Tetraazanaphthalene-based hypercrosslinked polymer for the photocatalytic synthesis of formamides from CO_2

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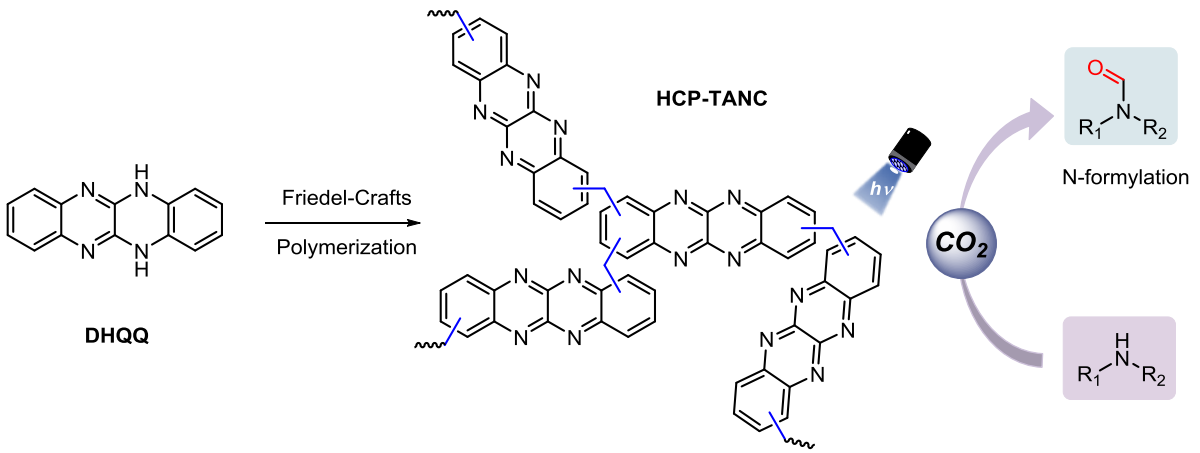
Hyper-crosslinked polymers (HCPs) are very interesting porous organic polymers (POPs) due to their easy preparation, robustness and versatility, high stability, high surface areas and large micropores volume.[1] These properties make HCPs promising materials for gas and energy storage, water splitting, catalysis, drug delivery and sensing. In addition, is possible to modulate and design these polymers to control the functionability and composition to develop a desired application.[2]

CO_2 is present in the atmosphere, but the uncontrolled emissions are a crucial factor in climate change and global warming. Nowadays, the emissions are increasing because of human activities, so it is really important to minimize the excess and, as a result, reduce the effects on the atmosphere.[3] The synthesis of formamides using CO_2, has high relevance in the synthesis of drug molecules, agrochemicals, or nitrogen-based heterocycles. Normally, to afford the N-formylation of amines, it is necessary the use of metals, high pressure of CO_2, high temperature and long reaction times. Therefore, the group had developed novel ion-liquid catalysts, supported on hyper-crosslinked polymers, enabling N-formylation of amines using CO_2 under mild conditions.[4]

Over the past years, photocatalysis research is growing up because of the ability to drive selective and sustainable chemical reactions allowing clean energy production, through a conversion of visible light into chemical energy. There are porous organic polymers (POPs) reported as metal-free heterogeneous photocatalysts due to the capability to modify the light absorption region and the charge transfer efficiency.[2]

It is known that π-π stacking in organic conjugated molecules can increase the absorption spectrum and decrease the band gap. 5, 12- Dihydroquinoline [2,3-b] quinoline (DHQQ) derivatives are known as organic photocatalysts with good absorption of visible light and excellent redox properties.[5] This work focuses on a promising tetraazanaphthalene-based hyper-crosslinked polymer (HCP-TANC) prepared from DHQQ as high robust and recyclable heterogeneous photocatalyst in the N-formylation of different amines with CO_2 at low pressure, phenylsilane as a hydrogen donor, and DMF as a crucial polar additive, at room temperature obtaining excellent yields.



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Vers l'élaboration de métaux supportés sur phosphates de terres rares : des matériaux tolérants à l'eau pour la valorisation de la biomasse

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La transformation de la biomasse en molécules d'intérêt se présente comme un enjeu majeur pour le développement d'une chimie durable, visant à s'affranchir au maximum de l'utilisation de ressources fossiles. Toutefois, la conversion de produits biosourcés bruts en composés à forte valeur ajoutée nécessite le développement de catalyseurs capables de promouvoir des réactions à la fois sélectives et efficaces en milieu aqueux. Plusieurs matériaux ont déjà été décrits dans la littérature, présentant de bonnes performances. Néanmoins, ces systèmes catalytiques demeurent souvent coûteux et leur stabilité est parfois limitée, notamment en raison de phénomènes de lixiviation. C'est dans ce contexte que s'inscrit cette thèse. Plus précisément, ce travail vise à développer des catalyseurs bifonctionnels reposant sur la combinaison d'un support de phosphates de terres rares ($LnPO_4$), connus pour leur stabilité et présentant des propriétés acides, et d'un métal supporté permettant une hydrogénation. L'exemple présenté ici concerne la transformation de la cellulose en sorbitol (Figure 1).

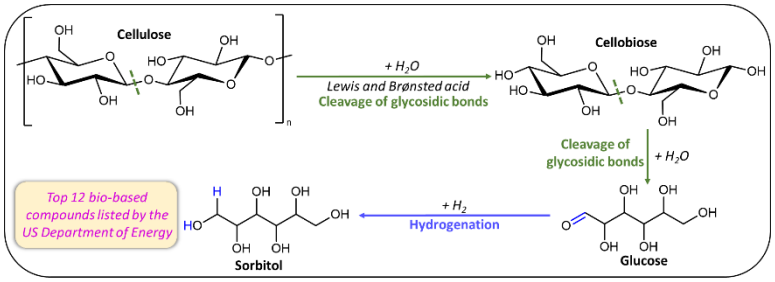

Figure 1 : Transformation de la cellulose en sorbitol

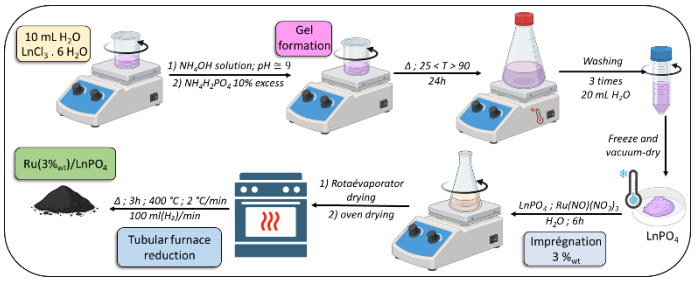

Figure 2 : Synthèse des catalyseurs Ru/$LnPO_4$

Les catalyseurs utilisés sont à base de Ruthénium supporté sur des phosphates de Lanthane, Erbium, et Scandium. Leur synthèse est présentée en Figure 2. Le protocole standard des réactions catalytiques est décrit en Figure 3.

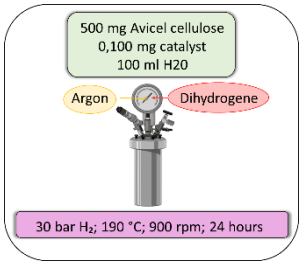

Figure 3 : Conditions de réaction catalytiques

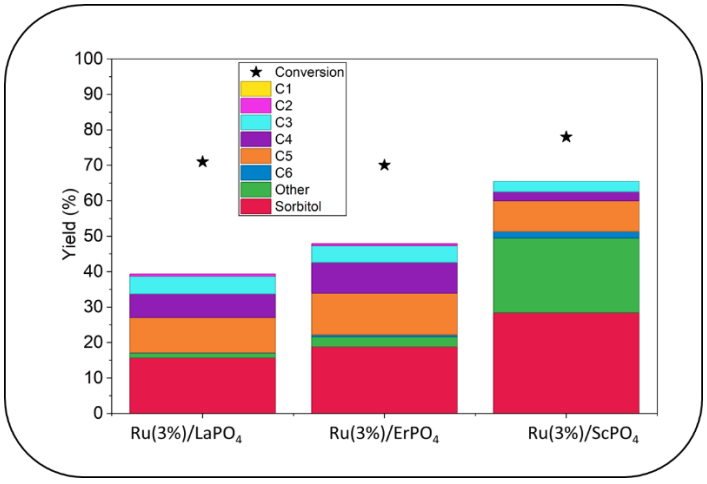

Figure 4 : Conversion de la cellulose et rendements avec trois catalyseurs différents

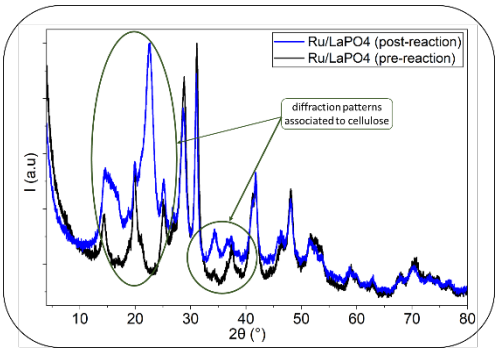

Figure 5 : Diffractogramme de Ru/LaPO4 avant (noir) et après (bleu) réaction.

La Figure 4 met en évidence des rendements en sorbitol intéressants, de l'ordre de 30%. Les performances de ces nouveaux catalyseurs, encore inédites dans la littérature pour ce type de réaction, se révèlent d'ores et déjà remarquables. Bien que ce travail n'en soit qu'à ses débuts, les résultats obtenus apparaissent encourageants et prometteurs, en particulier en ce qui concerne la stabilité hydrothermale de la structure (Figure 5). Au-delà de l'intérêt fondamental lié à la compréhension de ces systèmes catalytiques, ces matériaux se présentent comme une alternative prometteuse pour le développement de catalyseurs hétérogènes destinés à la transformation de la biomasse en phase aqueuse.

Enhanced CO_2 Methanation over NiO Catalysts Promoted by Noble Metals

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The combustion of hydrocarbons in industry, energy, and transport is a major source of CO_2 emissions, contributing to global warming and climate change [1]. Over the past 300 years, atmospheric CO_2 levels have increased by ~50% [2,3]. Recent technologies, such as carbon capture and storage (CCS) and direct air capture (DAC) implemented at the Orca plant, the Mammoth plant, etc. enable CO_2 removal from the atmosphere; however, efficient utilization of captured CO_2 remains a key challenge [4,5].

CO_2 methanation is a promising approach for CO_2 utilization, converting it into methane via hydrogenation—a process that can be viewed as the reverse of hydrocarbon combustion [6]. This reaction offers the potential for a closed carbon cycle.

Nickel oxide (NiO) is widely used as a catalyst for hydrogenation reactions. Its catalytic performance strongly depends on particle size, morphology, and surface properties. In this work, NiO micro- and nanoparticles were synthesized via a solvothermal method followed by thermal decomposition [7,8]. By varying synthesis conditions, different morphologies (microspheres, nanosheets, hexagonal particles, and nanodiscs) were obtained. Moreover, intercalation of nickel oxide with a small amount of noble metals (rhodium, platinum) improves catalytic performance.

Catalytic testing in CO_2 methanation showed high activity and selectivity toward CH_4. The best performance was achieved for NiO with disc-like and spherical morphology, reaching CH_4 selectivity close to 100% and CO_2 conversion up to ~93% [9,10].

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Synergistic Electronic and Supramolecular Stability in a Perimidine-Based Iron(II) Complex

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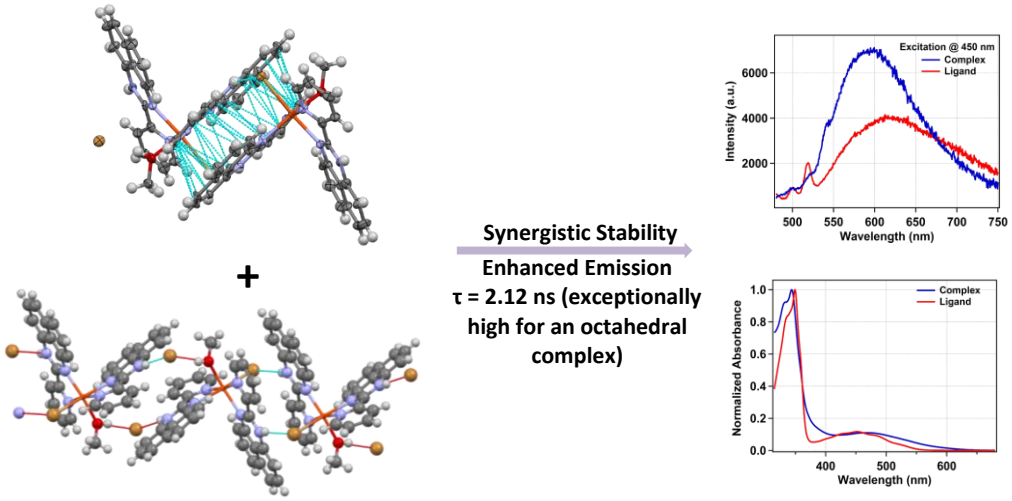
The rational design of transition-metal complexes with tailored photophysical and electronic properties relies heavily on synergistic non-covalent interactions and electronic communication. Herein, we report the synthesis and comprehensive characterisation of a perimidine-based ligand and its corresponding Iron(II) complex, achieved in high yields. Structural determination via single-crystal X-ray diffraction (SC-XRD) reveals a distorted octahedral geometry around the Fe(II) centre. Crucially, the solid-state architecture is highly stabilised by intermolecular π-π stacking interactions between adjacent perimidine moieties. Concentration-dependent and variable-temperature 1H NMR studies confirm that this robust supramolecular assembly, governed by a synergistic combination of π-π stacking and intermolecular hydrogen bonding, persists and dictates solution stability.

The complex demonstrates pronounced metal-to-ligand π-backbonding, which effectively delocalizes electron density and stabilises the metal centre. This is strongly supported by a low Mössbauer isomeric shift and a notably high metal-centred oxidation potential observed in cyclic voltammetry. Photochemical investigations reveal a broad metal-to-ligand charge transfer (MLCT) absorption band spanning the visible region. Upon selective excitation, the complex exhibits a dramatic increase in photoluminescence intensity relative to the free ligand, with a blue-shifted emission. This emissive behaviour, accompanied by a rapid excited-state lifetime, is attributed to the structural rigidity imparted by supramolecular interactions, which effectively minimise non-radiative decay pathways. Collectively, these findings provide critical insights into the interplay of electronic stabilisation and supramolecular architecture in perimidine-based Iron(II) complexes, with broader implications for the development of robust photochemically active materials.



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Supported gold catalysts for sustainable amide synthesis

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Amides are essential building blocks for the pharmaceutical, agrochemical and materials industries. However, their conventional synthesis relies on stoichiometric coupling agents that generate substantial amounts of toxic waste [1]. The direct oxidation of an alcohol in the presence of an amine constitutes a promising alternative, yet heterogeneous gold-based catalysts remain largely understudied, with existing works almost exclusively limited to carbon supports [2,3], leaving basic oxide supports largely unexplored.

This work investigates, for the first time systematically, the influence of preparation method on the performance of Au catalysts supported on basic oxides. Three methods were compared (impregnation, deposition-precipitation, PVA encapsulation), all followed by $NaBH_4$ reduction. The effects of solvent nature (EtOH, H_2O, EtOH/H_2O), volume ratios, and support nature (different hydrotalcites (HT), MgO, CaO, MnO, MnO_2) were investigated systematically. Catalysts were characterised, including XRD, ICP-OES and TGA. Catalytic tests were carried out in an autoclave under 20 bar O_2 at 50 °C with GC-FID quantification. The second axis examines the effect of the substituent nature and position on the starting benzyl alcohol (4-Me-Ph, 4-MeO-Ph, 2-MeOPh) on amide yield.

All three methods afford comparable performance, reaching 52% amide yield on Au/HT, with impregnation selected for its simplicity and reproducibility. The optimal solvent depends on the support. The 4-Me-Ph group leads to the highest amide yield (52%) (**Figure 1**), attributed to its electron-donating character through inductive and mesomeric effects. MeO-Ph groups, although electron-donating through mesomeric effects, exert a slight electron-withdrawing inductive effect, resulting in lower yield (31% and 37%). The position of the methoxy group (*ortho* vs *para*) has no significant impact on performance.

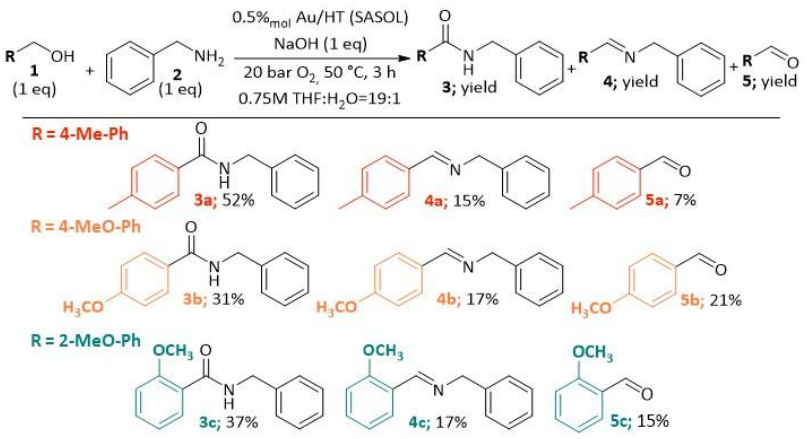

Figure 1. *Amide (**3**), imine (**4**) and aldehyde (**5**) yields obtained for three substituted benzyl alcohols.*

By establishing clear links between preparation conditions, support nature and catalytic performance, this work lays the groundwork for sustainable amide synthesis via heterogeneous gold catalysis.

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Dithienoquinoxaline photocatalyst: Mechanistic insights and applications

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Photoredox catalysis enables redox transformations under mild conditions through light-induced activation of substrates. At the heart of this strategy lies a photocatalyst that captures light energy and mediates single-electron transfer processes.[1] Common classes of organic photoredox catalysts include xanthene dyes (e.g., eosin Y and rhodamines), acridinium salts, flavins, and dicyano(hetero)arenes.[2] In 2014, we have introduced X-shaped dicyanopyrazine (DPZ) photocatalyst and subsequently explored both its synthesis[3] and synthetic applications.[4] Recent photophysical and theoretical investigations clarified the mechanism of its catalytic activity.[5] We later discovered that under blue-light irradiation, DPZ undergoes a Mallory-type cyclization to form dithienoquinoxaline (DTQ), which represents the actual catalytically active species. The doublet excited state $DTQ^{\bullet-}$ exhibits exceptionally strong reducing power ($E_{red}^* \approx -3$ V vs SCE), ranking it among the most potent organic photoreductants reported to date. Importantly, DTQ displays dual catalytic behaviour: it can function as a one-electron oxidant via its triplet excited state (^{3}DTQ) and as a powerful reductant in its radical anion excited state ($^*DTQ^{\bullet-}$), both accessible using a single light source. The remarkable reducing capability of $^*DTQ^{\bullet-}$ was exploited in a chemodivergent reduction of nitroaromatic compounds, selectively affording nitroso, bis-(*N*,*O*-diacetyl)-*N*-arylhydroxylamine, azoxy, azo, and aniline derivatives shown in Figure 1. This transformation addresses a fundamental challenge in both synthetic organic chemistry and large-scale chemical manufacturing.

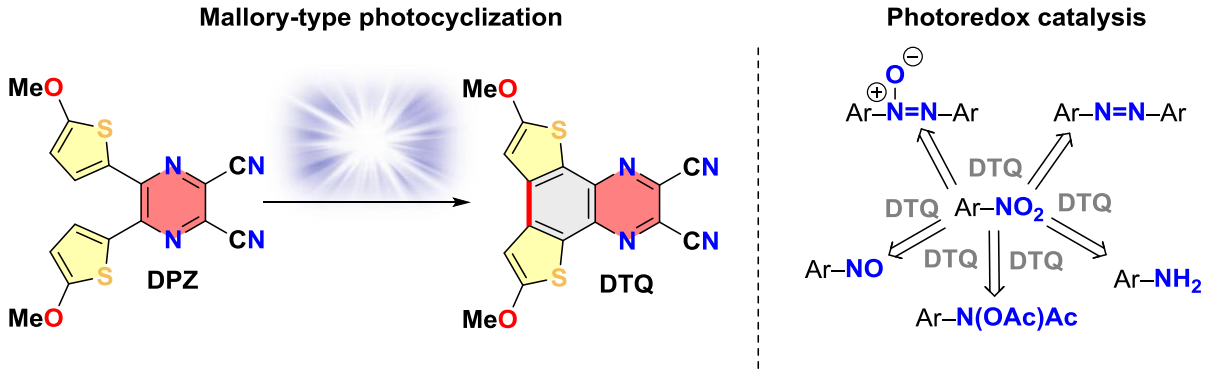

Figure 1. Mallory-type photocyclization of DPZ to DTQ and its chemodivergent reduction of nitroaromatics.

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The Role of Metal Dispersion in the Performance of Metal-Modified Graphitic Carbon Nitride for Photocatalytic Ammonia Cracking

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The development of catalytic materials for the production of green hydrogen (H_2) has received significant attention in recent years, with photocatalysis also playing a role since the discovery of the Honda-Fujishima effect. However, common photocatalysts such as TiO_2, ZnS, and ZnO are activated by UV light, accounting a small percentage of the total solar spectrum. Employing a photocatalyst capable of harnessing visible light, such as graphitic carbon nitride (g-C_3N_4), would allow green H_2 generation under direct solar irradiation, not from water splitting but from ammonia (NH_3) cracking, as NH_3 possesses higher H_2 content by weight (17.8%) compared to water (11.2%) and its decomposition reaction is thermodynamically more favourable [1]. Hence, the present work investigates the potential of exfoliated g-C_3N_4 (GCN-T) loaded with metal particles (M/GCN-T, M = Au, Pd, Pt, Ru) for the photocatalytic NH_3 cracking. The photocatalytic materials were prepared by the incipient wetness impregnation method, with a metal precursor solution added dropwise to GCN-T under sonication. Photocatalytic experiments were conducted on a batch reactor coupled with an LED system (λ_{max} = 420 nm). An ammonium hydroxide (NH_4OH) solution was used as the source of NH_3 with a nominal concentration of 0.5 M. The highest H_2 generation was observed after 6 h of irradiation at a catalyst loading of 1 g/L for Pd/GCN-T (0.8 mmol/g_{cat}), which also showed the highest NH_3 conversion (36%), followed by Ru/GCN-T and Au/GCN-T. No H_2 was detected when pristine GCN-T was used, establishing the importance of the metal co-catalysts for the reaction. The H_2 generation capability of Pd/GCN-T is comparable to that of the reference material Pt/GCN-T, but the latter exhibits a much lower NH_3 conversion value (19%). The superior activity observed for Pd/GCN-T compared to the other tested materials can be explained by the predominance of metal single-atoms, as observed by scanning transmission electron microscopy, which constitutes a significant advantage in terms of metal atom utilisation efficiency and electronic properties [2]. In addition, Pd/GCN-T exhibits the lowest electrochemical impedance, indicating lower resistance to charge carrier transport, as well as the highest current values for both reduction and oxidation potentials measured by cyclic voltammetry. The decomposition of NH_3 is thought to proceed by the formation of $\cdot NH_2$ radicals originating from the reaction of NH_3 with a photogenerated hole (h^+) in the valence band, suggested by the presence of hydrazine (N_2H_4) produced by the self-coupling of said radicals. N_2H_4 is further decomposed into N_2 and H^+, which are reduced by photogenerated electrons (e^-) to H_2 in the conduction band [3]. Considering the direct dependence on both photogenerated e^- and h^+ for the reaction to occur, the current values at redox peak potentials measured for Pd/GCN-T support the observed photocatalytic performance.

This work was supported by project 2022.04682.PTDC -SuN2Fuel - Photo-assisted production of green ammonia-based fuels - (DOI: 10.54499/2022.04682.PTDC). This research was also supported by Fundação para a Ciência e a Tecnologia, I.P./MECI through national funds: LSRE-LCM, UID/50020/2025 (https://doi.org/10.54499/UID/50020/2025); and ALiCE, LA/P/0045/2020 (https://doi.org/10.54499/LA/P/0045/2020). MJS acknowledges FCT funding under the Scientific Employment Stimulus - Institutional Call (DOI:10.54499/CEECINST /00010/2021/CP1770/CT0011). RCC acknowledges the PhD research grant from FCT, Ref. 2025.05272.BDANA.

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Ethane dehydroaromatization using LDH-Derived mixed oxides of Ga and Zn, and Mg over HZSM-5 zeolite

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The conversion of ethane to BTX is a promising approach to upgrading abundant feedstock into important petrochemical intermediates. LDH-derived Ga-Zn-Mg mixed oxides were anchored on HZSM-5 zeolite to obtain bifunctional catalysts for ethane dehydroaromatization. XRD patterns in Fig. 1a confirmed the presence of MgO- and ZnO-related phases after calcination, while Ga species were highly dispersed in the oxide structure. Catalytic tests revealed that ethylene selectivity is maximized at near-zero conversion, whereas aromatics result from consecutive reactions on the zeolite as conversion increases. To further clarify the reaction mechanism, *in situ* DRIFTS studies were carried out, as shown in Fig. 1b. Bands at 2978 and 2882 cm^{-1} were assigned to C-H stretching modes of CH_2/CH_3, while bands at 1250, 1150, and 1070 cm^{-1} correspond to alkoxy-type surface species, which were formed by the reaction of zeolitic -OH with ethylene. Mechanistically, C-H bond scission in ethane occurs on Ga and Zn sites, producing surface ethyl species (C_2H_5), which further decompose to ethylene via beta-H elimination. The resulting ethylene then reacts with Brønsted sites to produce alkoxy-type species that undergo oligomerization and cyclization, yielding aromatic compounds. The oxide/zeolite ratio affected product selectivity, as shown in Fig. 1c. Overall, catalysts with high oxide content favored ethylene formation due to high dehydrogenation activity, whereas high zeolite content favored BTX formation due to high Brønsted acidity, while minimizing methane formation. BTX selectivity of about 31.5% and ethane conversion of 13.2% were achieved using the 5Z-1cLDH catalyst.

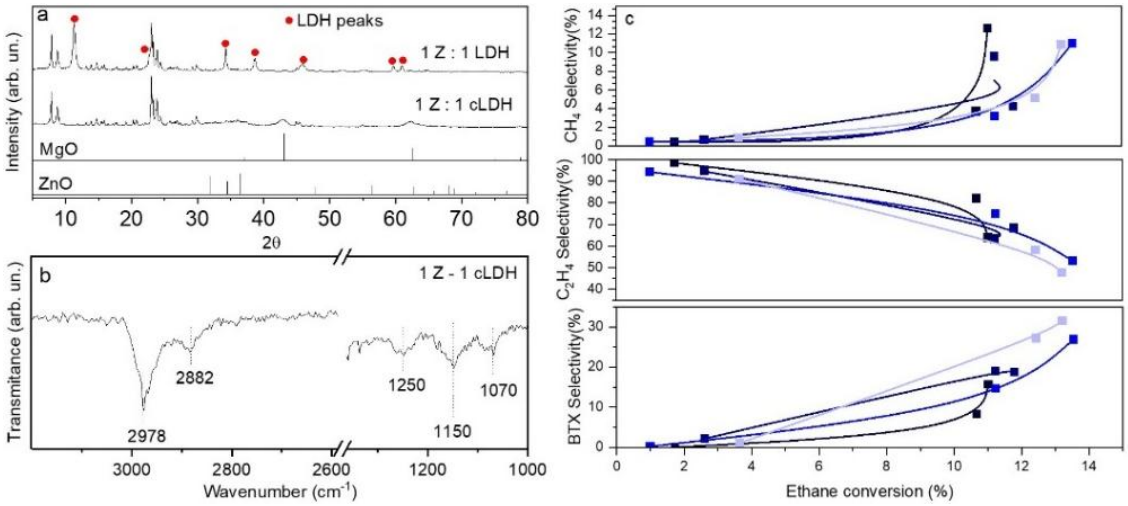

Figure 1: (a) XRD patterns of LDH-derived materials before and after calcination at 600 °C. (b) *In situ* DRIFTS spectra after ethane adsorption at 300 °C. (c) Product selectivities (CH_4, C_2H_4, and BTX) as a function of ethane conversion using 5 Z - 1 cLDH (bright blue), 3 Z - 1 cLDH (light blue), 1 Z - 1 cLDH (blue), and 1 Z - 3 cLDH (navy blue) catalysts. Reaction conditions: 600 °C, cat. 30-275 mg, ethane pressure: 101.325 kPa. Samples were denoted as *xZ : yLDH* or *xZ : ycLDH*, where *Z* is H^+-ZSM-5 (Si/Al=28), *LDH* is the precursor (mole ratios M^{2+}/Ga^{3+} = 3, and Mg^{2+}/Zn^{2+} = 3), and *cLDH* is the calcined mixed oxide. The numbers indicate the zeolite-to-mixed-oxide weight ratio (e.g., 1Z:1cLDH = 1:1).

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Ni_xCo_y for RWGS: A composition study

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The concern over rising CO_2 levels on the atmosphere has been shaping world politics and science, promoting a circular carbon economy, to reduce our overall carbon footprint. The intrinsic thermodynamic stability of CO_2 has historically rendered it as a waste product from the combustion of organic matter and more specifically fossil fuels [1,2]. However, advances in science technologies (power-to-gas, power to liquid) have given CO_2 a new value as it is becoming an important C1-feedstock precursor in the industry. The Reverse Water Gas Shift (RWGS) enables the conversion of CO_2 into CO, which has an important role in industry, for instance, in the Fischer-Tropsch reaction [3,4]. Traditionally, the RWGS has been catalysed by noble metal-based catalysts, [5]. On the other hand, despite their abundance and lower prices, non-noble metal-based catalysts, , are usually less active and/or selective than their noble metal counterparts. Nevertheless, the combination of two different non-noble metals into a bimetallic catalyst might result in a synergistic effect, boosting activity and enhancing selectivity [6]. The RWGS, a complex reaction that is affected by the composition of the catalyst active phase, can be used to probe the effects of bimetallicity. We will present the synthesis via the organometallic method, the characterization (fig.1) and their performance in the RWGS, of nickel-cobalt bimetallic catalysts (Ni_xCo_y/SiRAlOx and Ni_xCo_y/TiO_2),. Our results show that modification of the Ni:Co ratio results in changes in the electronic and structural properties that lead to different selectivity and catalytic activity (fig. 2).

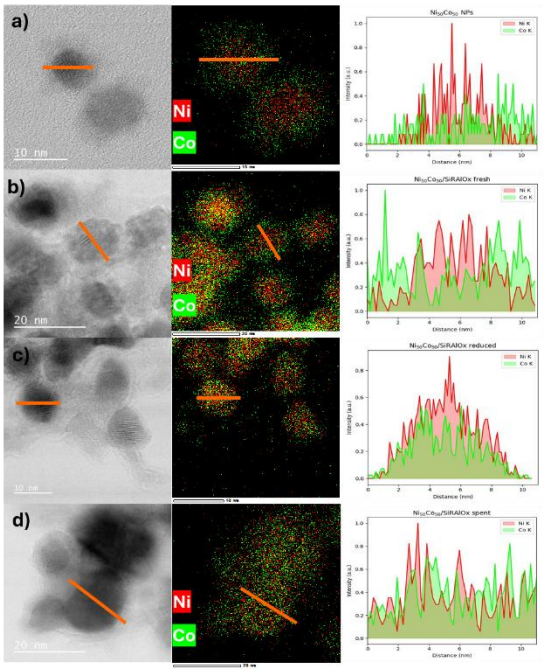

Figure 1. HRTEM, EDX-map and EDX-line analysis of a) $Ni_{50}Co_{50}$ NPs, b) Fresh, c) Reduced and d) Spent $Ni_{50}Co_{50}$/SiRAlOx.

New copper - red mud supported catalyst for organic transformation reactions: studies of model reactions employing H_2O_2 as an oxidizing agent in liquid phase oxidation - an insight into selectivity and structure-activity relationship

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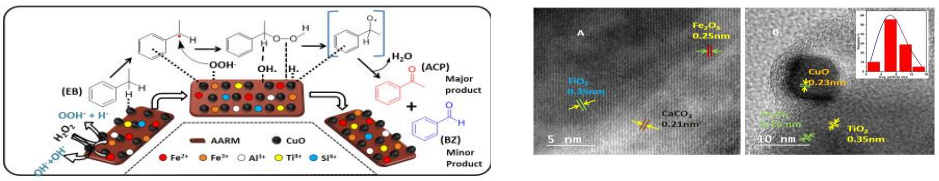
Industrial production of acetophenone is carried out by oxidation of ethyl benzene in presence of molecular oxygen as an oxidant. In this process, cobalt cycloalkanecarboxylate/cobalt acetate [$Co(OAc)_2.4H_2O$] is used as a catalyst in acetic acid solvent.[1,2] It is known that transition metal-based heterogeneous catalysts are recognized as environmentally benign and these materials are capable of generating powerful hydroxyl radicals [$E^o(^*OH/H_2O) = +2.8\ V_{NHE}$]. Our research work, herein, reports facile synthesis of a new heterogeneous catalyst (CuO supported on activated red-mud, CuO_AARM) for oxidative conversion of ethylbenzene to acetophenone using H_2O_2 as an oxidant. The catalyst promotes benzylic C – H bond oxidation in ethyl benzene to form acetophenone in optimized reaction conditions (Temp.: 75°C; solvent: mixture of H_2O and acetonitrile (1:1)). The electron deficient metal species could abstract hydrogen from hydroperoxide to produce alkyl peroxide which rapidly decomposes to yield acetophenone (Scheme-1).



Scheme-1: Mechanism of surface catalyzed oxidation of ethyl benzene to acetophenone using CuO_AARM.

DFT study shows that the optimized geometrical structure favors the reaction *via* hydroperoxyl radical formation in an endergonic process. The catalyst shows good kinetic control over the decomposition of H_2O_2. The synergy between the atomically dispersed CuO nano-particles and components in red-mud support promotes a facile and robust approach towards development of a recyclable and reusable heterogeneous catalyst with 86.0% conversion efficiency and 74.0% selectivity using green chemistry route.

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A 3D-AFM-Based Method for Isolating Short-Range Molecular Interaction Forces on Catalytic Surfaces

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Cobalt phthalocyanine (CoPc) has been identified as a uniquely active and selective electrocatalyst for CO_2 reduction to CH_3OH [1]. Its activity is tunable via substituent groups and support interactions. Low-temperature non-contact atomic force microscopy (LT-NC-AFM) has been used to isolate how these factors affect the interaction of the key CO intermediate with the catalyst. Data have been collected for CoPc and NH_2-functionalized CoPc on Ag(111) and Au(111) supports. In these measurements, a CO-functionalized tip is used to collect three-dimensional data of the local force interactions between the tip and the sample as a function of x, y, and z from a series of frequency-shift images acquired at different tip–sample distances over an individual catalyst molecule. Here, the CoPc/Au(111) system is used as a representative platform to demonstrate a general methodology for isolating the short-range interaction forces between the tip-terminating CO molecule and the CoPc molecule from the three-dimensional atomic force microscopy (3D-AFM) data collected during the experiment. Such isolation is necessary because the raw data does not solely originate from the CO–CoPc interaction, which is the contribution that is of catalytic importance, but results from the combined effect of multiple pairwise interactions reflecting the complete tip–sample system [2]. It is therefore necessary to isolate the CO–CoPc force by systematically separating the remaining contributions.

In our methodology, discrete frequency shift data are first densified by interpolation to obtain a continuous $\Delta f(z)$ curve at each (x,y) pixel, thereby reconstructing the complete 3D dataset [3]. Subsequently, the data are converted first into potential energy and then into force [4]. At the same time, the contributions from the metal tip–substrate and tip–molecule interactions are identified as being long-ranged. This allows characterizing these contributions at large tip–sample distances where short-range interactions are negligible. This long-range component is then extrapolated toward shorter distances to reconstruct its contribution over the full z range. This yields a corresponding frequency-shift dataset for these contributions, which is subsequently converted into potential energy and force. In the final step, the long-range background contribution is subtracted from the total force to yield 3D force data corresponding solely to the CO–CoPc interaction.

The fundamental importance of this study lies not only in presenting results for the CoPc/Au(111) system, but also in establishing a general method that systematically isolates chemically relevant short-range interactions from 3D-AFM data; the availability of such data then allows quantitatively comparing different systems and the effects of specific changes on the overall interaction. This approach provides a framework applicable to a wide range of molecular catalyst systems at surfaces.

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Predicting Stereoselectivity in γ-Lactonization through a Simple Computational Model of the Reactant Complex

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The stereoselective oxidation of non-activated C(sp^3)–H bonds is one of the most challenging yet powerful transformations in organic synthesis, as it enables direct access to stereochemically rich oxygenated scaffolds. However, because C(sp^3)–H bonds are ubiquitous in organic molecules, controlling site, diastereo, and enantioselectivity remains highly challenging. Recently, Costas and co-workers reported the site- and stereoselective γ-lactonization of non-activated primary and secondary C(sp^3)–H bonds by Mn complexes using H_2O_2 as the oxidant(Call et al. 2023; Call et al. 2022) To fully exploit the potential of such bioinspired C(sp^3)–H oxygenation reactions, identifying the factors controlling selectivity, together with the development of predictive models, is of critical importance.

Herein, we present a simple, predictive, and robust computational methodology that, based on the analysis of the most stable reactant species, predicts the site of C(sp^3)–H oxidation. The predictive power of the model is consistent with the experimentally observed stereoselectivities and is further supported by the calculation of the reaction Gibbs free energy barriers. The methodology was evaluated on a series of chiral and prochiral carboxylic acids. Collectively, our results show that the site of oxidation can be rationalized by the relative orientation of the accessible γ- C(sp^3)–H bonds with respect to the reactive Mn-oxo unit.

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Mechanistic Investigation of Magnetically Induced Catalytic Processes

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Catalysis plays a crucial role as the backbone of the chemical industry, enabling the rapid and efficient synthesis of a vast array of chemicals and materials. Catalysts usually require activation from an external energy source, traditionally heat generated from fossil fuels. In this context, magnetic induction heating of catalyst materials is an emerging and promising alternative heating method which promotes sustainability by electrifying the chemical industry. In magnetically induced catalysis (MICat), alternating current magnetic fields (ACMFs) are used to heat and activate magnetically-responsive materials (Fig. 1). In contrast to conventional heating, heat is generated directly at the active sites, removing the need to heat the whole reactor and improving energy efficiency. The rapid and localized catalyst activation enabled by MICat allows rapid on/off switching of catalytic activity, making it suitable for intermittent power supply, a characteristic of renewable energy sources. Notably, commercial ACMF generators are already employed in the metallurgical industry, suggesting a possible transfer of MICat from laboratory to scales relevant for the chemical industry.[1]

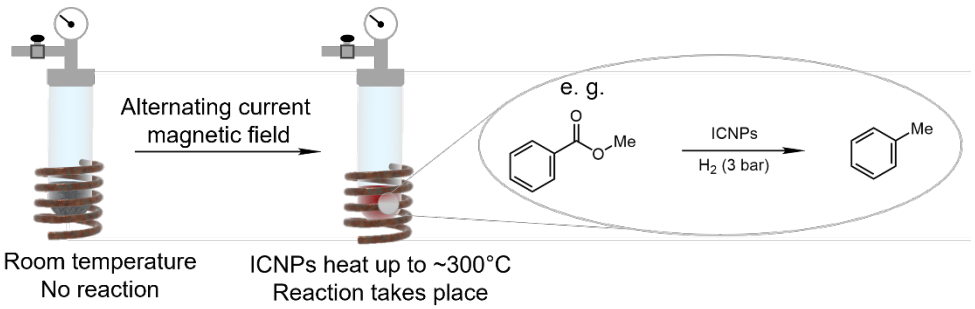

Figure 1: Scheme of conducting MICat experiments using iron carbide nanoparticles as heating agents and catalyst.

In the past few years, our group and a few others have started lifting the veil on the promises of MICat. For example, we recently demonstrated that MICat can enable challenging liquid- and gas-phase transformations (e.g. amide hydrogenation[2], (poly)ester hydrodeoxygenation[3], reverse water gas shift[4]) under very mild conditions. However, the true potential of magnetic induction heating in chemical processes is still unclear, and many fundamental and practical questions remain.[1] A key research question relates to the potential occurrence of non-thermal effects in MICat processes, which have been investigated in a few recent studies.[5] Despite the potential importance of such effects for both mechanistic understanding and practical applications, their occurrence, identity, and origin remain largely elusive.
I will give a general introduction on MICat, give an insight on the requirements for conducting MICat experiments, as well as discuss possible non-thermal effects in MICat and how these could be verified.

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Active-Phase Engineering in NiFeS for Enhanced Alkaline Water Splitting

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Nickel–iron sulfides (NiFeS) are attractive non-noble electrocatalysts for water splitting due to their tunable electronic structure and high conductivity. Solvothermally synthesized NiFeS enables controlled composition and uniform Ni/Fe dispersion. Under Oxygen Evolution Reaction (OER) conditions, the catalyst undergoes sulfur leaching, reconstructing into NiFe-LDH oxyhydroxides that act as the true OER-active species [1–2]. In contrast, during Hydrogen Evolution Reaction (HER), the sulfide framework remains structurally stable, maintaining efficient charge transfer and sustained proton-reduction activity [3]. This dual behavior S-driven activation in OER and stability in HER highlights NiFeS as a promising catalyst for overall water splitting.
The NiFeS catalyst exhibits the highest activity and stability for both OER and HER among all tested materials (NiS, FeS, NiFe, NiFeS). Its low OER Tafel slope (38 mV dec^{-1}), HER Tafel slope (123 mV dec^{-1}), and reduced overpotentials highlight the strong synergistic interaction between Ni, Fe, and S. Chronopotentiometry confirms long-term operational stability. Raman analysis further reveals that NiFeS reconstructs into NiO/FeO oxides under OER, while NiS sulfides remain the active phases during HER, explaining the catalyst's performance.

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Combustion synthesis of CeO_2 Nanoparticles for catalyst applications

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The study presents a green synthesis approach for fabricating nanoceria (CeO_2 NPs) using the solution combustion synthesis method. The synthesized CeO_2 nanoparticles were characterized using various sophisticated instruments and methods to determine their detailed properties. The UV-Vis spectra showed a characteristic absorbance peak at 242 nm and a band gap (E_g) of 3.05 eV. Simultaneously, Fourier transform infrared spectra of CeO_2 NPs displayed bands at 418 cm-1, 991 cm-1, 1382 cm-1, 1658 cm-1, 2306 cm-1, 3288 cm-1, and 3643 cm-1, which indicates the presence of phytochemicals that facilitate the reduction and stabilization of CeO_2 NPs. The major peaks for cubic CeO_2 NPs were obtained with a crystalline size of 9.6 nm by X-ray diffraction. The microscopic analyses revealed irregular, ovoid, and aggregated morphologies with sizes ranging from 3 to 10 nm. The XPS analysis revealed the presence of Ce 3d, C 1s, and O 1s states, along with their corresponding atomic percentages. Therefore, this investigation focuses on synthesizing catalysts that demonstrate both thermal stability and high catalytic activity for the oxidation of CO and the reduction of NOx

Supported Copper and Cobalt Nanoparticles for Acceptorless Dehydrogenation via Plasmonic Photocatalysis

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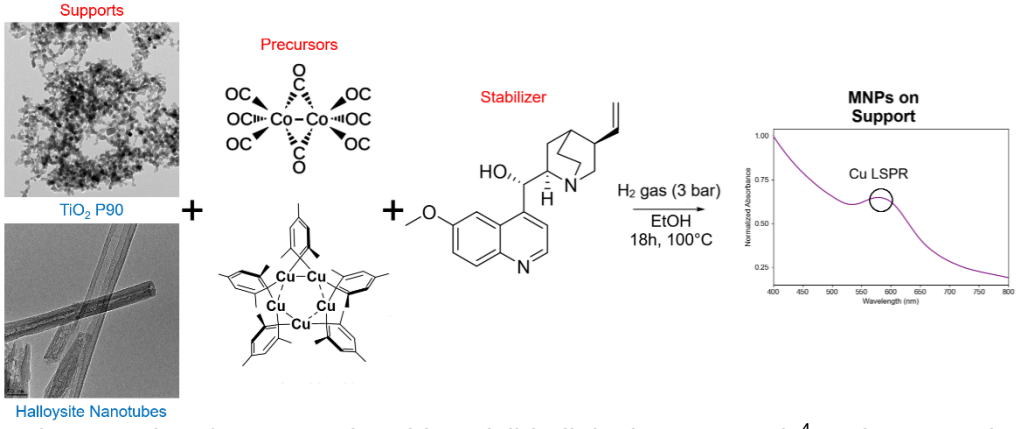
Acceptorless dehydrogenation has gained increased attention in recent years as a means of generating both value-added oxidized products as well as H_2 gas. Photocatalysis using plasmonic metal nanoparticles (PMNs) allows harsh stoichiometric oxidants to be avoided in favour of simply using light. PMNs can either act directly as the photocatalyst by providing electrons and holes, excited via localized surface plasmon resonance (LSPR), for the reaction, or indirectly by enhancing the photocatalytic activity of semiconductors through hot electron injection.[1] Noble metal nanoparticles such as Ag and Au have traditionally been the material of choice for PMNs as they exhibit strong LSPR due to their high density of free charge carriers.[2] However, first-row transition metals have also been emerging as a lower-cost alternative.[3] Here, we report our ongoing work on the synthesis and characterization of plasmonic Cu and Co NPs on both semiconductor and insulator supports, with the aim of catalysing the acceptorless dehydrogenation of alcohols. XRD, UV-Visible spectroscopy, ICP, XPS, TEM, BET and TGA were employed to fully characterize the nanocomposites.



The complementarity of Cu NPs absorbing visible light (ca. 560 nm),[4] and Co NPs in the UV region (280 nm),[5] confer these systems attractive properties for applications in photocatalysis as they can use solar energy. In the present work, we decorate TiO_2 NPs, a known photocatalyst for H_2 production[6], with Cu NPs to extend its absorption range to the vis-NIR range. Co NPs have previously been shown to catalyse the thermal dehydrogenation of alcohols[7] but their application in plasmonic photocatalysis remains unexplored. Formerly thought to be non-plasmonic, strong LSPR with quality comparable to Au NPs have been reported in Co NPs in recent years, achieved by controlling the inter-particle distance to avoid the interactions between adjacent NPs which degrade the resonance quality.[5] Our approach in this work is to support the Co NPs on different materials and tune the loading amount to achieve the appropriate inter-particle distance for LSPR.

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Enhancing Hydrogen Production via Ni-P Catalysts on Lead-Free Halide Perovskite Photoelectrodes.

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The development of sustainable and efficient hydrogen production is crucial to moving towards a clean energy future. Photoelectrochemical (PEC) hydrogen evolution, driven by solar energy, offers a promising route to the generation of sustainable renewable fuels. Tin-based perovskites, with their lower optical band gaps and higher charge mobilities, compared to lead based materils, offer an eco-friendly pathway for solar-driven PEC applications[1,2]. Despite these advantages, their performance is often limited by sluggish HER kinetics. Transition metal phosphides, such as nickel-phosphide (Ni-P), with low overpotentials and excellent stability[3], are highly effective at enhancing photocurrents from formamidinium tin iodide ($FASnI_3$)-based photocathodes.

This study explores the integration of Ni-P catalysts with FASI-based photocathodes for PEC hydrogen generation, demonstrating enhanced photocurrent densities with an anodic shift in the onset potential and longer operational times. The work aims to provide a framework for the development of stable, lead-free PEC systems for green hydrogen production.

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Hydrotalcite derived Mixed Metal Oxide based Dual Functional Material for CO_2 Trapping and Methanation

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Abstract

CO_2 capture and utilization has evolved as a powerful strategy to mitigate CO_2 emissions, with CO_2 to methane using renewable H_2 as a prime focus [1]. Hydrotalcite derived Mixed Metal Oxides (MMO) have been emerged as promising candidate for CO_2 capture and methanation application, owing to their unique properties such as high surface area, tunable basicity, uniform atomic level metal distribution etc [2]. However, identifying materials with superior trapping/methanation performance at isothermal conditions (Figure 1) still remains a key challenge.

This work developed and compared various metal loadings of RuNi/MgAlTi for CO_2 capture and methanation application. The influence of other noble metals such Pt and Pd were also examined. The synthesised materials were systematically characterized using XRD, N_2 physisorption, HAADF-STEM and XAS and the CO_2 trapping and release efficiency were analyzed using TGA. The results suggested that with RuNi incorporation, ≈24% CO_2 can be absorbed at 300°C, which can further increase to 33% at room temperature. The high surface area and increased basicity of MgAlTi support provides abundant sites for CO_2 adsorption as well as better dispersion of Ru and Ni. The methanation studies highlighted the synergistic interaction between Ru and Ni, confirmed with rapid increase in CO_2 conversion and CH_4 selectivity with even small amounts of Ru (0.1%), which aids in Ni reduction and enhanced H_2 spillover. The optimum catalyst for CO_2 trapping and methanation was found to be 1Ru9Ni/MgAlTi with ≈19% CO_2 adsorption, 98% CO_2 conversion and 87% CH_4 selectivity at 300°C. Among the noble metals, Ru was found to be the most efficient for CO_2 methanation. The superior performance of 1Ru9Ni can be attributed to the optimal metal dispersion, active phase interaction and availability of basic sites on the surface. Overall, these findings pave the way for rational design of DFMs with superior CO_2 trapping – methanation efficiency, positioning this approach in the forefront of sustainable carbon management.

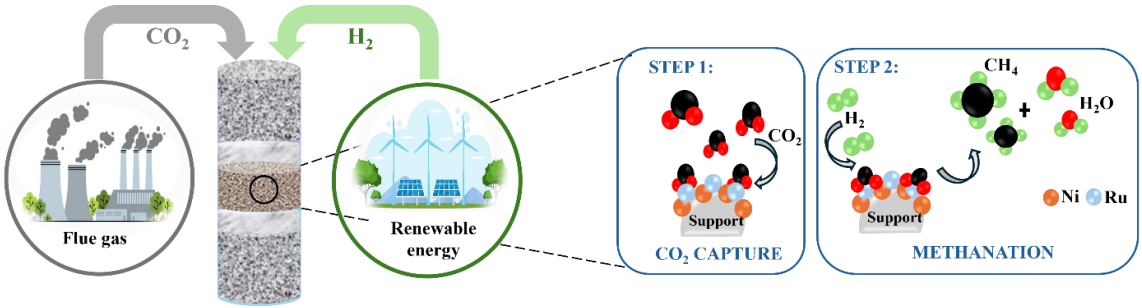

Figure 1 Schematic representation of CO_2 capture and methanation

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Production d'hydrogène par reformage à sec du biogaz assisté par un catalyseur à base de biochar riche en fer dopé à l'hydroxyapatite

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Dans un contexte de tension énergétique et de prise de conscience des limites environnementales terrestre, les vecteurs énergétiques renouvelables, tels que l'hydrogène vert, sont appelés à jouer un rôle crucial afin de réduire la dépendance des ressources fossiles. Actuellement, l'hydrogène est massivement produit par reformage à la vapeur d'eau du gaz naturel d'origine fossile. Il est donc nécessaire de décarboner au maximum sa production. Le reformage à sec du biogaz ($CH_4 + CO_2 \rightarrow 2H_2 + 2CO$, $\Delta_rH°_{298K}$ = 247kJ/mol) apparaît particulièrement pertinent en offrant une production d'hydrogène biogénique à partir de CH_4 et CO_2 obtenus par fermentation de bioressources. Le reformage à sec nécessite généralement des catalyseurs commerciaux utilisant des métaux nobles (Ru, Rh). Cependant, des catalyseurs biosourcés à base de biochar riche en fer ont prouvé leur efficacité dans la production d'hydrogène jusqu'à 500°C, où les métaux alcalins et alcalino-terreux ont montré leur rôle crucial en tant que promoteurs catalytiques [1]. Les principaux défis de l'utilisation de biochar en reformage à sec sont la stabilité et l'efficacité du biochar en tant que catalyseur, et la réduction du dépôt de carbone, principalement dû au craquage du méthane $CH_4 \rightarrow C + 2H_2$, $\Delta_rH°_{298K}$ = 75kJ/mol et à la réaction de Boudouard $CO + CO \rightarrow C + CO_2$, $\Delta_rH°_{298K}$ = -173kJ/mol. Lors de travaux précédents, l'hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), céramique stable jusqu'à 1400°C, a été utilisée en tant que catalyseur dans le reformage à sec [2], [3]. Cependant, le catalyseur se désactive rapidement par dépôt de carbone. L'objectif de ces travaux est de combiner un biochar riche en fer avec de l'hydroxyapatite afin de proposer un catalyseur biosourcé qui résiste plusieurs cycles catalytiques de reformage à sec de biogaz, tout en étudiant son mécanisme de désactivation et de régénération.

Des catalyseurs biosourcés ont été préparés à partir de biomasse ou de biochar (pyrolyse, 800°C, sous N_2) de fougère et de fucus co-broyés avec de l'hydroxyapatite. Ils ont été caractérisés chimiquement (CHNS/O, ICP-OES, TPx) et physiquement (ATG, BET, DRX, Raman, MEB). Ensuite, leurs performances ont été testées en reformage à sec dans un réacteur à lit fixe à 800°C, à 1bar, sous une atmosphère CH_4/CO_2 (ratio molaire 1/1) et avec un débit massique de 4.5 $L/h/g_{catalyseur}$. Les résultats obtenus en reformage à sec sont reliés à la composition physicochimique du catalyseur et à son évolution avant et après réaction.

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Adsorption sites diversity and reactivity in colloidal Iron Carbide nanoparticles for Fischer-Tropsch Synthesis

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Fischer–Tropsch synthesis (FTS) continues to draw considerable interest for the production of a wide range of hydrocarbon products; yet despite extensive characterization and computational studies, the FTS mechanism, surface adsorbate stoichiometry, and catalyst structure under reaction conditions are still unresolved. [1 - 4] Our group has recently reported the use of colloidal amorphous dodecylamine-capped iron carbide nanoparticles (DDA-Fe_xC NPs) as a functional model for FTS catalysts. [5] Our nanoparticles exhibit catalytic activity for low-temperature FTS without any pretreatment. *In situ* Transmission Fourier Transform Infrared (FTIR) spectroscopy enabled direct observation of surface H and CO, and surface H was quantified through its complete removal using molecular reagents. In this work, we investigate the diversity of adsorption sites and hydrogen reactivity of these iron carbide nanoparticles by combining different spectroscopic techniques. [5][6]

Surface adsorbates were studied using FTIR spectroscopy, revealing the formation of ν(C–D) stretching bands upon exposure to D_2 and indicating the formation of at least four distinct C–D surface species (Figure – A). Exposure to CO produced a single broad ν(CO) band that shifted to higher frequencies with CO coverage (~24 cm^{-1}) or co-adsorption of H_2 (~70 cm^{-1}). Combined with DFT calculations, these results showed that the thermodynamically preferred adsorption sites are surface carbon atoms for H and surface iron atoms for CO (Figure – B).

Treatment of the nanoparticles with H_2 followed by D_2 exposure led to complete surface H–D exchange, corresponding to an H: total Fe ratio of 0.17:1 (~40 H atoms *per* NP). Stoichiometric surface dehydrogenation of the nanoparticles using different reagents led to complete or partial removal of surface H. These results indicate a diversity of C–H bonds with differing reactivity, likely due to differences in their C–H bond dissociation free energies. Preliminary FTIR studies showed that partial dehydrogenation can be linked to distinct ν(C–D) bands. For DDA–Fe_xC NPs treated with D_2, reaction with weak hydrogen acceptors predominantly decreased the lower-frequency bands. Conversely, reaction of as-prepared nanoparticles with a weak D-atom donor resulted primarily in formation of the higher-frequency bands. These insights provide a basis for correlating adsorption site diversity with reactivity. Next, we aim to extend this understanding to catalytic conditions.

This work provides a new view of surface intermediates and their diversity in Fischer–Tropsch synthesis, offering insight into the mechanism of a century-old catalytic process.

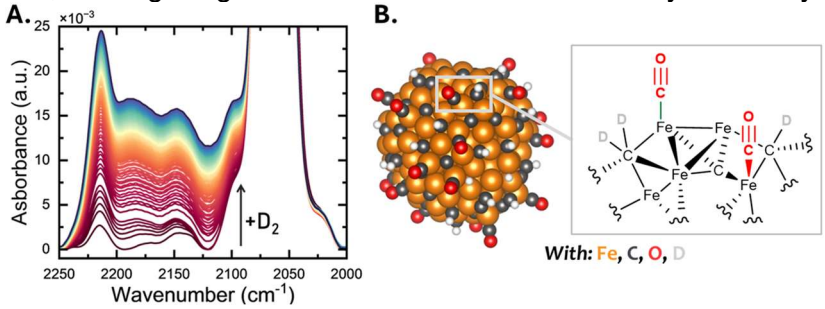

Figure 1. (A) FTIR spectra of DDA-Fe_xC NPs exposed to D_2 (25 bar) and monitored *in situ* over time. (B) Fe_xC NPs (without DDA, for clarity) with a zoom on primary adsorbates in FTIR spectra under 25 bar D_2 followed by CO. [5][6]

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Photocatalytic Degradation of Dinaphthophenazine Textile Dye: Investigated by UV-Vis-NIR Absorption Spectroscopy

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Toxic dye-containing wastewater is a major problem globally. Synthetic dyes that do not bind to fabric are discharged by textile industries untreated in millions of tonnes as effluents which are known to persist in the environment and deleterious to aquatic life. The treatment of the dye-contaminated wastewater discharge using ultraviolet (UV)-induced photodegradation, metal oxides and photocatalysts had gained increased attention over the recent years among chemists towards improving these technologies for environmental protection. In this study, a Dinaphthophenazine (DNPz.) textile dye was subjected to degradation experiments to characterise its degradation rates and highlight the photocatalytic degradation effect of manganese (IV) oxide (MnO_2) on it by comparing the kinetics of UV-induced degradation against MnO_2 – catalyzed photodegradation. Figures 1 and 2 shows results of kinetic experiments that were conducted by acquiring time-dependent wavelength scan absorption spectra at intervals using double beam UV-Vis-NIR spectroscopy to monitor the photodegrdation process. A decrease in absorbance over time depicts photodegradation of the dye under UV illumination.

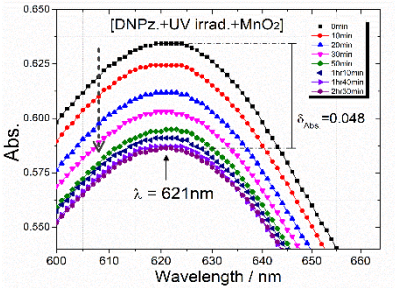

Fig. 1

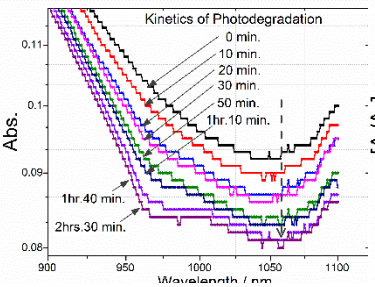

Fig. 2

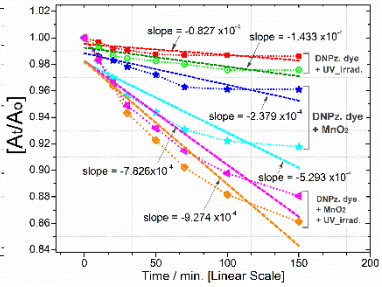

Fig. 3

Figure 3 shows a multicurve plot analysis of the all the three experiments: exposure of DNPz to UV irradiation [DNPz.+UV irrad.], exposure of DNPz to MnO_2 only [DNPz.+MnO_2], and the exposure of DNPz to a similar doze of MnO_2 in presence of UV 254 nm irradiation [DNPz.+MnO_2+UV irrad.]. Pseudo-1st Order kinetic modelling shows that the rate of decrease in absorbance over time is greatest in the case of [DNPz.+MnO_2+UV irrad.]. This effectively characterizes the photocatalytic effect of MnO_2 in the degradation of the DNPz organic textile dye.

Conclusion: The exposure of DNPz to both MnO_2 and UV irradiation enhance the photodegradation rate of DNPz molecule by about nive (9) tiimes based on our optimised experiemental conditions.

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Catalytic Activity of Ti_3-doped Goldene for Nitric Oxide Reduction Reaction – A First-Principles Study

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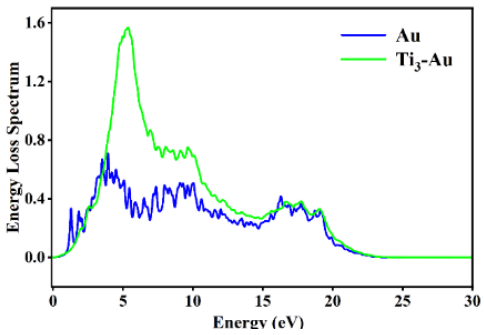
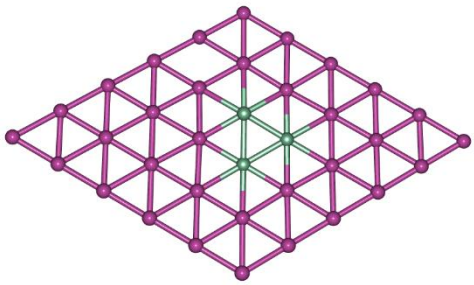
Nitric oxide reduction reaction (NORR) offers a sustainable alternative to the energy-intensive Haber-Bosch process by converting the pollutant NO into valuable NH_3 under ambient conditions.Using density functional theory (DFT) calculations, we investigated Ti_3 -doped goldene (Ti_3 -Auene) for NORR. Ab initio molecular dynamics (AIMD) simulations in solvent medium (10 ps at 500 K) confirmed its thermal stability. Electronic structure analysis showed strong hybridization between Ti 3d and goldene states, introducing Ti 3d orbitals near the Fermi level. This significantly enhances visible-light optical absorption and surface plasmon excitations (evident from enhanced EELS), making Ti_3 -Auene promising for bifunctional electro(photo)catalysis.The Ti_3 active sites improve NO adsorption and activation, delivering efficient NORR performance with a limiting potential of 0.89 V. Surface Pourbaix diagrams confirm its electrochemical stability across a wide pH range under *O, *OH, and $*H_2O$ coverages.Overall, Ti_3 -Auene emerges as a highly promising bifunctional catalyst for electrocatalytic and photocatalytic NO-to-NH_3 conversion.





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Effect of H_2O on NH_3-SCO over calcined hydrotalcite-zeolite composites

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Air pollution is one of the major global environmental issues, strongly affecting ecosystems and human health. Ammonia (NH_3), emitted from combustion processes, fertilizer production, agriculture and industry processes significantly contribute to eutrophication, acidification and air pollution (1,2). Selective catalytic oxidation of ammonia (NH_3-SCO) is a low-temperature catalytic process (≤ 400 °C) and is considered as a very promising method for the removal of ammonia from waste gases, in which ammonia is selectively converted to non-toxic nitrogen (N_2) and water vapor (H_2O) in oxygen-containing gas mixtures with low NH_3 concentrations (2). This work presents calcined hydrotalcite-zeolite composites as effective catalysts for this process. In the composites, zeolite ZSM-5 with different Si/Al ratios served as the support, while Cu-Mg-Al hydrotalcite acted as the precursor of the active phase. Materials were synthesized via the co-precipitation method (3,4) and subsequently calcined at 550 °C to form catalysts with desired structure. *In-situ* thermal decomposition leads to the transformation of the hydrotalcite-type precursors into mixed metal oxides and to the formation of highly dispersed copper oxides, which constitute active catalytic sites with a high specific surface area on the given zeolite support. The prepared composites were analysed using several techniques, including AAS, XRD, H_2-TPR, NH_3-TPD and N_2O-RFC. Their catalytic activity was evaluated in the NH_3-SCO reaction. XRD results verified the formation of the hydrotalcite phase and confirmed that the ZSM-5 zeolite structure remained intact. No distinct reflections of CuO or spinel phases were observed, suggesting that copper species are highly dispersed and thus under detection limit of XRD. Reduction behaviour studied by H_2-TPR revealed low-temperature peaks (below 250 °C), which are associated with the reduction of finely dispersed copper species (5). All catalysts exhibited high NH_3-SCO activity compared to unsupported counterparts, achieving over 80% NH_3 conversion at 300 °C (WHSV = 1000 $mL \cdot min^{-1} \cdot g^{-1}$). On the other hand, N_2 selectivity above 90% over the entire temperature range was observed only for composites with low zeolite Si to Al ratio (Si/Al = 6). Based on these results, additional experiments were carried out to evaluate the influence of H_2O on the catalytic behaviour. The presence of water led to a decrease in NH_3 conversion compared to dry conditions. The effect of H_2O was only partially reversible, as a slight irreversible loss of activity was observed upon the first exposure, while subsequent cycles showed stable catalytic performance. This suggests that a minor fraction of active sites undergoes irreversible deactivation during the initial contact with water, whereas the remaining sites are affected reversibly.

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Understanding the Role of Metal-Support Interactions in Au-M/TiO_2 (M = Co, Ir, Rh, Ni, Pd, Pt, Cu, Ag) Catalysts

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The metal-support interface plays a key role in determining the catalytic performance of metal nanoparticles supported on titania (TiO_2) [1]. Experimental studies have shown that incorporating a second metal into gold nanoparticles leads to a pronounced synergistic enhancement in the catalytic activity for CO oxidation relative to monometallic Au [2]. However, the origin of this effect and the nature of the active sites remain unclear. Here, we present a systematic computational screening of Au_xM_y bimetallic nanoparticles, both in vacuum and supported on the TiO_2(001) anatase surface, using DFT+U calculations under periodic boundary conditions. Structural, electronic, and interfacial properties were analyzed to identify reliable descriptors of chemical reactivity. Oxygen vacancy formation energies were computed to assess how bimetallic composition influences the reducibility of the oxide support. Distinct adsorption trends emerge from the screening: systems containing lighter transition metals (Co, Ni, Cu) preferentially bind via direct M-TiO_2 interactions, whereas heavier metals (except for Ag) favor interfacial configurations involving the Au-M ensemble. Additionally, nanoparticle fluxionality and charge transfer effects were evaluated to elucidate their role in modulating catalytic behavior. Overall, this descriptor-driven comparative analysis provides fundamental insight into metal-support interactions and establishes guiding principles for the rational design of efficient bimetallic catalysts.

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Beneficial Role of SnS Incorporation in MoS_2 Thin film for Enhanced Alkaline Hydrogen Evolution Reaction

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Two-dimensional transition metal chalcogenides (TMDs), particularly MoS_2, have been extensively studied as promising electrocatalysts for the hydrogen evolution reaction (HER) due to tubable electronic structures and remarkable catalytic activity [1,2]. However, their catalytic performance is often limited by poor intrinsic conductivity and a low density of active sites in the basal plane [3,4]. Some studies suggest that introduction of Sn into MoS_2 structure in the form of Sn doping and SnS_2 incorporation can improve the condutivity, water adsorption, and HER activity under alkaline condition by tuning their charge redistribution and electronic properties [5,6]. Despite theoretical predictions indicating that SnS-MoS_2 heterostructures could enhance water splitting [7], the role of SnS on MoS_2 structure for HER has not been systematically investiated experimentally.

In this study, MoS_2-SnS heterostructures were prepared on Si (100) wafers by varying the Sn/Mo ratio using the modulated elemental reagents (MER) method in a molecular beam epitaxy (MBE) system to investigate the effect of SnS incorporation on MoS_2 thin films for alkaline HER. Cyclic voltammetry (CV) reveals that the increasing Sn content leads to enhenced current density as well as current nomalized by total metal loading, indicating the improvement of catalytic activity. The turnover frequency (TOF) shows a strong correlation with increasing Sn content, providing clear evidence that the HER performance is improved from intrinsic catalytic activity. Moreover, the decrease in charge transfer resistance (R_{ct}) obtained from electrochemical impedance spectroscopy (EIS), with increaseing the Sn contents suggests improved charge transfer. Furthermore, Tafel analysis shows reduced slopes correlated with Sn contents, indicating facilitated reaction kinetics.

These results collectively demonstrate that Sn incorporation enhances HER performance through both improved charge transfer and reaction kinetics.

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Functionalized ruthenium catalysts for sustainable catalytic oxidation of organic substrates

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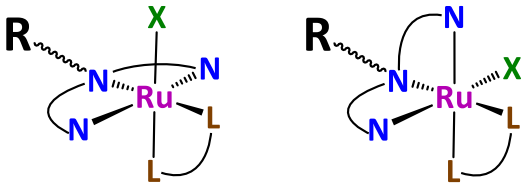
Chemical catalysis is fundamental to the transition towards green chemistry, requiring the optimization of reaction conditions to meet the global demand for renewable energy and environmental protection.[1] This work focuses on the development of functionalized ruthenium complexes specifically designed for the sustainable synthesis of cyclic compounds, primarily through the selective epoxidation of olefins.[2] We detail the synthesis of novel Ru catalysts featuring carboxylic acid (-COOH) functionalities within their ligand frameworks to evaluate their impact on catalytic efficiency and their potential to activate sustainable oxidants like hydrogen peroxide. Ru-complexes also exhibit photochemical properties that allow for photoactivated reaction schemes using visible light as a clean activator. To further enhance sustainability and system reusability, these catalysts are anchored onto mesoporous silica nanoparticles (MSN), which provide high surface area and stability while minimizing catalyst aggregation. This study evaluates the catalytic performance of Ru-complexes and their corresponding heterogeneous composites in the oxidation of alcohols and the formation of cyclic epoxides, investigating the effects of different solvents, green oxidants, and visible light activation on their activity and turnover numbers.



R = COOH or H
X = Cl or H_2O
L = C or N donor atom

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From Metallic Phases To Metal Borides: Exploring New Bifunctional Catalysts For Sustainable Aviation Fuels Via Guerbet Reaction

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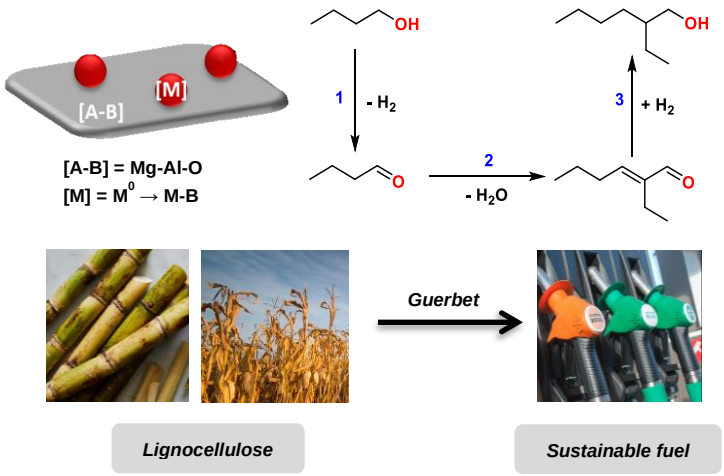
Abstract

The transition towards bio-sourced molecules from petrochemistry requires an efficient method to convert biomass-derived short-chain alcohols into long-chain alcohols to attain the kerosene fraction of hydrocarbons (C_{12}-C_{16}).[1] The multi-step Guerbet reaction is a key tool for this chain extension, and is composed of a bifunctional catalyst: a metallic phase for (de)hydrogenation (Steps 1 and 3) and acidic-basic sites for aldol condensation (Step 2).[2] Existing catalysts often suffer from limited selectivity due to the formation of undesired products such as esters (Tischenko reaction) and acetals.



Representative mechanism of the Guerbet reaction for the conversion of n-butanol to 2-ethylhexanol

Our research explores metallo-covalent phases, such as borides, as alternatives to the metallic phase.[3] Introducing boron allows on one hand to precisely adjust the electronic structure of the active sites, thus influencing the adsorption energies of the reagents and changing selectivity, and on the other hand to create more active coordinatively unsaturated sites (CUS) than in pure metals. To achieve this, we study a series of metal boride nanoparticles supported on a neutral support (SiO_2, Al_2O_3) or a basic support (Mg-Al-O). These catalysts are synthesised by a robust method that involves coprecipitation and calcination of a layered double hydroxide, yielding a porous mixed oxide Mg-Al-O,[4] and support wet impregnation followed by chemical reduction with $NaBH_4$ for metal borides. The performances of catalysts are assessed using the model reaction of n-butanol condensation to 2-ethyl hexanol in a batch liquid phase reaction (250 °C).

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Morphology-driven metal-support interactions in Co/CeO_2 catalysts for enhanced CO oxidation

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Carbon monoxide (CO), a toxic product of incomplete combustion, is a major air pollutant associated with serious environmental and health impacts, accounting for a large fraction of urban air contaminants in rapidly growing megacities[1]. Its catalytic oxidation is widely employed both as an emission-control strategy and as a model reaction for understanding structure-property relationships[2]. In this study, cobalt oxide (Co_3O_4) catalysts supported on hydrothermally synthesised ceria (CeO_2) nanorods (NR) and nanocubes (NC) were comparatively explored to evaluate the effect of support morphology on CO catalytic performance. Ceria was selected due to its facile Ce^{3+}/Ce^{4+} redox cycling and high oxygen storage capacity[3], while cobalt addition further enhances these properties through strong metal-support interactions[4]. Both bare supports and Co/CeO_2 catalysts were characterized by N_2 physisorption, XRD, SEM/TEM, TPR, XPS, Raman and TGA. The results show that nanorods, predominantly exposing {100} and {110} facets, exhibit improved structural and redox properties compared with nanocubes, which correlates with higher catalytic activity. Cobalt addition enhances CO oxidation for both supports while preserving the morphology-dependent trend of bare ceria, underscoring the dominant role of support shape. Notably, Co is highly dispersed as surface nanoclusters on CeO_2 nanorods, whereas on nanocubes Co accumulates mainly at edges and corners, leading to moderate metal-support interactions and active site distributions. As a result, Co/CeO_2-NR achieves complete CO conversion at around 165^{o}C, significantly lower temperature than Co/CeO_2-NC (197^{o}C). Consequently, support morphology control is an effective strategy to tune metal-support interactions and in turn affect oxidation performance.

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Optimization of Composition and Structure of MoS_2 thin films via Molecular Beam Epitaxy for Hydrogen Evolution Reaction

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Molybdenum disulfide MoS_2 is an earth-abundant, promising catalyst for hydrogen evolution reaction (HER) owing to its tunable electronic properties [1]. Its layered structure facilitates charge transfer and exposes active sites primarily at the edge. Precise control over defects, stoichiometry and structural ordering can create additional active sites thereby enhancing HER activity [2]. However, achieving precise control in the growth of MoS_2 utilizing conventional synthesis methods remains a significant challenge.

To address this limitation, we employed molecular beam epitaxy (MBE) to precisely tailor the MoS_2 structure. Samples were synthesized by optimizing Mo/S ratio, layer number and post-annealing temperature. In-situ reflection high-energy electron diffraction (RHEED), Raman spectroscopy, X-ray diffraction and X-ray absorption fine structure (XAFS) confirmed structural modifications. It is observed that higher annealing temperatures and increased layer number improve crystallinity but decrease edge-site density and electronic conductivity, thereby reducing HER activity [3]. Intermediate layer number attained better HER due to better conductivity while sulfur-deficient conditions yielded MoS_2 containing residual metallic Mo and sulfur vacancies [3]. These defects activate inert basal planes while providing conductive pathways, yielding optimal HER performance [3]. These findings highlight that MBE growth provides a versatile platform for tailoring the catalytic activity of MoS_2. This approach offers a promising pathway for innovation in sustainable hydrogen production technologies.

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Synergistic Effect of Bimetallic Spinel $CuFe_2O_4$ Nanoparticles in a Bipyridine-Based Covalent Organic Framework for Robust Water Oxidation

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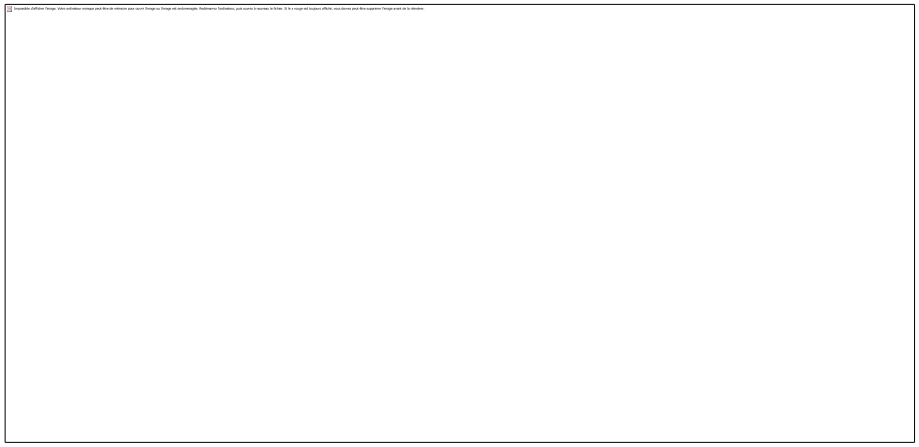
Covalent Organic Frameworks (COFs), owing to their highly crystalline and porous nature, have attracted attention for electrocatalytic oxygen evolution reaction (OER) applications. However, their intrinsic OER activity is often limited due to the lack of sufficient catalytic active sites and conductivity.[1] To tackle this limitation, COF-based composites incorporating metallic nanostructures have emerged as promising electrocatalysts because of their improved conductivity, enhanced charge mobility, and structural stability.[2,3] Herein, we conceptualized in-situ synthesis of a highly active and stable COFs composite (Py-Bpy-COF@30%CFO) by incorporating a varied ratio of spinel bimetallic copper ferrite (CFO) nanoparticels into a bipyridine-based Covalent Organic Framework.[4]



The spinel bimetallic system is effectively confined within the COF's pore network through coordination interactions with the bipyridine moieties. Each COF composite was systematically evaluated for OER application, and an optimized Py-Bpy-COF@30%CFO delivered high OER performance at a current density of 10 mA cm^{-2} with a low overpotential of 379 mV with high stability of 40 hrs. The enhanced performance is attributed to the synergistic interaction between the spinel $CuFe_2O_4$ catalyst and the COF framework, which provides a large surface area, abundant active sites, improved conductivity, and enhanced charge transport and mass transfer during the OER process. It developed COF composites as highly efficient and stable OER catalysts superior to pristine COF and bimetallic systems. This study provides insights into the design of efficient and durable COF-based electrocatalysts for sustainable energy applications.

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DTQ Immobilization: Bridging Homogeneous and Heterogeneous Photoredox Catalysis

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Photoredox catalysis represents a powerful and sustainable approach for driving redox transformations under mild conditions using visible light.[1] However, homogeneous systems often suffer from difficult catalyst recovery and limited recyclability. Immobilization strategies therefore provide an attractive solution, enabling catalyst reuse and facilitating integration into continuous-flow processes.[2]
In 2014, our group introduced the organic photocatalyst dicyanopyrazine (**DPZ**),[3] which was later found to undergo a Mallory-type photocyclization under blue-light irradiation to form dithienoquinoxaline (**DTQ**). **DTQ** exhibits unique redox behaviour by acting either as an oxidant or highly potent reductant (E_{red}* ≈ –3 V vs SCE) via PET or conPET and using a single light source.[4] To enhance its practical applicability, **DTQ** was immobilized via copolymerization with styrene, affording a polymer-supported photocatalyst (**iDTQ**). The resulting material retained the key photophysical and catalytic properties of homogeneous **DTQ** and proved effective in heterogeneous photoredox reactions under both batch and continuous-flow conditions, with improved recyclability.[5]

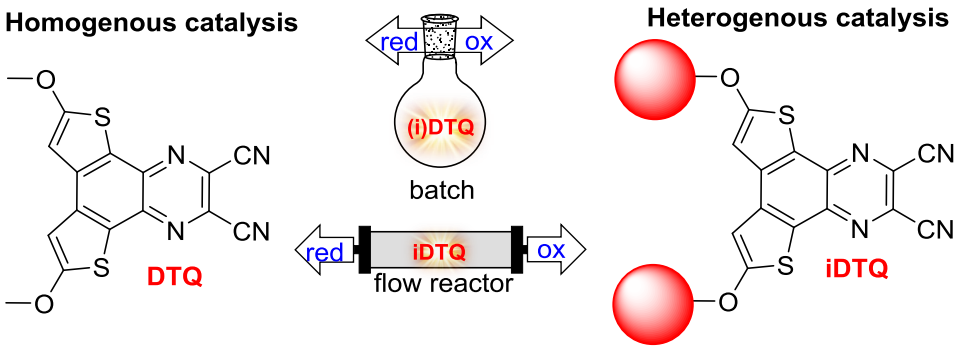

Figure 1. Homogeneous **DTQ** vs. heterogeneous **iDTQ** photocatalysis in batch and flow reactors.

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Silver-Modified Lemon Peel Biochar for Adsorption–Catalytic Removal of Parabens

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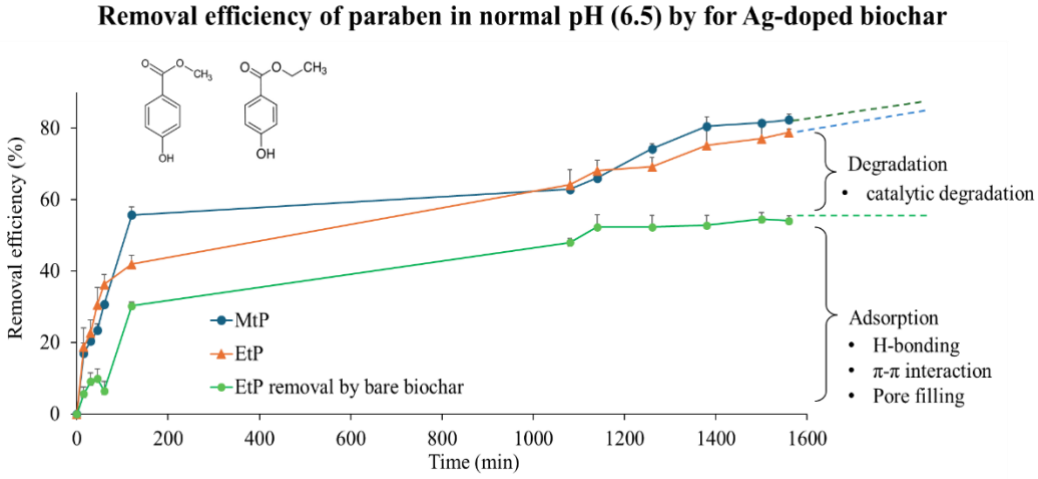
Silver-modified biochar derived from lemon peel waste was developed as a catalytic material for the removal of parabens from aqueous systems, using methylparaben (MeP) and ethylparaben (EtP) as model contaminants. The biochar support was prepared under optimized pyrolysis conditions at 500°C, as established in prior work [1], to ensure suitable porosity and surface functionality for subsequent modification. Silver incorporation was carried out via two approaches: (i) chemical reduction using glucose as a reducing agent to generate pre-formed silver nanoparticles, and (ii) direct impregnation of silver precursor followed by thermal treatment without an external reducing agent. Comparative results indicated that the non-reduced route led to a more effective catalytic system, likely due to stronger interaction between silver species and the biochar matrix. The silver-modified biochar exhibited enhanced removal performance compared to bare biochar, highlighting the contribution of catalytic transformation pathways in addition to surface interactions. The reaction behavior followed pseudo-second-order kinetics, suggesting that surface-mediated processes govern the overall removal. Mechanistically, paraben removal is attributed to combined adsorption–catalytic processes, including electron transfer facilitated by silver species, along with π–π interactions and hydrogen bonding. The stability of silver on the biochar surface supports its function as a heterogeneous catalyst. This study demonstrates that waste-derived biochar integrated with silver can serve as a promising low-cost catalytic material for the treatment of emerging contaminants such as parabens.



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g-C_3N_4/$Cs_3Bi_2Br_9$ Photocatalysts for Visible-Light-Driven *p*-Anisaldehyde Synthesis

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Replacing traditional organic synthesis processes with efficient alternatives that can operate at ambient conditions is essential for the transition towards a more environmentally responsible chemical industry. Photocatalysis appears as an alternative, using light as a source of energy instead of conventional energy-intensive processes. Graphitic carbon nitride (g-C_3N_4, here referred to as GCN) is a metal-free photocatalyst with high stability and low cost, but its practical efficiency is often limited by a high charge-carrier recombination rate and low specific surface area [1]. To overcome these challenges, this work explores the development of GCN-based composites with $Cs_3Bi_2Br_9$ (CBB), leveraging the exceptional visible-light absorption and photoelectric properties of these lead-free perovskites [2]. The production of *p*-anisaldehyde (*p*-AAD), a high-value compound used in the pharmaceutical, food, and fragrance industries, from the respective alcohol was selected as a model reaction.

The synthesis of the hybrid materials involved the thermal polymerisation of dicyandiamide at 550 ºC to produce GCN, which was added in different amounts to a solution of N,N-dimethylformamide containing the CBB precursors (CsBr and $BiBr_3$) at 60 ºC. The synthesised xGCN/CBB (x = 50-98 wt.%) photocatalysts were characterised through different methods, such as diffuse reflectance ultraviolet-visible (DRUV-Vis), solid-state photoluminescence (PL) and Fourier transform infrared (ATR mode) spectroscopies, scanning electron microscopy (SEM) and X-ray diffraction (XRD). Photocatalytic experiments were conducted under visible-light LED irradiation using a 1 g L^{-1} catalyst load in 40 mL of a 5 mM anisyl alcohol (AA) solution for 1 hour. High-performance liquid chromatography (HPLC) was employed to identify and quantify AA and *p*-AAD in samples taken periodically from the reaction medium. To enhance the practical applicability of the system, the most promising catalyst was immobilised on a 3D polyethylene terephthalate structure by a simple deposition method using polyvinyl alcohol, which acted as an adhesive agent to anchor the catalyst onto the support.

SEM micrographs of the hybrid materials revealed the formation of hexagonal CBB crystal plates with irregular sizes, directly grown on stacked GCN sheets. DRUV-Vis and PL spectroscopies confirmed that the incorporation of CBB extends light absorption further into the visible range of the spectrum, while slowing charge-carrier recombination and improving charge separation efficiency. xGCN/CBB materials exhibited a remarkable synergistic effect with enhanced AA conversion, significantly outperforming pure GCN. Among the prepared materials, the 70GCN/CBB composite showed optimal photocatalytic performance, providing the best balance between high activity and structural stability. Once immobilised, this material maintained consistent performance across three consecutive 2-hour reaction cycles, for a total of six hours of stable operation. These findings show that immobilised 70GCN/CBB provides an effective and environmentally friendly alternative for *p*-AAD production under mild conditions, without the need for additional separation steps, and support further studies on safer and greener photocatalytic organic synthesis systems.

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Transition-Metal–Incorporated tunable Redox-active Polyoxometalate-Stabilized TiO_2 Nanocores for Visible-Light-Driven Photo-, Electro-, and Photoelectrocatalytic HER

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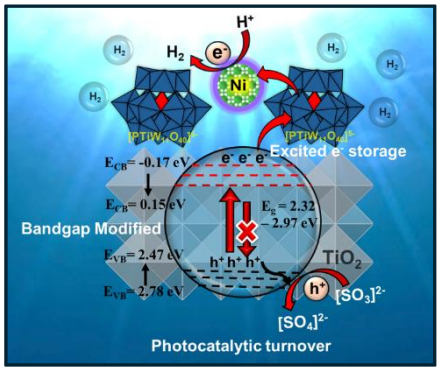
Abstract

Water-soluble molecular metal-oxide cluster anions, specifically polyoxometalates (POMs), which exhibit distinct redox activities and serve as covalently bonded inorganic ligands on anatase TiO_2 nanocrystals. These complexes represent a unique class of anionic clusters that occupy an intermediate position between discrete macroanions and conventional colloidal nanoparticles. The research primarily focuses on Keggin-type ions, represented as $Na_{(12-n)}[\alpha\text{-}X^{n+}W_{11}O_{39}]$, where the heteroatom X^{n+} varies among P^{5+}, Si^{4+}, and Al^{3+}. Post-synthesis characterisation reveals an average binding of approximately 55 ± 10 α-$[PW_{11}O_{39}]^{5-}$ anions per nanocrystal, acting as pentadentate ligands stabilising Ti(IV) centres while maintaining coordination to the underlying anatase TiO_2 core via a sixth coordination site. The surface-anchored POM anions function as reversible electron acceptors with redox potentials that can be modulated by heteroatom substitution, shifting toward more negative potentials upon replacing P^{5+} with Si^{4+} or Al^{3+}. These findings suggest that POM cluster anions can modulate the redox behaviour and reactivity of metal centres in nanostructured materials, offering a route to precise control over charge-transfer processes. To improve the absorption in the visible regions, impregnation of transition metals(such as, Fe, Ni, Cu, Ag, Au) onto the surface of self-doped TiO_2 crystals notably enhances the visible-light-driven photocatalytic performance of these hybrid POM-TiO_2 systems, offering promising avenues for optimised photo-, electro- and photoelectrocatalytic applications.



Keywords: Polyoxometalates, Self-doped TiO_2 hybrid, Lacunary Kegging, Photocatalytic HER, electrocatalytic HER,

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Evaluation of CuO-Layered Double Hydroxide for Oxygen capture

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Argon, an inert gas widely used in the chemical industry, can be liquefied at −186 °C at atmospheric pressure. Currently, a consumption of about 70,000 tons of liquid argon is expected at the facilities of Fermilab for neutrino research [1]. However, trace amounts of O_2, H_2O, and N_2 can compromise this process [2]. Therefore, oxygen removal is critical. This work aimed to synthesize, pelletize, and evaluate the potential of CuMgAl-LDH (layered double hydroxide) and CuMgAlCe-LDH materials for O_2 capture in liquid argon (LAr), comparing their performance with CuO-BASF, commonly used in this process. Both materials, prepared with 10% Cu via coprecipitation at constant pH, were filtered, washed, and dried. They were then extruded, dried, cut and finally calcined at 500 °C in air for 2 h. The X-ray diffraction (XRD) patterns of the synthesized LDHs (Fig. 1a) show characteristic peaks of basal reflections, indicating a well ordered structure [3]. For CuMgAlCe-LDH, the XRD indicates the formation of CeO_2, this segregation is attributed to the large ionic radius of Ce^{3+} compared with Al^{3+}, hindering its incorporation into the LDH structure [4]. Furthermore, the XRD patterns of the pellets (Fig. 1b) show that the LDH structure is maintained after extrusion. On the other hand, for the calcined pellets (Fig. 1c), the lamellar structure collapses, leading to the formation of a periclase MgO (Mg(Al)O) structure. The absence of peaks corresponding to crystalline copper indicates that the copper species are well dispersed within the LDH structure. To determine the oxygen capture capacity of the pellets, consecutive reduction and oxidation cycle tests were performed. For this, it was assumed that the fresh pellet were reduced according to reaction $CuO + H_2 \rightarrow Cu^0 + H_2O$, followed by oxidation of Cu^0 species ($2Cu^0 + O_2 \rightarrow 2CuO$). The results (Fig. 1d) show that the CuMgAl-Pellet exhibited the highest O_2 capture capacity approximately 60%, even compared with the CuO-BASF. This behavior is attributed to the larger external surface area, improving dispersion of the Cu^0 particles, resulting in superior efficiency [4,5]. Thus, CuMgAl-LDH to be a promising material for purification of oxygen impurities from liquid argon.

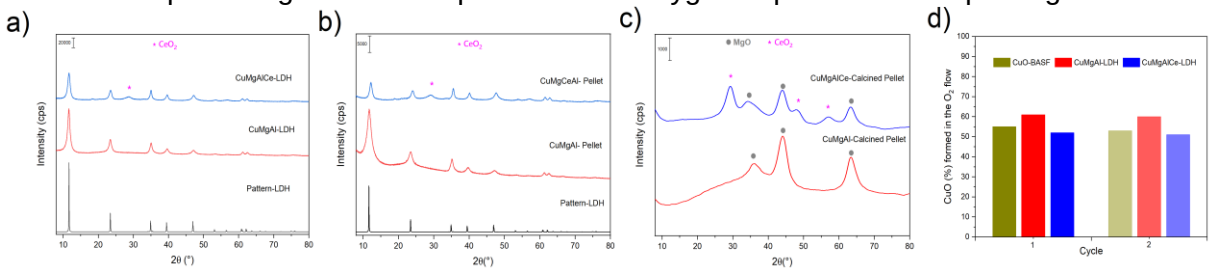

Figure 1. XRD patterns of (a) as-synthesized LDHs, (b) extruded pellets, and (c) calcined pellets, comparing calcined CuMgAl and CuMgAlCe pellets with CuO-BASF. (d) O_2 capture capacity evaluated by reduction and oxidation cycling.

Acknowledgment
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Environment-Dependent Evolution of Silver Species on TiO_2 under UV

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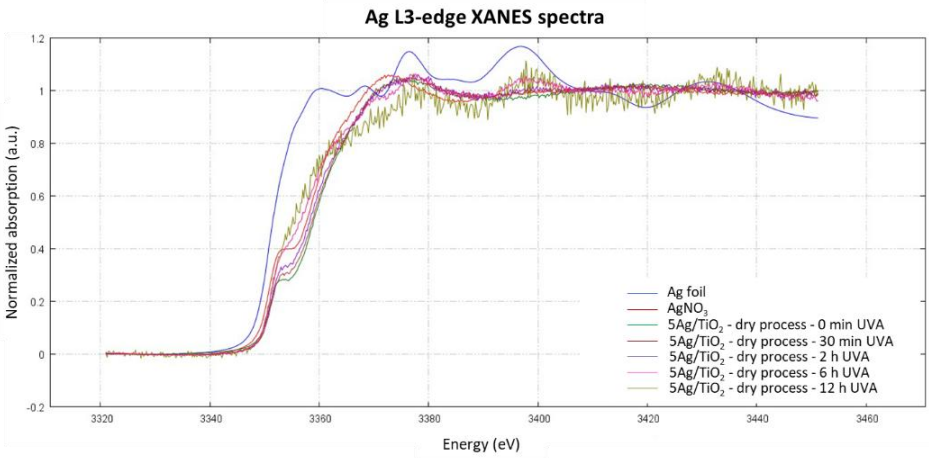
Silver-modified TiO_2 is widely used in photocatalytic applications, yet the chemical nature and evolution of silver species on the TiO_2 surface remain not fully understood. In our previous work, silver nanoparticles were generated via a reduction process prior to deposition onto TiO_2, followed by thermal treatment to remove residual organics. This approach consistently resulted in stabilized silver species on TiO_2, highlighting strong interactions between Ag and the support [1]. Building on this understanding, the present study investigates whether UV irradiation alone can induce the transformation of silver species on TiO_2 without the need for thermal treatment, and how the irradiation environment affects this process. Ag/TiO_2 samples were prepared from a silver nitrate precursor and subjected to UV irradiation under both dry and wet preparation conditions. The evolution of silver species was probed using synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy, supported by X-ray photoelectron spectroscopy (XPS). The results reveal a clear environment-dependent behavior. Under dry conditions, prolonged UV irradiation (30 min to 12 h) progressively shifts the silver species toward a more reduced state, approaching metallic Ag^0. In contrast, under wet conditions, no significant spectral change is observed even after extended irradiation (12 h), indicating that the presence of liquid-phase components suppresses or alters the transformation pathway. These findings demonstrate that UV irradiation can effectively drive the evolution of silver species on TiO_2 without thermal treatment, while the transformation strongly depends on the surrounding environment. This work provides direct spectroscopic evidence of environment-dependent silver evolution on TiO_2 and suggests that commonly assumed preparation–structure relationships may be significantly altered under irradiation conditions.



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Maximizing Loading of Rh Single-Atom on CeO_2 for Hydroformylation reaction

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Keywords: Single atom catalyst, CO DRIFTS, Hydroformylation.

Background and motivation.
The increasing demand for aldehydes can be met through industrial hydroformylation reaction, in which cost-effective, recyclable Rh single atom catalysts (SACs) can catalyze as analogues to Rh molecular catalysts.[1] The key step in hydroformylation is the migratory CO insertion step, for which Rh is highly effective in thermal catalysis.[2], [3] Although SAC has high atomic efficiency with low metal loading, increasing metal content is crucial to achieve higher yield. However, SACs are prone to agglomeration due to their high surface energy and therefore, complementary characterization is necessary to confirm the existence of isolated atoms at higher metal loadings.[4] From this perspective, we aim to find the maximum possible loading at which Rh forms single atoms using CeO_2 as support for the hydroformylation reaction.

Materials and methods. Rh/CeO_2 catalysts were prepared with different Rh loading via the precipitation method. The catalysts were characterized with powder X-ray diffraction (PXRD), Raman spectroscopy, aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM), energy dispersive X-ray spectroscopy (EDS) and X-ray absorption spectroscopy (XAS). Catalytic testing has been carried out with Styrene and Synthesis gas (CO: H_2 = 1:1) with hydroformylation reaction conditions.

Results and discussion. The Rh/CeO_2 catalysts with Rh loadings of 0.5, 1, 2 and 5 wt% have no detectable Rh_2O_3 peaks in their PXRD patterns, indicating a high dispersion of Rh (fig. 1 (a)). The high dispersion of Rh can further be visualized by AC-HAADF-STEM images and EDS mapping. The X-ray absorption near edge spectra (XANES) at the Rh K-edge (fig. 1 (b)) showed that Rh is in the +3 oxidation state for all the catalysts, and the extended X-ray absorption fine structure (EXAFS) spectra (fig. 1 (c)) revealed Rh–O as the first coordination shell without any Rh–Rh scattering up to 5 wt% Rh. The Raman spectra further verified the existence of the Rh–O–Ce bonds. Catalytic testing has confirmed that the Rh/CeO_2 SAC are highly active catalysts for hydroformylation of styrene. As an outlook, further investigation is underway to determine the maximum Rh single atom dispersion threshold on CeO_2 and its influence on catalytic performance.

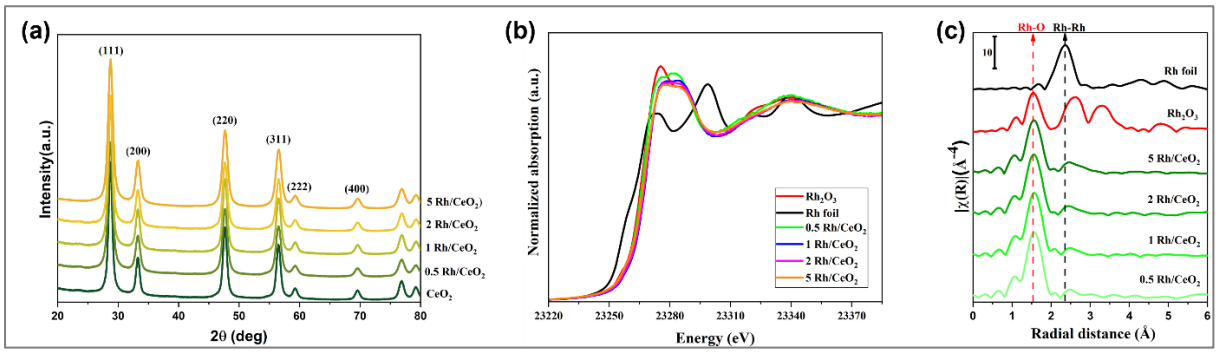

Figure 1. PXRD (a), XANES Spectra (b), EXAFS Spectra of X Rh/CeO_2, X = 0.5-5 wt%.

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Promoting the synthesis of sustainable aviation fuels (SAFs) over exposed heterointerfaces

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Sustainable aviation fuels (SAFs) from renewable biomass provide a viable, circular alternative to fossil fuels, but upgrading biomass-derived molecules such as furfural into C_8-C_{16} hydrocarbons remains challenging.[1–4] Aldol condensation is strategically positioned to address this by enabling controlled C–C coupling and oxygen removal.[5–9] However, industrial catalysts often depend on corrosive acids/bases, or expensive noble metals that require extensive purification.[7,10–13]

Alternatively, bifunctional acid-base catalysts promote these reactions through cooperative interactions under milder conditions.[10,14] In my research, I develop a new concept for engineered acid-base bifunctional catalysts using purely inorganic heterointerfaces. Using Area-Selective Atomic Layer Deposition (AS-ALD), I create thin basic oxide surface phase rafts (SPRs) on an acidic support. The exposed heterointerface is expected to provide both acid and base sites in close proximity, inducing bifunctionality (**Figure 1**). This bottom-up strategy ensures high reproducibility and structural stability, overcoming traditional catalyst limitations.

Preliminary results established a reproducible SBA-15 synthesis, providing a uniform support for precise ALD validation. An optimized ALD protocol achieved significant internal coating, balancing pore accessibility with practical reaction times. Current work focuses on an area-selective salt masking strategy; optimized deposition parameters developed for silicon wafers will also be applied to SBA-15 to create targeted heterointerfacial sites after ALD and salt removal.

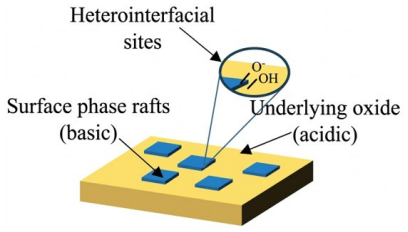

Figure 1: Bifunctional basic SPR on acidic support.

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NiZnCeAl-LDH catalysts applied to methane dry reforming

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Biogas is a mixture composed of CH_4 and CO_2 obtained through anaerobic digestion processes of biomass [1]. An alternative for the direct utilization of biogas is in the syngas production through the dry reforming of methane (DRM) reaction. This reaction uses CO_2 as an oxidizing agent, however the formation of carbon throughout this process is highly challenging [2], which leads to the continued development of economically viable catalysts resistant to deactivation under operational conditions [3]. Here, the properties of materials containing Ni/ZnO/CeO_2/Al_2O_3 (NZCA), derived from layer double hydroxide (LDH) structures, prepared under different pH values (8 and 10) with and without hydrothermal treatment (HT) were evaluated. The catalysts were characterized by TGA, XRD, N_2 physisorption, elemental analyses and evaluated in the DRM. In sum, the pH had a significant impact on the crystallinity of the materials. HT enhanced the crystallinity of the materials at both pH. Samples prepared at pH10 exhibited peaks characteristics of Ce species, indicating that this pH promoted Ce segregation. In contrast, for samples prepared at pH8, the presence of Ce phase, could not be identified, indicating its higher dispersion in the material. Thermal treatment led to the collapse of LDH structure and the formation of a mixture of oxides. The NZCA-pH8 sample, without HT, was the only that did not promoted the segregation of CeO_2 phase, indicating that these synthesis conditions improved the dispersion of this phase. The results of physisorption showed values of specific surface area between 252 – 85 $m^2.g^{-1}$ (NZCA-pH8= 252; NZCA-pH8HT=213; NZCA-pH10=13; NZCA-PH10HT= 85). All materials were evaluated in the DRM at temperatures of 650, 700 and 800°C and results indicated that the carbon deposition rate was lower for the NZCA-pH8 catalyst. The results suggest that the greater catalytic activity and lower carbon production on NZCA-pH8 are probably related to the high dispersion of cerium, associated with a high specific surface area, which promoted a greater Ni-Ce interface and favoured the gasification of carbon species.

Table1. Catalytic test results

Material	Conversion [%]		Productivity [$mol.g_{cat}^{-1}.h^{-1}$]		Carbon [$g_c.g_{cat}^{-1}.h^{-1}$]
	CH_4	**CO_2**	**H_2**	**CO**	
Temperature: 650°C					
NZCA-pH8	49	61	3.3	4.3	0.005
NZCA-pH8HT	46	59	3.0	4.0	0.1
NZCA-pH10	38	52	2.3	3.2	0.1
NZCA-pH10HT	34	47	2.2	3.1	0.3
Temperature: 700°C					
NZCA-pH8	50	65	3.4	4.4	0.1
NZCA-pH8HT	60	71	4.2	5.2	2.5
NZCA-pH10	73	81	4.9	5.8	1.3
NZCA-pH10HT	51	60	2.9	3.7	3.3
Temperature: 800°C					
NZCA-pH8	82	89	5.8	6.7	0.01
NZCA-pH8HT	78	84	5.4	6.2	0.2
NZCA-pH10	85	89	5.5	6.5	0.1
NZCA-pH10HT	91	93	6.2	7.1	0.1

Acknowledgment
The authors acknowledge FAPESP (22/10615-1) and CNPq (300454/2025-2) for the financial support.
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Tuning Co–Mn Bimetallic Catalysts for Selective C_3–C_4 Hydrocarbon Formation from CO_2

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With the growing urgency to combat climate change, converting CO_2 into useful products such as LPG (C_3–C_4) has gained considerable attention. Liquefied petroleum gas (LPG) is a vital component of the global energy mix, serving households, industries, and petrochemical plants alike[1]. However, CO_2 hydrogenation typically favors C_1 products, making the selective production of higher hydrocarbons such as C_3–C_4 a significant challenge and an important research focus.

The relevant chemical reactions are as follows –

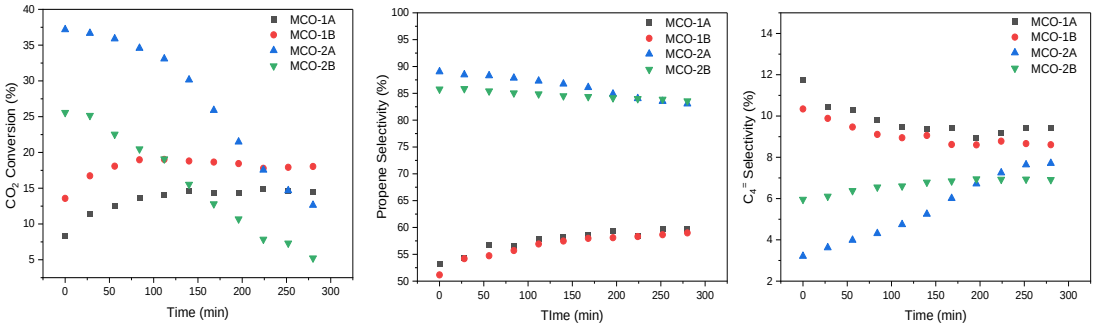
$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \quad \text{……(R.1)}$$

$$n\ CH_3OH + H_2 \rightarrow CH_3(CH_2)_{n-2}CH_3 + n\ H_2O \quad \text{……(R.2)}$$

$$n\ CH_3OH \rightarrow CH_2{=}CH(CH_2)_{n-3}CH_3 + n\ H_2O \quad \text{……(R.3)}$$

The reactions **R.1** to **R.3** are considered as possible reaction pathways[2].

Previous studies using Zn- and Zr-based zeolite catalysts show limited CO_2 conversion[3]. In this work, we report a highly crystalline bimetallic Mn–Co mixed oxide catalyst synthesized via a hydrothermal method using a mixture of different precursor salts. Based on this, the catalysts are defined as MCO-1A, 1B, 2A, and 2B. The catalysts were characterized by XRD, H_2-TPR, ICP-OES, and HR-SEM, confirming high crystallinity and the formation of mixed oxides. Figure 1 shows preliminary activity results, where the MCO-2 series exhibits



higher C_3 selectivity than MCO-1, while C_4 selectivity shows the opposite trend.

Figure1: The catalyst activity test was conducted with GHSV = 117.88 l/g_{cat}-h, Reduction temp = 350 ℃, H_2:CO_2:Ar = 3:1:6, and Reaction condition 350 ℃, 20 bar.

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PoliHIPE Supported Heterogeneous Pt−NHC Catalysts for Sustainable Silicon Industry Applications

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Platinum (Pt) catalyzed hydrosilylation of alkenes has known as the most efficient reaction method for the synthesis of industrial functional silicones and has emerged as one of the largest applications of industrial homogeneous catalysis over the last 50 years [1]. In the context of the evolving silicon industry, the need for sustainable and efficient catalytic processes that can replace commercial homogeneous Pt catalyst such as Speier and Karstedt is paramount. In order to reduce the catalyst cost of the Pt-catalyzed alkene hydrosilylation, studies to develop a heterogeneous catalyst design in which the Pt metal can be reused with minimal activity loss are therefore is very crucial. Among the heterogeneous catalyst support materials, styrenic polyHIPEs stand out with their relatively low cost and facile synthesis method. Their dual-sized macro-dimensional porosity can be upgraded to homogeneously dispersed meso-micro porosity by hypercrosslinking method. Free alkyl halide functional groups originating from vinyl benzyl chloride monomer present on the surface of hypercrosslinked polyHIPE (HCLPH) can be utilized for chemical binding of the metal-ligand complex to provide catalytic activity. This research presents novel heterogeneous Pt catalysts which are hierarchical porous HCLPH support containing Markó-type NHC-Pt complex structures designed specifically for industrial alkene hydrosilylation applications. In depth chemical and morphological characterization of novel Pt catalyst have been performed by using X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Thermogravimetric Analysis (TGA), and BET surface area and porosity analysis techniques. Comparative studies with industry standard Speier and Karstedt catalysts for the alkene hydrosilylation monitored with GC-MS and ^{1}H-NMR reveals that these novel catalysts not only match the catalytic performance of commercial catalysts with the same amount of Pt, but also provides at least ten catalytic cycles without any loss of activity. The unique hierarchical architecture of the support facilitates superior mass transfer and active site accessibility, resulting in enhanced catalytic performance. This research underlines the potential of these novel heterogeneous Pt catalysts to contribute to sustainable silicon production by maximizing resource utilization in industry while maintaining high efficiency alkene hydrosilylation.

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Influence of reducible metal oxides on alkane molecule adsorption

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Global plastic production continues to rise annually, yet less than 10% of plastic waste is mechanically recycled. Current chemical recycling strategies predominantly rely on combustion and pyrolysis, processes that are energy-intensive, poorly selective, and contribute significantly to environmental pollution. The development of more sustainable recycling approaches is therefore urgently needed.

Catalytic strategies offer a promising pathway to address these challenges by enabling polymer depolymerization at lower temperatures with enhanced selectivity. One such approach involves catalytic oxidative dehydrogenation (ODH) of polymers. When ODH is conducted over metal catalysts supported on reducible oxides, the reaction can proceed via a Mars–van Krevelen (MvK) mechanism, wherein lattice oxygen from the support participates directly in the reaction with adsorbed species. The resulting oxygen vacancies are subsequently replenished by gas-phase oxidants, thereby regenerating the active sites and sustaining catalytic activity.

In this work, we investigate the reactive adsorption and catalytic transformation of model short-chain alkanes under mild conditions as a proxy for polyolefin deconstruction. We synthesize both monometallic (e.g., Ni) and bimetallic alloy (e.g., NiCo) catalysts supported on reducible oxides and probe their physicochemical properties using temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) of heptane. Complementary in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is employed to elucidate surface intermediates and correlate molecular-level interactions with catalytic performance.

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Electrochemical oxidation of methanol at $Ni(OH)_2$-supported Pd electrocatalysts for direct methanol fuel cells

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Direct methanol fuel cells (DMFCs) have acquired considerable attention owing to high energy density, structural simplicity, fast operation and low pollution. However, their industrial application remains limited by some of their drawbacks, such as low fuel efficiency conversion, slow methanol oxidation and poisoning of catalytic active sites by carbonaceous intermediates[1]. To address these challenges, in this study $Ni(OH)_2$ was hydrothermally synthesized and composited with metallic Pd nanoparticles, obtained by chemical reduction, to synthesize $Pd/Ni(OH)_2$ composite with different Pd : Ni ratio. Various physiochemical techniques such as X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) were used to evaluate the structural, morphological and chemical properties of $Pd/Ni(OH)_2$ catalyst. XRD analysis confirmed that $Pd/Ni(OH)_2$ composite showed the characteristic peaks of nickel hydroxide and metallic Pd. While SEM-EDS results displayed the presence of agglomerated and irregular $Ni(OH)_2$ flakes along Pd nanoparticles and uniform distribution of all constituent's elements in $Pd/Ni(OH)_2$ samples. XPS patterns further confirmed the existence of metallic Pd, with Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks observed at 335.00 eV and 340.22 eV binding energies.

Cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) were used to investigate the electrocatalytic behavior of $Pd/Ni(OH)_2$ material for methanol oxidation in alkaline solution. The $Pd/Ni(OH)_2$ exhibits significant catalytic activity towards MOR relatively to $Ni(OH)_2$ due to synergistic effects of both the Pd active sites and $Ni(OH)_2$ support. Among the investigated composites, Pd : Ni (1:0.5) catalyst showed highest forward peak current density (31.10 mA cm^{-2}) and normalized mass activity (450 mA mg^{-1}_{Pd}) compared to other similarly synthesized catalysts. However, Ni-rich composites $Pd/Ni(OH)_2$ (1:1) and (1:3) showed larger I_f/I_b ratio (~1.4), lower Tafel slope (134 mV dec^{-1}) and τ_{LF} values, attributed towards less deactivation of active sites responsible for fresh methanol oxidation in alkaline media. Increasing the Ni content led to a decrease in catalytic activity for MOR due to larger resistance and reduced electronic conductivity. To overcome this, the Ni-rich composite (1:3) was mixed with 20 wt% carbon black, showing significant decreased in τ_{LF} values confirmed by EIS and 35% increase in direct methanol oxidation current. Overall, the obtained $Pd/Ni(OH)_2$ material presents a cost effective, promising, durable anode catalyst.

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Electron Traps in Thermal Heterogeneous Catalysis: Fundamentals, Detection, and Applications of CO2 Hydrogenation

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Abstract:

Defect engineering has become a key strategy in heterogeneous catalysis; however, the role of electron traps (ETs) in thermally driven catalytic processes remains insufficiently explored. This work presents a comprehensive perspective on ETs as fundamental electronic states that connect lattice defects with catalytic performance, with particular relevance to CO_2 hydrogenation.

Electron traps, defined as localised electronic states within the band gap, regulate charge storage, transfer, and release under reaction conditions. Their characteristics, including depth, density, spatial distribution, and dynamics, directly influence key catalytic steps such as reactant activation, intermediate stabilisation, and redox turnover. This work integrates fundamental concepts of ET formation and characterisation with advanced spectroscopic techniques, including thermally stimulated current (TSC), deep-level transient spectroscopy (DLTS), thermoluminescence (TL), electron paramagnetic resonance (EPR), photoluminescence (PL), and reversed double-beam photoacoustic spectroscopy (RDB-PAS), providing a unified framework for probing trap states.

Through selected case studies of metal oxides and supported catalysts, ETs are shown to act as dynamic electron reservoirs that modulate reaction pathways and lower activation barriers in thermocatalytic CO_2 hydrogenation. The interplay between defect structure and electronic properties is highlighted as a key factor governing catalytic activity, selectivity, and stability.

This work establishes electron traps as actionable design parameters and offers a framework for the rational development of next-generation thermocatalysts for energy-relevant transformations.

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Steering the Catalytic Mechanism via the Mott–Schottky Effect in $Fe_{0.64}Ni_{0.36}/Ni_{12}P_5$ Heterostructures

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Absract

Developing efficient and stable oxygen reduction reaction (ORR) catalysts is essential for high-performance zinc-air batteries [1,2]. Herein, we report a $Fe_{0.64}Ni_{0.36}/Ni_{12}P_5$ heterostructure catalyst in which the ORR pathway is effectively regulated from a two-electron ($2e^-$) process toward a desirable four-electron ($4e^-$) process through a Mott-Schottky effect at the metal/semiconductor interface. The formation of the heterointerface induces charge redistribution and an internal electric field, which optimizes the adsorption behavior of oxygen intermediates and accelerates electron transfer kinetics. As a result, the catalyst exhibits enhanced ORR activity, favorable reaction selectivity, and improved catalytic stability in alkaline electrolyte. When applied as the air cathode in zinc-air batteries, the $Fe_{0.64}Ni_{0.36}/Ni_{12}P_5$ catalyst delivers a higher power density and prolonged cycling stability compared with benchmark catalysts. This work demonstrates an effective strategy for steering ORR pathways via interfacial electronic modulation and provides insights into the rational design of advanced electrocatalysts for metal-air batteries.

Result

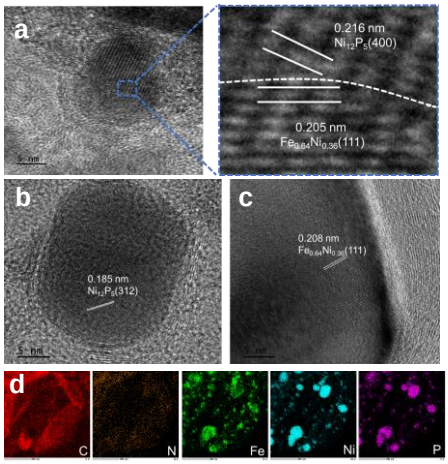

Fig.1 Structural characterization of the $Fe_{0.64}Ni_{0.36}/Ni_{12}P_5$ heterostructure.

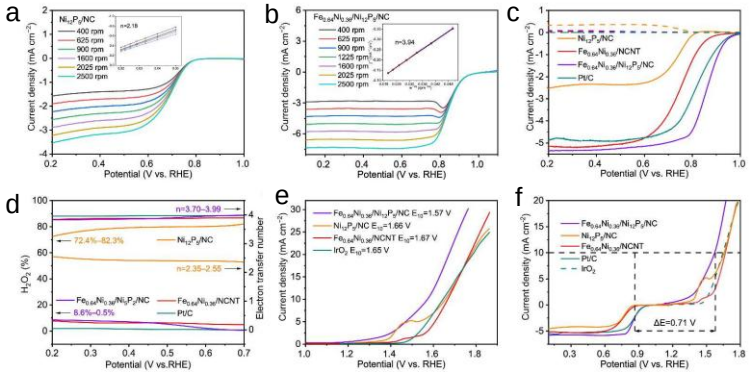

Fig.3 Electrocatalytic ORR and OER performance of $Fe_{0.64}Ni_{0.36}/Ni_{12}P_5$ /NC.

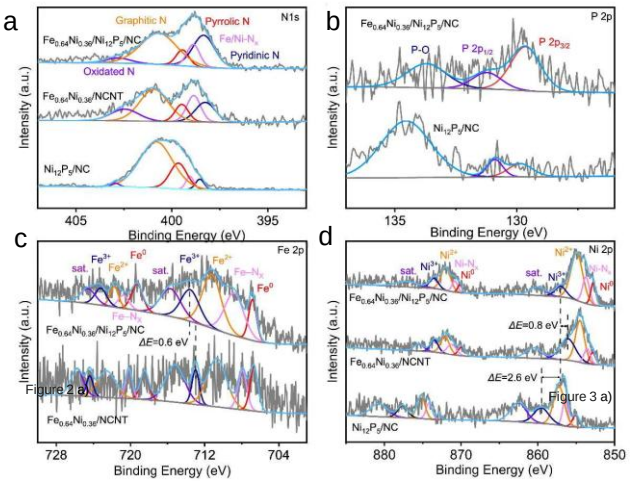

Fig.2 XPS analysis of electronic structure and interfacial interaction.

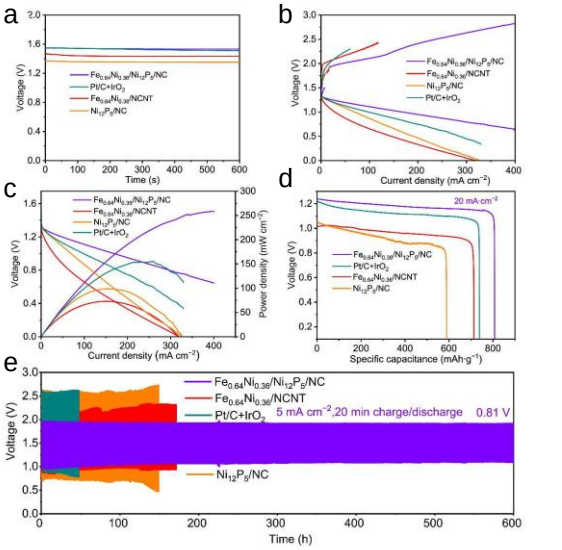

Fig.4 Zn–air battery performance based on $Fe_{0.64}Ni_{0.36}/Ni_{12}P_5$ /NC.

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Iridium Cluster Decoration on Amorphous Cobalt Oxide-Coated Carbon Nanotubes for High-Performance Lithium-Oxygen Battery Cathodes

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Absract

Lithium-oxygen batteries hold great promise for next-generation energy storage due to their exceptionally high theoretical energy density. However, their practical application is hindered by the sluggish kinetics associated with the oxygen reduction reaction and oxygen evolution reaction, resulting in severe voltage polarization and limited cycling stability. Herein, a simple solvent thermal reaction and a one-step reduction reaction is developed, where amorphous cobalt oxide (CoO) is uniformly coated on multi-walled carbon nanotubes (CNT) and further decorated with highly dispersed iridium (Ir) clusters. The amorphous CoO coatings preferentially nucleate at CNT defect sites, which not only passivates surface defects but also facilitates the homogeneous distribution of Ir clusters. This unique Ir/CoO@CNT architecture provides abundant active sites and promotes efficient electronic and ionic transport, thereby enhancing the electrocatalytic activity and overall battery performance. The synergistic effect between the highly active Ir clusters and the amorphous CoO, which accelerates reaction kinetics and stabilizes the electrode interface. As a result, the Ir/CoO@CNT cathode achieves a high discharge capacity of ≈6700 mAh g^{-1}, with a low overpotential of 0.96 V and exhibits excellent cycling stability, sustaining over 150 cycles under a limited capacity of 500 mAh g^{-1} at 500 mA g^{-1}.

Result

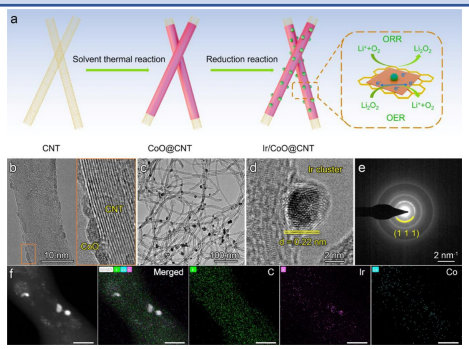

Figure 1 a) Schematic of the synthesis process. b,c) TEM images of CoO@CNT (b) and Ir/CoO@CNT (c). d) HRTEM image of Ir/CoO@CNT. e) SAED spectrum. f) EDS mapping of Ir/CoO@CNT, and the scale bar is 10 nm.

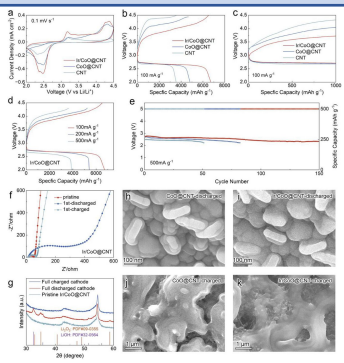

Figure 3 a) CV curves at 0.1 mV s^{-1}. b) First fully charged/discharged curves of CNT, CoO@CNT, and Ir/CoO@CNT batteries. c) First charged/discharged curves with a fixed capacity of 1000 mAh g^{-1} at 100 mA g^{-1}. d) Rate capabilities. e) Cycling performance and discharge final potential of CNT, CoO@CNT, and Ir/CoO@CNT with a fixed capacity of 500 mAh g^{-1} at 500 mA g^{-1}. f) Electrochemical impedance profiles of Ir/CoO@CNT batteries at various states. g) XRD patterns of the Ir/CoO@CNT electrode in their pristine, fully discharged, and fully charged states. h-k) SEM images of the electrodes of CoO@CNT and Ir/CoO@CNT batteries after fully discharged (h,i) and recharged (j,k).

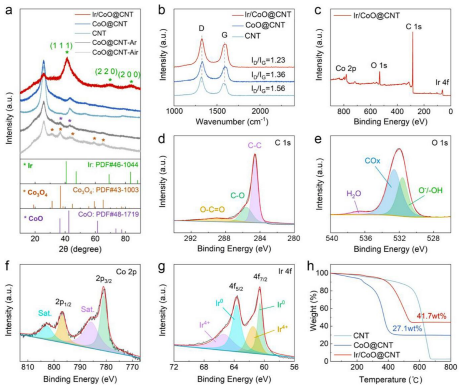

Figure 2 a) XRD patterns of CNT, CoO@CNT, CoO@CNT-Air, CoO@CNT-Ar, and Ir/CoO@CNT. b) Raman spectra of Ir/CoO@CNT. c) XPS survey spectrum of Ir/CoO@CNT. d-g) High-resolution XPS spectra of C 1s (d), O 1s (e), Co 2p (f), and Ir 4f (g). h) TG curves of CNT, CoO@CNT, and Ir/CoO@CNT under air atmosphere.

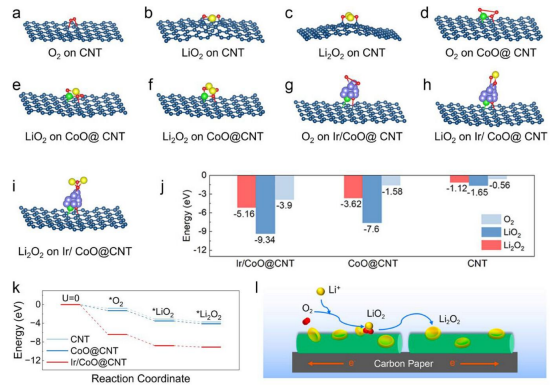

Figure 4 a-i) First-principles simulation results of O_2, LiO_2, Li_2O_2 adsorbed at CNT (a-c), CoO@CNT (d-f), and Ir/CoO@CNT (g-i), where blue atom represents Co, red represent O, yellow represent Li, and purple represent Ir. j) Adsorption energies. k) Free energy diagrams of battery reactions on cathodes. l) Schematic diagram of ORR reaction to generate Li_2O_2 on the cathode.

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Mechanistic Insights into the Catalytic Innovations in Biomass Valorization

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Catalysts are fundamental to enhancing biomass valorization processes, enabling selective and efficient conversion of lignocellulosic feedstocks into high-value bio-based chemicals and fuels. This study explores key catalytic strategies through experimental and theoretical investigations. The CO_2-assisted synthesis of PdNi nanoalloys demonstrates highly selective hydrogenation of 5-Hydroxymethylfurfural, promoting sustainable bio-refining [1]. Plasma-enabled catalysis facilitates the targeted synthesis of bio-based phenolics from lignin-derived feedstocks [2]. The catalytic fast pyrolysis of levoglucosan, furfural, and furan over HZSM-5 is analyzed using both experimental and theoretical approaches to reveal optimal reaction pathways [3][4]. Additionally, the role of bimetallic catalysts and Brønsted acid-supported metal sites in anisole hydrodeoxygenation is elucidated using density functional theory (DFT), offering a deeper understanding of deoxygenation mechanisms [5][6]. As show in Figure 1, The volcano relationship for bimetallic catalysts and catalyst supports have been clearly identified [1][7-11]]. By integrating catalytic advancements with mechanistic insights, this study provides a comprehensive framework for optimizing biomass conversion technologies, advancing sustainable biofuel and biochemical production within a circular bioeconomy.

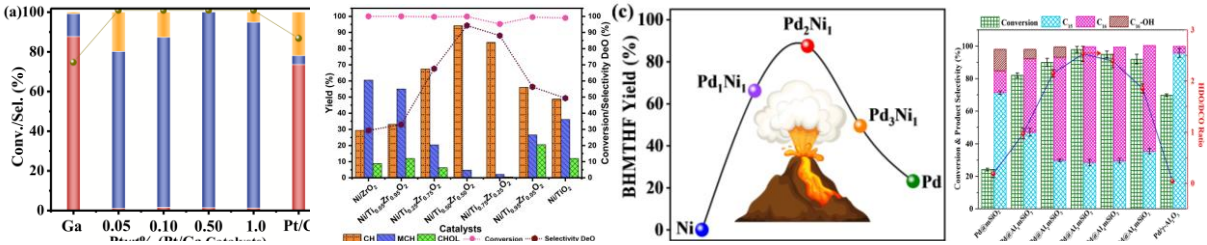

Figure 1. The volcano relationship for bimetallic catalysts and catalyst supports [1][9-11]

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