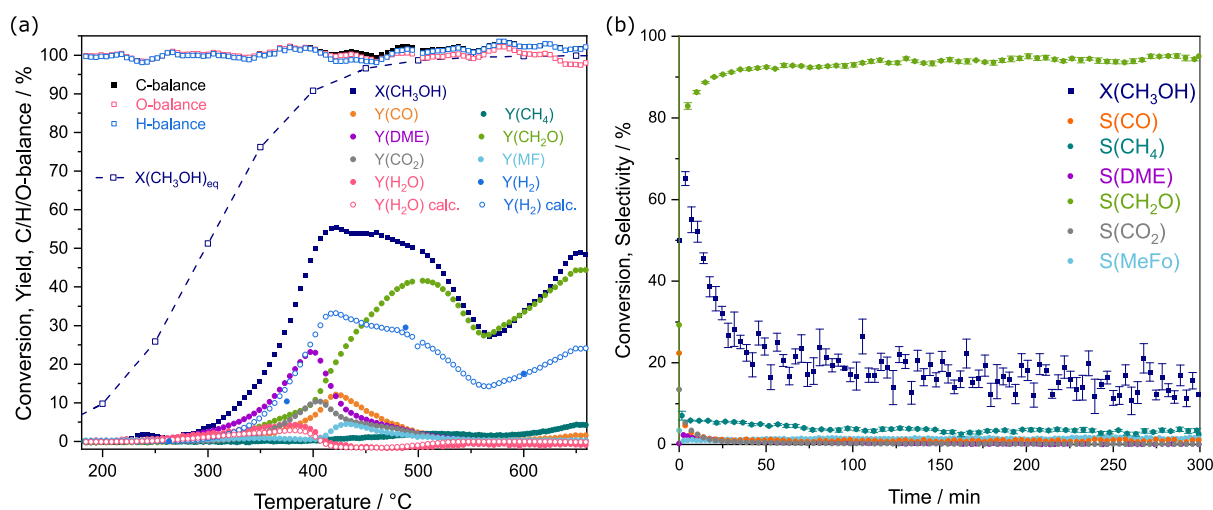


Figure 1. (a) Light-off curve for β -Ga₂O₃ at heating rate of 2 °C min⁻¹. (b) Catalytic activity of β -Ga₂O₃ in the dehydrogenation of CH₃OH during 300 min TOS at 550 °C. Reaction conditions: 2.6% CH₃OH in 300 STP mL min⁻¹ CH₃OH, GHSV 45500 h⁻¹, 50 mg of 250-355 μ m catalyst pellets in 450 mg SiC.

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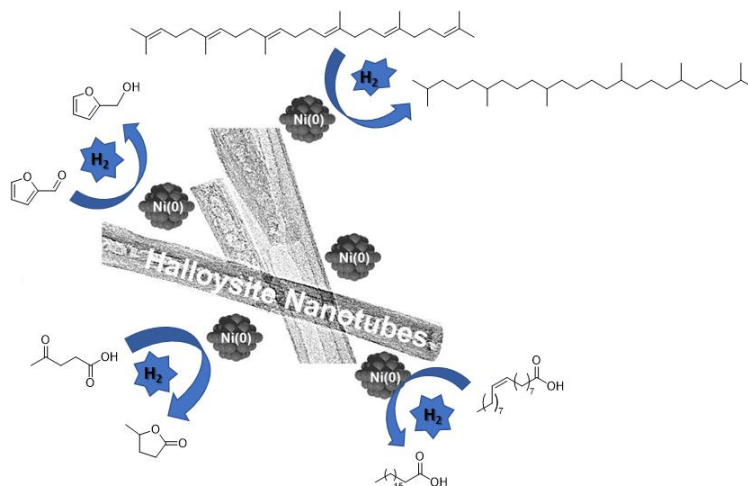
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NICKEL NANOPARTICLES IMMOBILIZED ON HALLOYSITE. AN OUTSTANDING CATALYST TOWARDS HYDROGENATION

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

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 design of sustainable processes.^[1] Herein, we report the synthesis of nickel nanoparticles supported on both natural and functionalized HAL clays, by one-pot methodology: reduction of $[\text{Ni}(\text{COD})_2]$ to Ni(0) nanoparticles (NiNP) in the presence of the halloysite acting as a support under smooth conditions (ethanol, 90 °C under 3 bar of H_2), based on the methodology previously described by our team;^[2] for unfunctionalized HAL, addition of a stabilizer was required (quinidine, quinine, triphenylphosphine, choline chloride, PVP...). These nanomaterials were fully characterized (by elemental analysis, TGA, DSC, ICP-AES, FTIR, XPS, PXRD and (HR)TEM) (Figure 1).



The as-prepared 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, highlighting the relevance of the nature of the support and the stabilizer in catalysis. Actually, NiNP-QUINIDINE@HAL catalyst was highly efficient towards a wide range of substrates, including fatty acids, squalene, furfural and levulinic acid. This catalyst was reused up to 5 times without activity loss.

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CO₂ capture and transformation into molecules of interest using a catalytic membrane system

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Greenhouse gas (GHG) levels continue to increase in the atmosphere, which is why in recent decades, the use of CO₂ as a C1 building block has become popular [1]. However, the development of efficient catalytic processes for its transformation into value-added products remains a challenge. Our strategy encompasses the design of a catalytic system based in a Hollow Fiber Catalytic Membrane Contactor (HFCMC) towards CO₂ activation via a dual activation with Lewis basic sites on the membrane in combination with metal nanocatalysts.

In the frame of the collaboration between LHFA and LGC laboratories concerning the design and applications of polymeric catalytic membranes [2], we present herein the grafting of DABCO derivatives through photoactivated polymerization as well as the synthesis of copper iodide nanoparticles towards the selective transformation of CO₂ into high added-value heterocycles.

Results of a tandem four-component reaction involving aldehydes, amines, alkynes and CO₂ will be presented as well as preliminary mechanistic insights (REACT-IR monitoring). Furthermore, studies on a stereo-selective hydrogenation will be shown to achieve saturated oxazolidinones, key structural scaffolds present in drugs with relevant uses as antibiotics or anticoagulants (Figure 1).

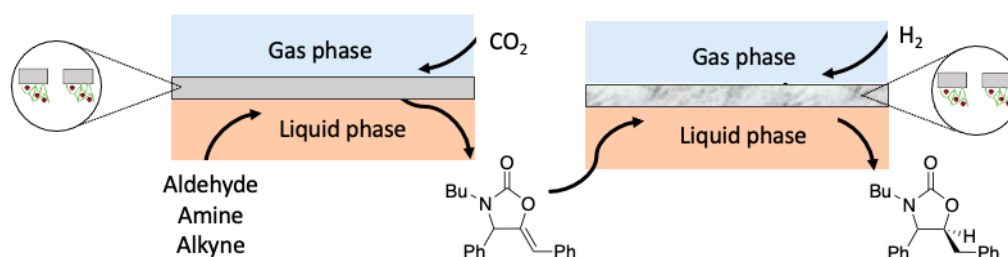


Figure 1. Polymeric catalytic membrane contactor for the stereo-selective synthesis of heterocycles.

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Metal–Polymer Heterojunction in Colloidal-Phase Plasmonic Catalysis

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Plasmonic catalysis has become a convenient strategy for solar fuel production in which all-metal architectures drive chemical transformation under a wide spectral range of incoming light.¹ Plasmons are basically collective oscillation of free electrons in metals. The characteristic wavelength of plasmons approaches that of visible light in particles in the colloidal domain, which makes them interesting for energy purposes. Plasmonic nanoparticles are thought to drive chemical conversion either by direct injection of hot carriers generated by the relaxation of localized surface plasmon resonance (LSPR) or by thermoplasmonic effect, where dissipation of plasmon energy increases the local temperature and thus the rate of a chemical reaction.^{2,3} Regardless of the true mechanism behind plasmonic catalysis, the experimental data indicate that these nanomaterials bring unprecedented opportunities in the development of so-called plasmonic photosynthesis.^{4,5} Plasmonic nanoparticles in solution needs to be stabilized to prevent aggregation by appropriate agents, the most common being molecular cationic surfactants. However, tight interaction with the metal often leads to a great inhibition of the photocatalytic activity.⁶⁻⁸ In this work, we show that water-soluble conjugated polymers can promote the formation of a metal–organic heterojunction on gold nanoparticles of different shapes, including spheres, cubes, rods, and bipyramids. We demonstrate that the polymers ensure both colloidal stability and noticeable activity in photoredox catalysis. In particular, a colloidal aqueous suspension of gold nanorods decorated with poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS) was successfully applied to the photoconversion of the biorelevant NAD⁺ to its highly energetic reduced form NADH in the presence of triethanolamine (TEOAH) as sacrificial electron donor (Figure 1). We foresee that the design of metal–polymer heterojunctions will drive plasmonic catalysis towards a new generation of photoactive nanomaterials, which will eventually allow to get rid of noble transition-metal co-catalysts.

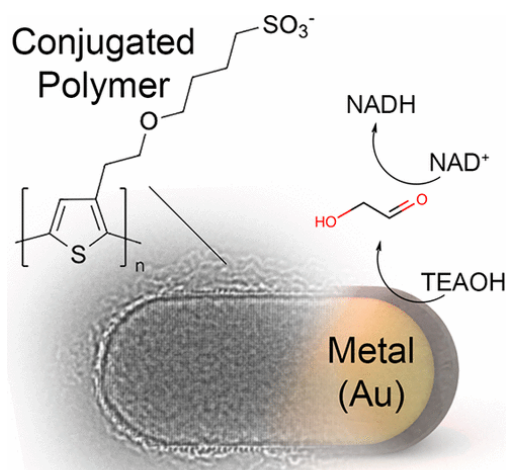


Figure 1: Water-soluble conjugated polymer covering gold nanoparticles promotes selective oxidation of electron donor molecules in the presence of light.

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Cobalt-based nanocatalysts for valorisation of fatty acids

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One of the most promising biomass sources for production of fuel and high added-value chemicals are the triglycerides from vegetable oils and animal fats. These triglycerides are generally composed of unsaturated fatty acids with a low degree of functionalization, making them an attractive renewable feedstock [1]. Under catalytic hydrogenation conditions, alcohols, hydrocarbons, and saturated fatty acids can be obtained, target compounds finding applications as food additives, biofuels, lubricants, detergents, stabilizers, polymers, etc. [2,3].

In recent years, much progress has been made in the use of supported noble metal catalysts for the valorisation of carboxylic acids. However, it is still a major challenge to effectively perform these reactions on carboxylic acids using more earth abundant and less toxic metals [4]. Recently, cobalt-based homogeneous catalysts have been reported for selective hydrogenation of alkenes [5,6], and reduction of carboxylic acids to alcohols with superior activity [7], leading to the research and development of heterogeneous Co-based catalysts to perform these transformations. Halloysite, a natural nano-structured clay, has emerged as an attractive support of nanocatalysts for its large surface area and tubular structure. Additionally, its low-cost, availability and biocompatibility represent crucial properties for its application in catalysis and industrial processes [8].

In this work, Co-based nanoparticles supported on halloysites will be presented, prepared by three different methods and applied as catalysts in hydrogenations of fatty acids derivatives. A correlation of stabilizer and the synthesis approach with catalytic results will be outlined (Figure 1).

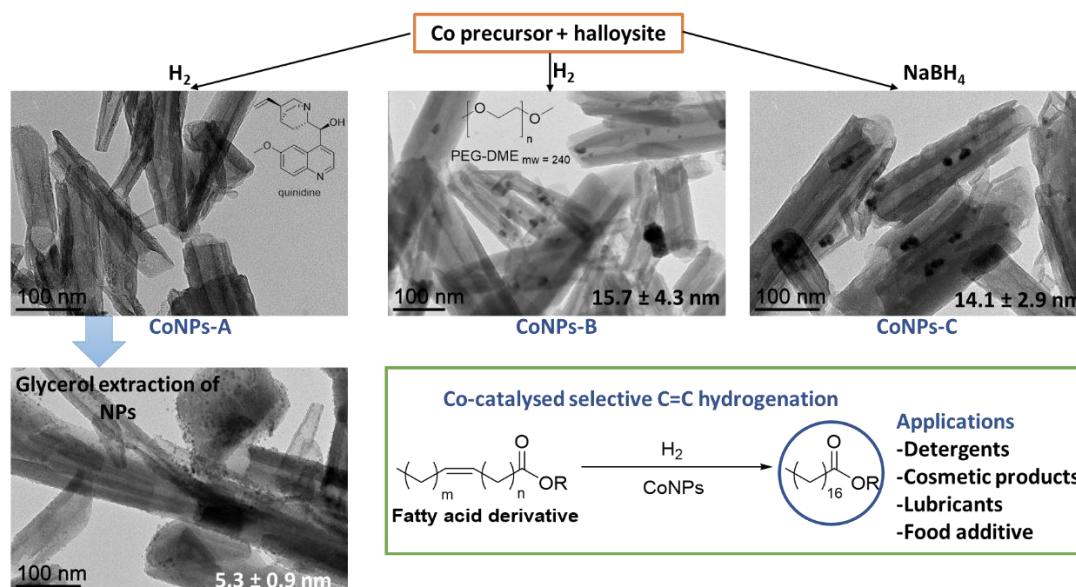


Figure 1. TEM images of Co-based nanoparticles supported on pristine halloysite prepared under different conditions (top), showing their application in hydrogenation of unsaturated fatty acids.

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Selective Hydrodeoxygenation of Aldehydes under Mild Condition using Copper-Decorated Iron Carbide Nanoparticle Activated by Magnetic Induction

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The selective hydrodeoxygenation of aldehydes to methylene units in the side chain of multifunctional aromatic substrates is an important transformation for the fine chemical and pharmaceutical industries as well as for the upgrading of biomass feedstock to value-added chemicals.[1] However, this requires the design of catalytic systems capable of hydrogenating and deoxygenating aromatic aldehydes, while leaving the aromaticity of the ring untouched. While promising results have been obtained in some cases for individual substrates, most of the traditional solid catalysts show severe limitations such as low hydrogenation selectivity, formation of side-products, and typically require harsh conditions ($> 150^{\circ}\text{C}$ and > 20 bar H_2). In the past years, pioneering groups including ours evidenced the potential benefits associated with the use of magnetic induction heating in catalysis (i.e. energy efficiency, localized heating, rapid heating and cooling, adaptivity to intermittent energy supply).[2-4] In particular, we reported recently the selective continuous flow hydrogenation of a wide range of aromatic ketones under mild conditions using a commercial catalyst ($\text{Cu}_2\text{Cr}_2\text{O}_5$) decorated with tailor-made iron carbide nanoparticles (ICNPs)[3] activated locally by magnetic induction.[4] In this work, we present the preparation and characterization of a novel multifunctional catalytic system composed of ICNPs decorated with small Cu NPs (Figure 1a and 1d-f). Using the resulting Cu@ICNPs activated by magnetic induction, aromatic aldehydes with a wide range of functional groups could be converted to valuable aromatic alkanes in excellent yields and selectivities under observable mild conditions ($\sim 100^{\circ}\text{C}$, 3 bar H_2). In contrast, Cu@ICNPs, ICNPs or Cu NPs show low activity when heated conventionally, even at 200°C . This work demonstrates the possibility to use magnetic induction heating to perform challenging hydrodeoxygenation reactions at low pressure and temperature with noble metal-free catalysts.

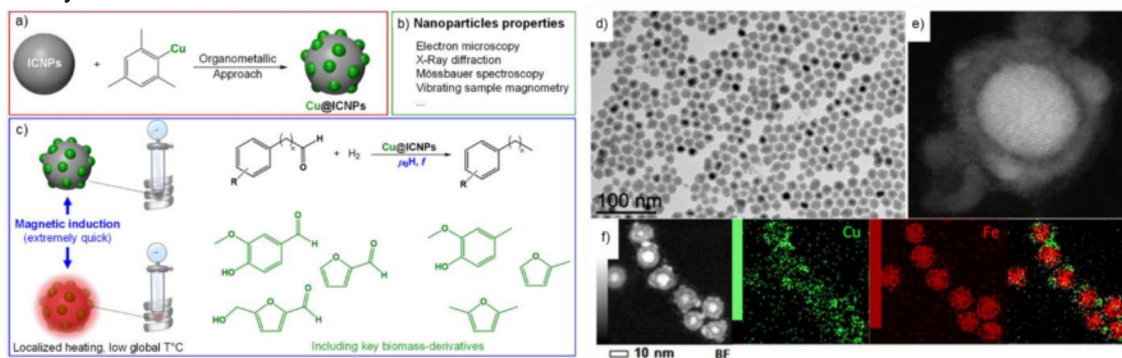


Figure 1. Illustration of the approach in this study (left). a) synthetic approach for Cu@ICNPs, b) characterization, and c) catalytic application using magnetic induction heating. Characterization of Cu@ICNPs nanoparticles (right). d) TEM, e) STEM-HAADF, f) STEM-HAADF-EDX.

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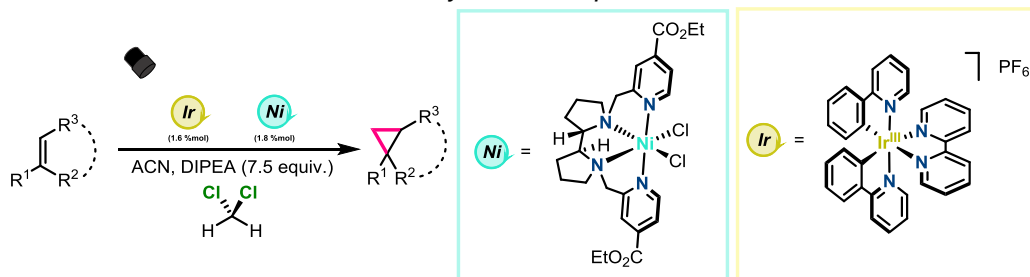
Cyclopropanation of Olefins Using Dichloromethane *via* Photoredox Catalysis

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The incorporation of a cyclopropyl group into organic skeleton has been drawn significant attention in organic synthesis and medical chemistry, enhancing metabolic stability, bioactivity and specificity.¹ Most classically, cyclopropanation is achieved by [2+1] cycloaddition, in which CH₂I₂ is used to generate a carbene specie that However, this reactivity presents some limitations. For this reason a procedure using ready available carbon sources such as dichloromethane (DCM) needs to be developed.

In this way, the use of DCM as reagent as building block is challenging, considering that the inertness of alkyl chlorides has precluded them as building blocks for organic methodologies. Our group achieved the activation of C_{sp³}-Cl bonds a dual metal catalytic system based on earth-abundant metals and using visible-light as energy source² that addressed dehalogenation of primary alkyl chlorides and an intramolecular reductive coupling of alkyl chlorides.³ Recently, tuning the previous conditions with a rational photocatalyst design, we developed a novel photoredox reductive cross-coupling reaction between alkyl chlorides and olefins.⁴

Following the same concept, herein we disclose a novel photoredox catalysis strategy of cyclopropanation using dichloromethane as common chlorinated solvent with a broad olefin scope. These results highlighted our system as a playground for the development of new cyclopropanation methodology

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Benzaldehyde-mediated oxidation of cyclohexane to K-A oil: a mechanistic investigation

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The selective oxidation of cyclohexane to K-A oil (a mixture of cyclohexanone and cyclohexanol) is a very important reaction in industrial chemistry, as it is the first step in the production of nylon-6 and nylon-6,6. However, the reaction is complicated by kinetic and thermodynamic constraints. In fact, inserting oxygen in the C-H bond of cyclohexane normally requires harsh conditions of T and P, but such conditions can lead to overoxidation of the K-A oil product. Moreover, the reaction proceeds through a complex free-radical mechanism[1]. The current industrial processes makes use of cobalt(II) salts as homogeneous catalyst and reaches limited conversions of cyclohexane in order to maintain a relatively high selectivity to K-A oil (around 80%), under 150°C and 10-15 bars of air [2,3]. Alternatively, in the current state-of-the-art, higher performances are generally obtained using expensive catalysts or expensive radical initiators, such as tert-butyl hydroperoxide (TBHP)[4–8]. This is where the obtainment of suitable heterogeneous catalysts would come useful, tuning the selectivity at milder conditions. In this work, the catalytic oxidation of cyclohexane to K-A oil under mild reaction conditions (120°C, 4 bar O₂) using a bimetallic AuCu system is presented. In fact, gold has been renowned for its activity in selective oxidation reactions (including cyclohexane oxidation) and for its efficacy in the activation of the C-H bonds of many molecules[9]. On the other hand, Cu was combined to favour the radical mechanism, being it able to undergo single electron switch. In this context, the reaction was carried out in the absence and in the presence of a 2wt% Au₁Cu₁/Al₂O₃ catalyst. The catalyst alone could not initiate the radical mechanism, but the addition of different amounts of benzaldehyde as an alternative, non-toxic radical initiator, allowed to study the influence of the catalyst on K-A oil production (Fig. 1). The role of benzoic acid and benzyl alcohol formation was also disclosed. Eventually, the catalyst was characterized by HAADF STEM-EDX and XPS, in order to assess its bimetallic nature.

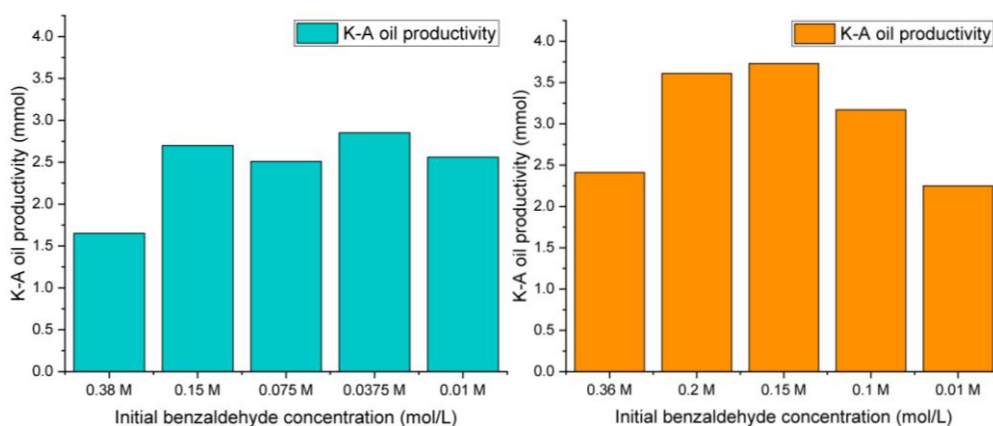


Fig. 1. Cyclohexane oxidation under mild conditions (120°C, 4 bar O₂) varying the initial concentration of benzaldehyde a) in the absence of the catalyst and b) in the presence of a 2 wt% Au₁Cu₁/Al₂O₃ catalyst (20 mg).

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Ru-Bipyridine Entrapped in the Supercages of EMC-1 Faujasite as Catalyst for the Trifluoromethylation of Arenes¹

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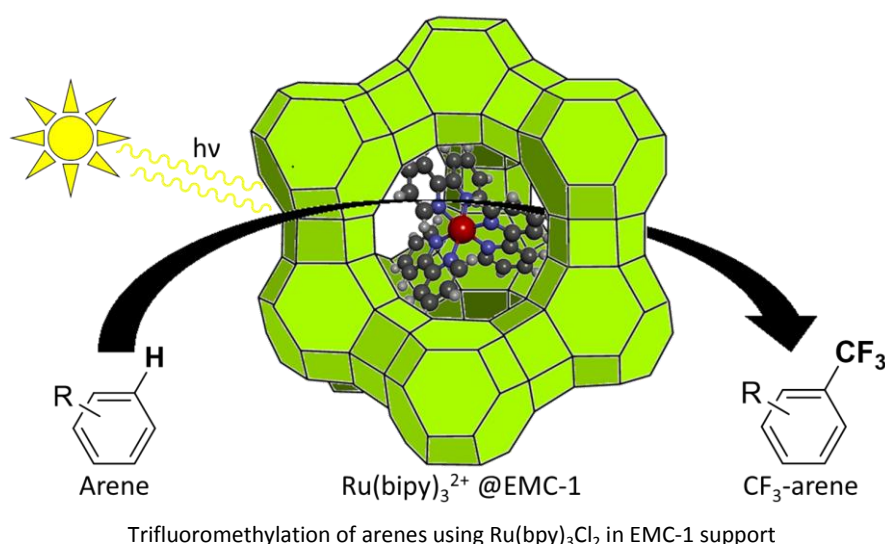
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Trifluoromethylation is an important reaction in the production of agrochemicals, pharmaceuticals and other functional materials. In pharmaceuticals and agrochemicals, the CF₃-group provides higher chemical/metabolic stability and enhances parameters such as lipophilicity and binding selectivity.² Currently, cross-coupling reactions are mainly used for the trifluoromethylation of arenes, which employ stoichiometric amounts of organometallic complexes or metal oxidants, expensive and corrosive CF₃-sources and require high temperature. Therefore photoredox catalysts, such as the well-known and well-studied Ru(bpy)₃Cl₂ are used to solve most of these problems. In this way, visible light is used as an energy source to activate economically friendly CF₃SO₂Cl, while working at room temperature. Recently, a homogeneous system with this photocatalyst was reported³, which still requires separation of the catalyst from the reaction products.

In this work¹, we incorporate the Ru(bpy)₃Cl₂ photocatalyst in the supercages of a FAU-type zeolite Y (EMC-1) via a “ship-in-a-bottle” technique. The formation of the complex inside the zeolite pores was confirmed with a variety of techniques including FTIR, UV-VIS spectroscopy and XAS. XRD measurements concluded that the support material was stable in acidified reaction environments and recyclability tests pointed out that the catalyst could be used multiple times without leaching and activity loss. A broad substrate scope showed that the newly developed catalyst can be used for the trifluoromethylation of different arenes, including some pharmaceutical relevant precursors, with yields above 70%.



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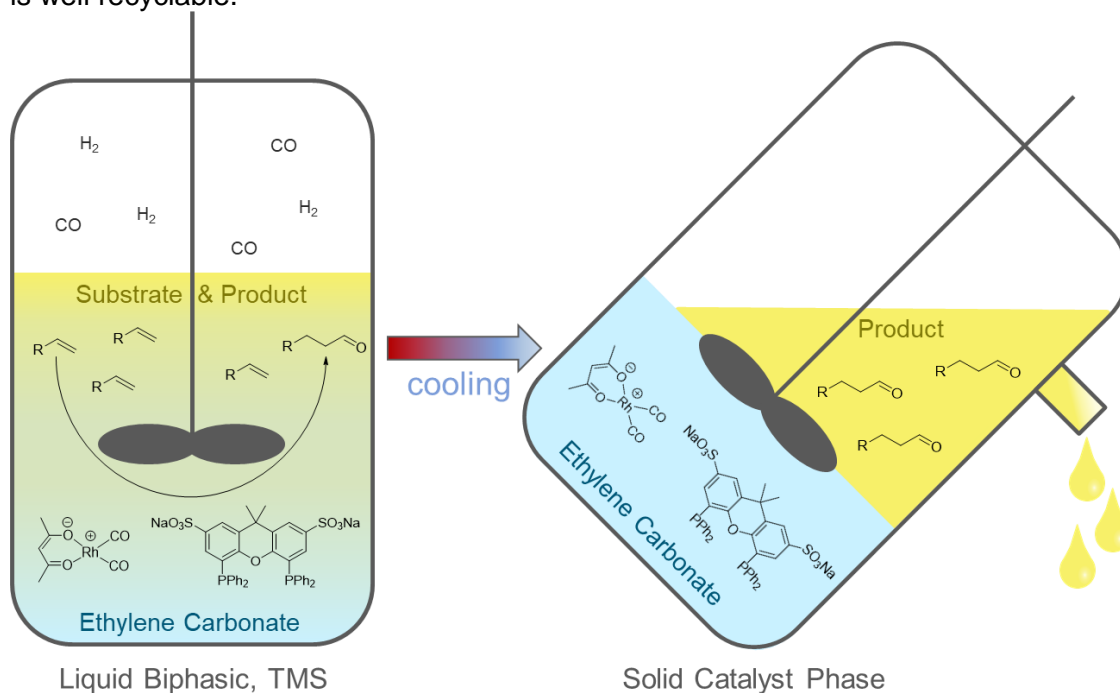
Hydroformylation of 1-Octene in TMS and biphasic Systems with Ethylene Carbonate and a Crystallization of the Catalyst Phase

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The hydroformylation reaction is one of the most important and most used homogeneously catalysed processes.^[1] Olefins react to aldehydes using transition metal complexes such as rhodium carbonyls modified with phosphine ligands. The recycling of such catalysts and their removal from the product are a focus in research and industry.^[2] A method to achieve this is through multiphase catalysis. A well-known system for the hydroformylation of short chain olefins such as ethylene and propylene is the Rhône Poulenc/Ruhrchemie process using water soluble ligands, resulting in the separation of a pure product phase from the catalyst phase.^[3-4] However, this method is not suitable for longer olefins.^[3] Less polar solvents for the catalyst phase such as glycols and carbonates need to be applied.^[5-6] Using two solvents with a smaller polarity gap additionally allows for the development of thermomorphic multicomponent systems (TMS). In these systems, the solvents are miscible at increased temperatures and turn biphasic again after the reaction. TMS combine the advantages of a fast reaction rate in single phasic mixtures with the recyclability in biphasic mixtures.^[7] Herein, we present the development of a TMS System based on ethylene carbonate as a green catalyst solvent with Rh/sulfoXantphos as a water-soluble catalyst in the highly selective hydroformylation of 1-octene. Ethylene carbonate and the reaction product Nonanal form a TMS System. However, the TMS is of a disadvantage in this reaction as it causes a precipitation of the catalyst past a certain nonanal yield. Modifications have been investigated in order to increase the thermomorphic temperature to remain in the biphasic regime. The addition of less polar solvents to the catalyst phase such as *n*-decane or the addition of water to the catalyst phase result in a slower but improved reaction system which is well recyclable.



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Quantum Yield Enhancement in Photocatalytic HCOOH Decomposition to H₂ under Periodic Illumination

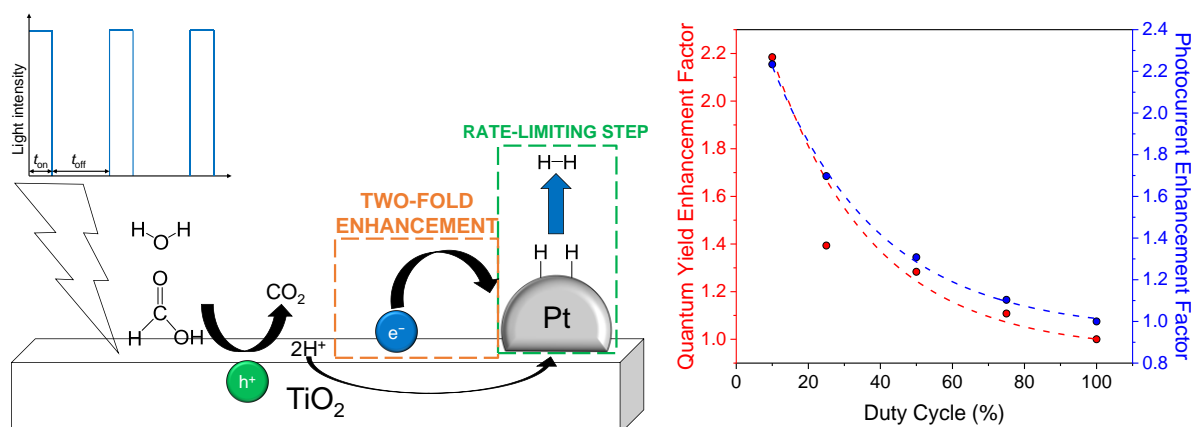
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Controlled periodic illumination has received significant attention as a promising approach to improve the quantum yield of photocatalytic processes. Despite numerous studies on controlled periodic illumination to improve the quantum yield of photocatalytic reactions, debates still exist on the dominating reason for the observed enhancements. Here, we studied the effects of periodic illumination on HCOOH dehydrogenation over TiO₂-supported noble metal photocatalysts. We demonstrated that intermittent illumination at moderate frequency of approximately 7 Hz and 10% duty cycle improved the quantum yield of H₂ production by more than 2-fold, regardless of type of metals on TiO₂. In conjunction with photoelectrochemical characterisation techniques, we suggest that the promotion mechanism in periodic illumination involves enhancement in the electron charge transfer kinetics for more efficient electron migration to the metal nanoparticles for subsequent proton reduction. This explanation is suggested by the linear correlation between quantum yield and photocurrent enhancement factors as functions of duty cycles, which seems to be generalisable among different photocatalysts under periodic illumination. Kinetic isotope effect (KIE) studies suggest that Pt-H cleavage to be a rate-limiting step for H₂ productivity under both continuous and periodic illumination.



Synthesis, Characterization and Catalytic Application of Colloidal and Supported Mn Nanoparticles

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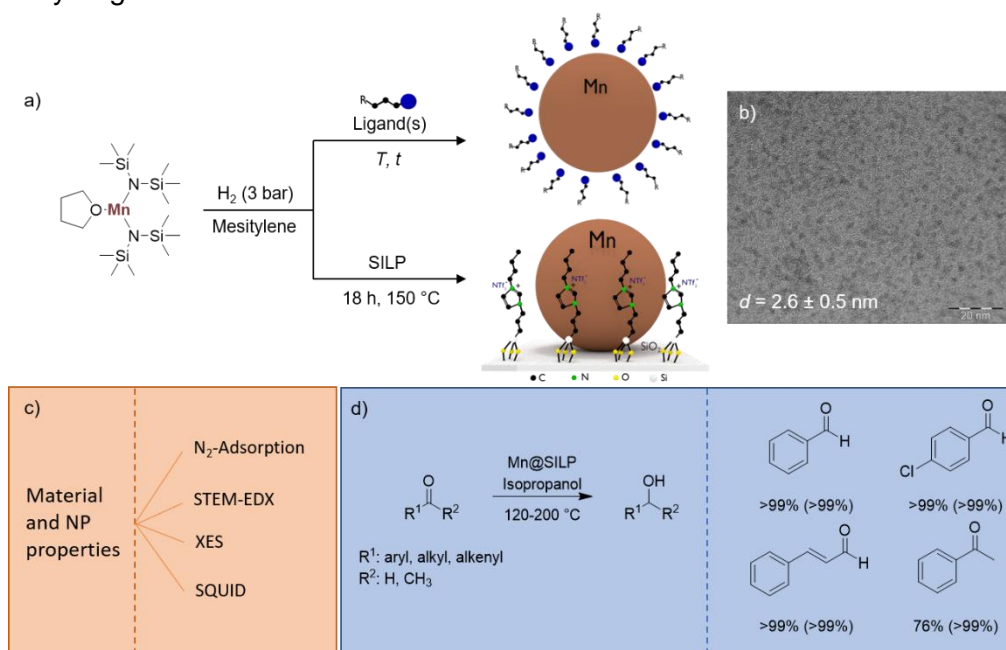
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Catalysis represents one of the most important tools of modern chemistry to improve the sustainability, efficiency and profitability of any given chemical process.^[1] In this context, transition metal nanoparticles (NPs) are recognized as efficient catalysts in a variety of chemical transformations;^[2] however, in recent years an increased effort has been made to replace toxic and precious metals with biocompatible and earth-abundant metals. Although Manganese shows great potential in homogeneous catalysis, metallic Mn NPs have been rarely considered in catalysis due to their high oxophilicity.

In this context, our work focuses on the preparation of various Mn NP based materials, their characterization and application in catalysis. Firstly, an organometallic synthetic approach was developed to access small (1-3 nm) and monodisperse colloidal Mn(0) NPs (Figure 1a-b). The influence of various synthetic parameters (e.g. stabilizing ligands, reaction time and temperature) on the NP properties was investigated. The resulting NPs were characterized using a combination of techniques (Figure 1c).

The Mn NPs were successfully immobilized on various carbon- and silica-based supports using different *in-situ* and *ex-situ* approaches. In particular, Supported Ionic Liquid Phases (SILPs) were considered as supports since they were shown to be suitable matrices for the synthesis and stabilization of a wide range of monometallic and bimetallic to produce multifunctional NPs@MMS catalysts with tailor-made reactivity.^[3] Mn@SILP catalysts showed very good activity and selectivity in the catalytic transfer hydrogenation of various aldehydes and ketones using isopropanol as a hydrogen source (Figure 1d). Mechanistic studies revealed that the reaction involves a direct hydrogen transfer opposed to metal-mediated hydrogenation.



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