

Porous Phenazine-bridged Tetraoxa[8]circulenes for Selective Gold Recovery and Heterogeneous Catalysis

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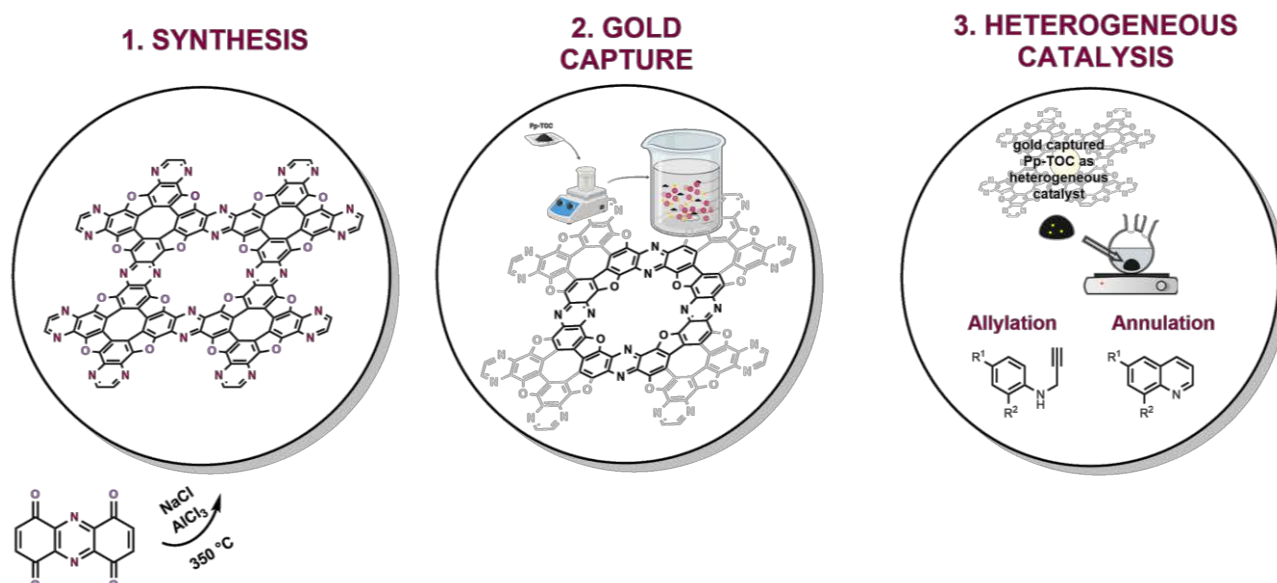
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To secure strategic resources and reduce the environmental impact of mining, we must sustainably recover precious metals. Selectively extracting gold from electronic waste is appealing yet challenging. In this study, we report on the synthesis of phenazine-based porous tetraoxa[8]circulene (Pp-TOC), which incorporates crown ether moieties that efficiently capture gold. Pp-TOC has a high surface area of over 1,200 m²/g, crown-ether-like cavities, and a high heteroatom content. These properties enable high gold uptake capacities of up to 860 mg/g under acidic conditions and up to 1250 mg/g under light irradiation. Importantly, the polymer can selectively capture gold from electronic waste even in the presence of high concentrations of competing metal ions such as copper. The recovered material contains a mixture of Au(III), Au(I), and Au(0) species and can be used directly as a heterogeneous catalyst in a sequential alkylation-annulation reaction. Switching from aprotic toluene to protic ethanol redirects the reaction outcome from alkylation to annulation. Thus, divergent product selectivity can be achieved with the same heterogeneous catalyst simply by changing the solvent.



Continuous-flow regeneration of enzyme immobilisation supports via thermally reversible Diels–Alder chemistry

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Enzyme immobilisation underpins industrial biocatalysis but generates persistent polymer waste, as the carrier (typically >90% of the catalyst mass) is discarded once the bound enzyme is exhausted.^[1] Building on our recent efforts to render immobilisation supports reusable through reversible chemistries,^[2] we have developed a thermally cleavable Diels–Alder (DA) cycloadduct that converts commercial C2-amine methacrylate beads into a regenerable carrier amenable to repeated load–use–cleave–reload cycles in batch. Here, that chemistry is translated into a continuous-flow format, in which a single packed-bed column is armed, loaded, used, and regenerated *in situ*, removing the need to replace the resin between enzyme generations (Fig.1).

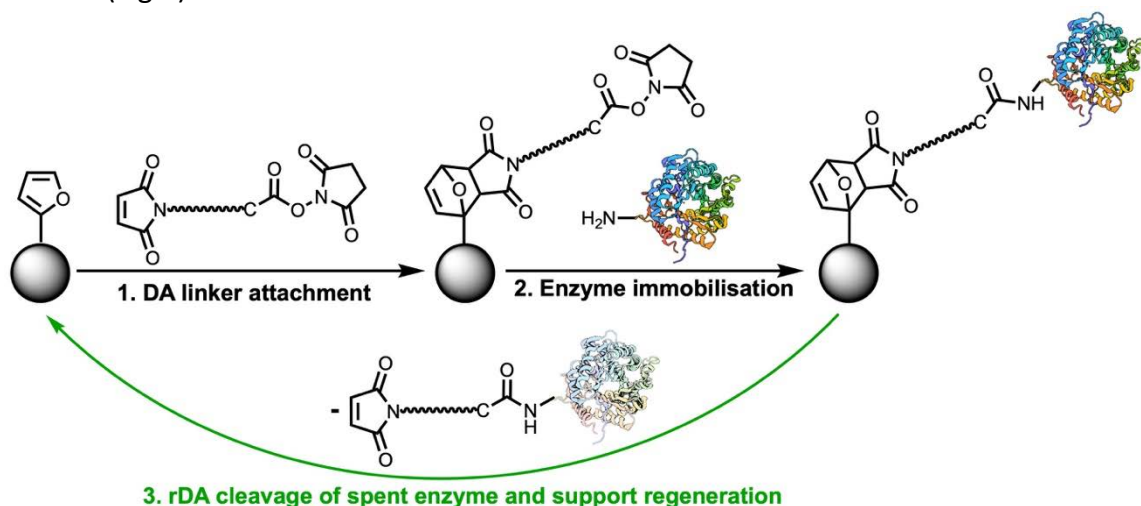


Figure 1: Three-step reusable enzyme immobilisation cycle on a furan-decorated methacrylate bead: (1) Diels–Alder attachment of the bifunctional maleimide–NHS linker, (2) enzyme immobilisation through NHS coupling to a surface lysine, and (3) retro-Diels–Alder (rDA) cleavage of the spent enzyme–linker conjugate, regenerating the furan-decorated support for the next cycle.

A glass column was packed with the furan-decorated resin and primed by recirculating the bifunctional MAL-PEG₂-NHS linker in DMAc at 37 °C for 72 h in loop mode, installing reactive NHS termini through the forward DA reaction. The target enzyme was then immobilised onto the activated bed under aqueous flow and used directly in continuous biocatalysis. Once the immobilised biocatalyst was exhausted, single-pass perfusion of 10% aqueous SDS at 100 °C cleaved the oxanorbornene adduct *via* the retro-DA reaction, washing out the spent enzyme–linker conjugate and regenerating the furan-decorated bed in place. A second loop-mode infusion of fresh linker re-armed the same column for the next immobilisation cycle. By confining every step of the carrier life cycle to a single packed bed, this workflow turns a consumable methacrylate support into a reusable flow platform and meaningfully extends carrier lifetime, addressing one of the most persistent sources of polymer waste in immobilised biocatalysis.

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Controlled and continuous precipitation of calcium silicate hydrate with a segmented flow tubular reactor

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Calcium silicate hydrate (CSH) is the main hydration product of Portland cement and the most abundant synthetic phase on planet earth [1]. The nucleation and growth of CSH controls the early hydration reaction and consequently the strength development, at later hydration times it forms a nanoporous network that controls ion transport which reduces the durability of concrete and causes structural degradation [2].

Cement hydration is a process where multiple reactions happen simultaneously. Consequently, obtaining phase pure CSH with cement relevant conditions is challenging. While many synthesis methods are used to produce synthetic phase pure CSH, only the direct precipitation method of Harris et al. [3] allows for the synthesis of CSH with cement paste relevant properties (Ca/Si ratio > 1.7). However, this batch reactor method appears to yield a non-uniform CSH structure due to changing solution conditions (namely pH).

To synthesize phase pure CSH at constant conditions in large enough quantities that allow for an extensive structural characterization we made use of the segmented flow tubular reactor (SFTR) [4]. In the SFTR reactor (Figure 1) the two reactants are introduced through a Y-mixer which is followed by a T-junction where the inflowing gas separates the solution into small “batch reactors” that allow for better mixing conditions. Through this we could successfully synthesize phase-pure CSH with Ca/Si = 2.0 and elucidate the surface structure of CSH [5].

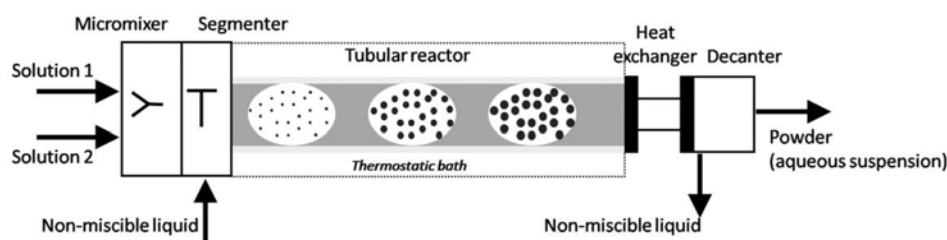


Figure 1. Schematic representation of the SFTR reactor [4].

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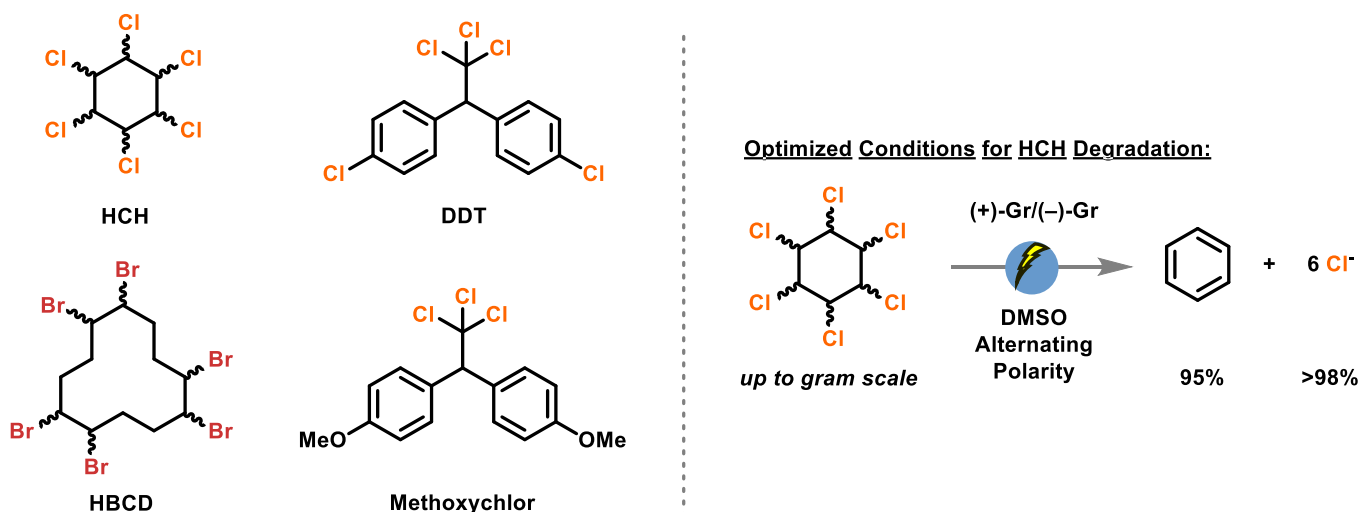
Electrochemical Degradation and Valorization of Persistent Organic Pollutants Enabled by Alternating Polarity

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Persistent Organic Pollutants (POPs) are highly recalcitrant and toxic compounds that pose a profound threat to ecosystems across the world. One of the most notorious representatives of this class of chemicals is hexachlorocyclohexane (HCH) – a known human carcinogen – a specific isomer of which was used as the insecticide Lindane. While the 2001 Stockholm Convention outlawed the manufacture and use of HCH and other POPs, millions of tons of production wastes throughout Europe alone are still left untreated in warehouses and landfills. Significant research has been carried out on various approaches to remediate such POP wastes. However, high cost, non-scalability, and the formation of ecotoxic by-products have hitherto stymied the application of these methods on industrially meaningful scales.^[1-3]

In 2021, the Morandi group disclosed a vicinal dihalide shuttle reaction under electrochemical conditions, with which HCH could be fully dechlorinated.^[4] In the present work, instead of transferring chlorine to another molecule, we sought to sequester it as an innocuous inorganic chloride salt, which is preferable for large-scale application.^[5] This was achieved using cheap graphite electrodes and DMSO as the solvent, which also acts as a sacrificial reductant. A key discovery was that the frequent alternation of electrode polarity suppressed unwanted side reactions and, crucially, maintained the structural integrity of the cathode. We furthermore show that with slight modifications, our conditions are also applicable to the complete dehalogenation of other POPs such as DDT, HBCD, and methoxychlor.



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Industrial continuous-flow access to explosive Grignard reagents and their downstream reactivity.

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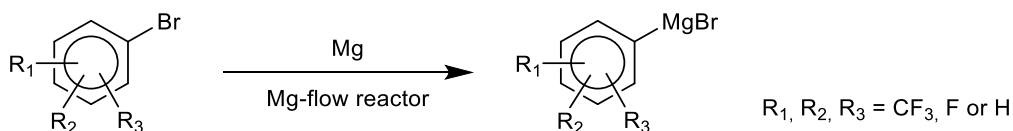
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Flow chemistry is increasingly gaining interest in industrial applications due to its many advantages. It provides accurate control over reaction parameters, enhances process safety, helps in process automation, facilitates the scale-up operations [1]. Flow chemistry is particularly suitable for dealing with exothermic reactions such as those observed in the synthesis of Grignard reagents. These organometallic compounds are used in a wide range of industries like pharmaceuticals, cosmetics, flavors and fragrances, and agro-chemicals [2,3]. Since their discovery in the 1900's their synthesis has relied on batch process in which exothermicity is sometimes delicate to absorb, and several incidents have been reported.

Fluorinated aromatic Grignard reagents, in addition to the hazards typically related to Grignards, suffer from thermal instability, in which thermal run-away and explosion may happen [4-6]. The instability of this Grignard family is not fully understood, it is believed to be due to the potent thermodynamic driving force of MgF_2 generation, which has a lattice energy of about $3000 \text{ kJ}\cdot\text{mol}^{-1}$.

CHEMIUM, a Belgian ChemTech specialized in fine chemistry, is operating a proprietary Flow reactor (*MgFlow*[®] Technology) for the industrial manufacture of Grignard for several years. This technology offers better reaction control, high quality of product, and most importantly, safe operating conditions. Production at the hundreds-of-kilograms scale proceed flawlessly with our equipment, yielding materials of dramatically improved purity compared to batch manufacturing. Given the facilitated scalability of flow chemistry, heat sensitive fluoro Grignard reagents are as of now available at a multi-ton scale from CHEMIUM.



Scheme 1: Example of fluorinated Grignard reagent prepared with the *MgFlow*[®] Technology by Chemium.

The inherent risk associated with this family of compounds (instability and self-degradation) also calls for a direct consumption of the Grignard in a downstream reaction with an electrophile partner, avoiding the need for storage, manipulation and shipment of explosive compounds. Ongoing pilot studies already suggest significantly improved quality profiles in industrially relevant downstream applications.

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Heterogeneous Dissolved Gas Reactions

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Heterogeneous gas-liquid transformations involving 'energy' gases (e.g. H₂, O₂, CO₂) are increasingly shifting towards continuous processing due to the enhanced process safety, and improved mass and heat transfer compared to conventional batch systems [1]. However, scaling continuous gas-liquid flow reactors (e.g. HEL and H-cube reactors) remains challenging due to the complex interplay between mass transfer and hydrodynamics [2]. Consequently, understanding the underlying physical transport phenomena and reaction mechanisms is difficult, as key parameters such as space velocity and mass transfer rates do not scale linearly with reactor geometry [3].

This work, in collaboration with Johnson Matthey, proposes a new technology that separates the gas-liquid dissolution step from the liquid-solid reaction step. This facilitates better mechanistic and kinetic understanding, as gas-liquid limitations are removed, thus reducing the system to a classical packed bed problem. This study evaluates whether this approach enables (i) use of stoichiometric H₂ rather than large excess, (ii) improved selectivity, here in nitrobenzene derivative hydrogenations through precise gas concentration control and (iii) reduced catalyst usage via more efficient transport to the catalytic sites. Our detailed studies identified that hydrogenation kinetics is an interplay between the intrinsic reaction rates and the liquid to solid mass transfer. Over-hydrogenation can be partially controlled through the ratio of H₂/substrate, and residence time, while initial selectivity depends on the balance between catalyst-product decoupling and further hydrogenation of the catalyst-product complex.

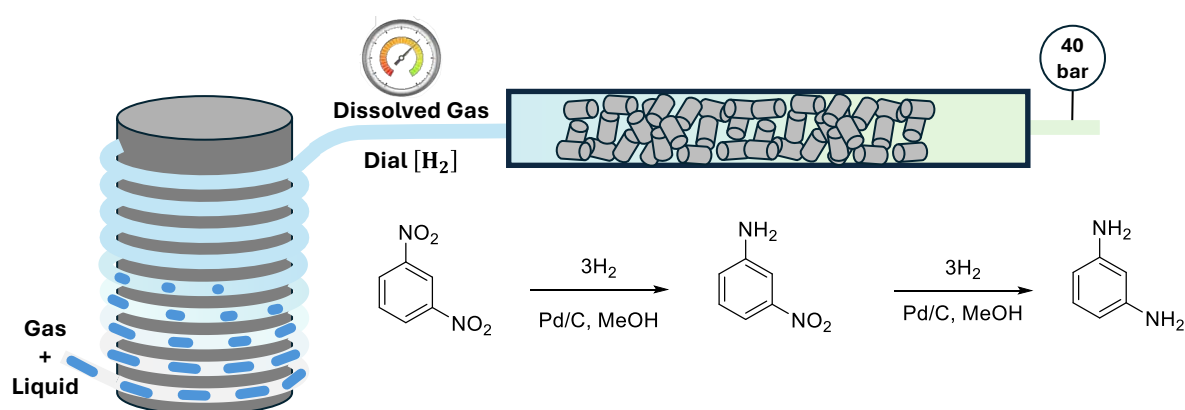


Figure 1. Schematic of a high pressure gas dissolver coupled to a heterogeneous packed bed reactor. A dissolved gas stream evolves from the coil with defined concentrations of hydrogen, before reacting with a model substrate, dinitrobenzene.

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Autonomously Optimised Flow Cascades for Upcycling of Polymer Waste

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Polymers in Liquid Formulations (PLFs) are a class of materials that underpin countless everyday products yet remain unknown to the public. Despite their prevalence, the manufacture and disposal of PLFs remain environmentally unsustainable. With little recovery post-use, an estimated \$125 billion USD of PLFs are lost each year^[1].

This work focuses on the unzipping of RAFT (Reversible Addition–Fragmentation chain Transfer) polymers to liberate discrete monomer units, enabled by the RAFT end-group^[2]. Under continuous-flow conditions, up to 65% of the constituent monomers have been regenerated within a 20-minute residence time.

The regenerated monomers are subsequently utilised in a Heck cross-coupling reaction, enabling access to drug-like molecular scaffolds relevant to contemporary pharmaceutical synthesis. This work lays the groundwork for a cascading flow process in which recovered monomers are directly incorporated into the synthesis of pharmaceutically relevant molecules. Preliminary studies focus on a simplified model substrate to address key chemical and engineering challenges, after which Bayesian optimisation will be applied to enable autonomous control and refinement of reaction conditions.

This strategy investigates the continuous conversion of polymer waste into high-value products, specifically a key fragment of the drug Lusutrombopag, which is used to treat bleeding associated with chronic liver disease.

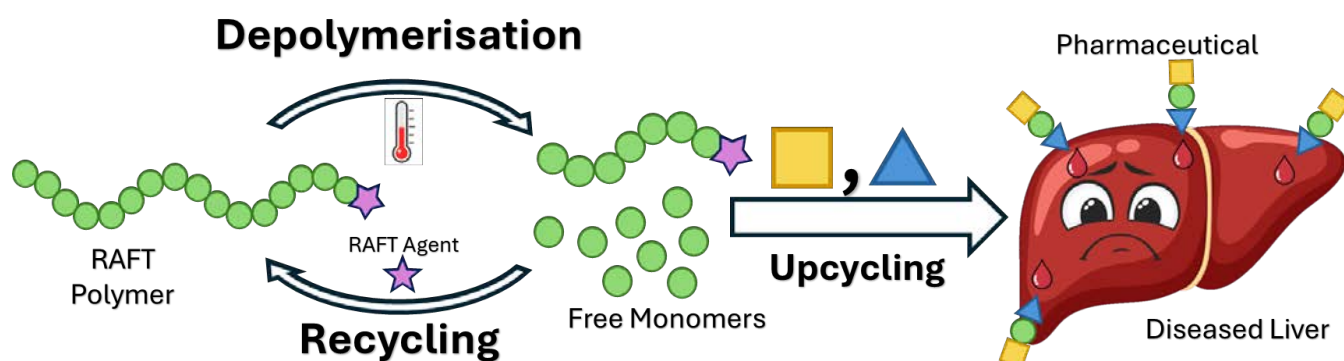


Figure 1. A simplified scheme of the proposed flow cascade

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Biocatalytic Reduction of Six-Membered Ring Heterocyclic Imines in Continuous Flow

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Heterocyclic amines are a key structural motif for the synthesis of pharmaceuticals (e.g., antibiotics) as well as pesticides and flavors. In this regard, imine reductases (IREDs) have recently emerged as a highly selective and sustainable alternative for asymmetric reductive amination reactions. Herein, we have applied six IREDs, two of which were newly identified, in the reduction of heterocyclic imines with either a *N*, *S*, or *O* substitution at C-4. Since IREDs are NADPH-dependent enzymes, a commercially available, supported glucose dehydrogenase was added as a cofactor-regenerating system [1]. IREDs were then immobilized on porous microparticles to further improve the efficiency and sustainability of the system.

The strategic combination of bioinformatic analysis and immobilization screening resulted in immobilized biocatalysts with 95% retained activity. This enabled the integration of the bienzymatic system into a continuous-flow reactor leading to >90% conversion of 50 mM of the *S*-heterocyclic amine, 5-methyl-3,6-dihydro-2*H*-1,4-thiazine, with a residence time of 30 min, and reaching space-time yields up to 14.3 g L⁻¹ h⁻¹. In addition, (*S*)- or (*R*)-stereoselectivity of the biocatalytic reduction of the 1,4-disubstituted heterocyclic imines was achieved by using the newly identified IREDs from *Goodfellowiella coeruleoviolacea* and *Labilithrix luteola*, respectively.

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Spectroscopic Insights into CO₂ Hydrogenation over Metal-Organic Framework Catalysts: From Gas-Phase to Liquid-Assisted Systems

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We investigate copper-zinc modified metal-organic framework catalysts for carbon dioxide hydrogenation to methanol, combining carbon dioxide adsorption in the porous structure with catalytic transformation on Cu(Zn) metallic domains. Batch experiments in a liquid solvent (dioxane) and gas-phase studies show that carbon dioxide and reaction products can be retained within the material under reaction conditions.

Using diffuse reflectance infrared Fourier transform spectroscopy, X-ray absorption spectroscopy, and ¹H nuclear magnetic resonance spectroscopy, we identify methanol-related intermediates and follow the evolution of copper species during reaction. Copper forms dispersed, structurally disordered domains without significant sintering, while the metal-organic framework remains stable.

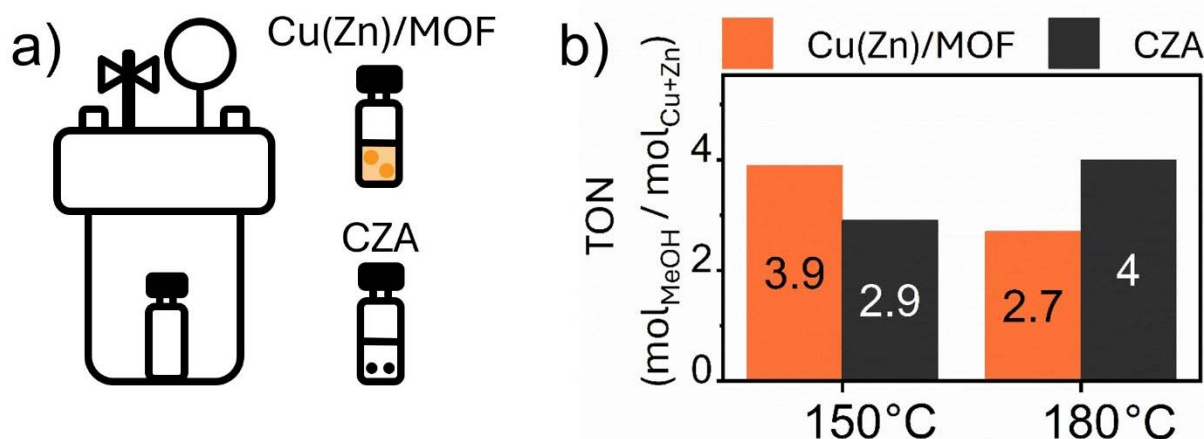


Figure 1. a) Schematic description of the batch autoclave setup for CO₂ hydrogenation; b) Catalytic tests in the batch autoclave of Cu(Zn)/MOF vs. CZA at 150-180 °C, 52 bar, CO₂:H₂ 1:26, 420 mL autoclave, 22 h in 1 mL dioxane, using 40 mg Cu(Zn)/MOF or 5 mg CZA.

The results indicate that adsorption and catalytic functions coexist in the composite, and that the presence of a liquid phase mainly facilitates product removal. This work provides a basis for further studies of such systems under liquid-phase and continuous-flow conditions.

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Pd–Cu Single-Atom Catalysts in Covalent Organic Frameworks for Sonogashira Cross-Coupling Reaction

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Bimetallic single-atom catalysts (SACs) offer opportunities for cooperative reactivity, yet controlling the spatial arrangement of distinct metal sites remains challenging. Here, we report a strategy to construct metallophthalocyanine-based covalent organic frameworks (COFs) with well-defined Pd and Cu single sites, extending our previously reported single-metal system [1] to a bimetallic architecture with spatially separated Pd and Cu sites. The material, Pd–Cu@pyPPC-NaCl, is synthesized via mixed-metal ionothermal polymerization of tetracyanopyrazine in a CuCl₂/ZnCl₂/NaCl melt, incorporating Cu into N₄ phthalocyanine cavities, followed by Pd introduction into the pores by wet impregnation. This approach yields atomically dispersed Pd and Cu sites with high loadings (16.2 wt% Cu, 6.2 wt% Pd).

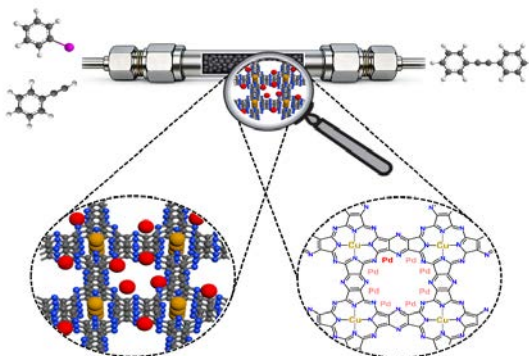


Figure 1. Pd–Cu@pyPPC-NaCl for cooperative flow catalysis

In the Sonogashira–Hagihara coupling, Pd–Cu@pyPPC-NaCl delivers >95% yield in batch and maintains >90% under continuous-flow conditions. Kinetic and time-on-stream studies show enhanced reaction rates and superior performance compared to monometallic analogues. The catalyst remains stable over 18 h with no significant metal leaching, and its activity is readily restored by solvent flushing. These results support a cooperative mechanism in which Pd and Cu activate the aryl halide and alkyne, respectively. This work provides a straightforward route to spatially controlled bimetallic SACs in COFs for efficient and durable catalysis under flow conditions.

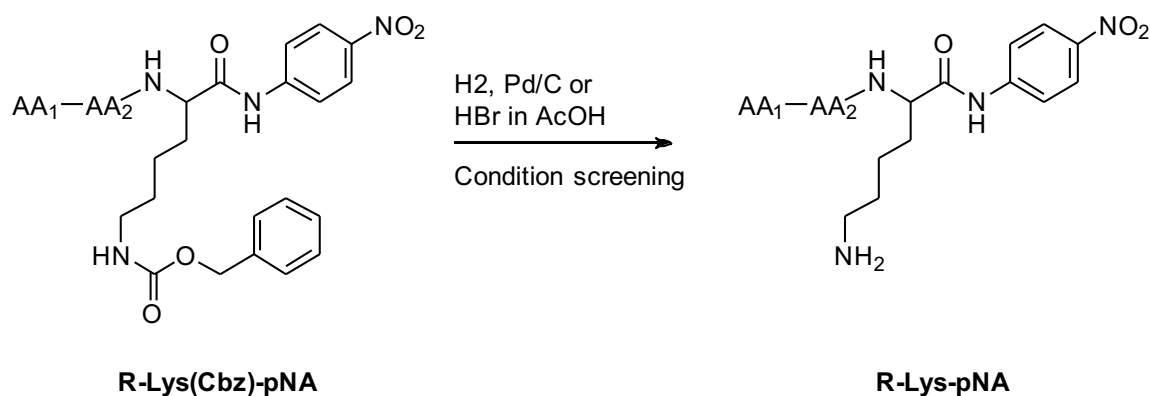
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Condition screening for challenging Cbz-deprotection on a tripeptide in flow chemistry

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Deprotection of Cbz-protected amino acids or peptides are usually carried out by hydrogenation over Pd/C. However, when a p-nitroaniline (pNA) moiety is present at the peptide C-terminus, pNA is also reduced during this procedure, leading to significantly lower yields and the formation of difficult-to-remove impurities. Deprotection by HBr in AcOH is a viable alternative approach, although less popular due to safety concerns. Since pNA is known to cleave under acidic conditions, the reaction conditions must be carefully tuned. Flow chemistry proved beneficial for handling hazardous substances and efficient for condition screening.



Flow-Based Spectroscopic Investigation of Zeolite Acidity

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Surface acidity in solid acids is commonly characterized by adsorption of a basic probe molecule followed by desorption in controlled temperature ramp to quantify the amount of acid sites. Spectroscopic methods can also be applied to identify the nature of the acid sites, i.e. Lewis vs Brønsted acid sites. Infrared (IR) spectroscopy is the most used technique for characterization of acid sites in solid catalysts, where the shift of characteristic vibrational modes of the adsorbed probe molecule with respect to the free molecule is observed. As a fundamental property of solid catalysts, characterization of acidity is well studied in gas phase experiments. However, it is poorly investigated in the liquid phase, where many catalytic reactions take place. There is thus a clear need in the development of acidity determination in liquid environments.

In this work, zeolite acidity is probed in liquid-phase conditions using *in situ* and *operando* spectroscopic techniques. By using pyridine as a probe molecule, the acidity of selected zeolites was studied by Attenuated Total Reflection Infrared (ATR-IR) and online UV-vis spectroscopy in liquid environments. The influence of solvent polarity, pore size, and presence of heteroatoms on probe-zeolite interactions was systematically evaluated, thus revealing key information on the presence and distribution of acid sites. Compared to conventional batch methods, the flow-based approach offers the ability to capture transient phenomena, and allows real-time observation of acid site accessibility, strength, and heterogeneity under flow conditions. The approach can also be used to study reaction mechanisms of acid catalyzed reactions with the aim to selectively block acid sites.

Overall, this methodology establishes a versatile foundation for studying zeolite acidity under realistic liquid-phase conditions, with potential applications in mechanistic studies and process optimization in heterogeneous catalysis.

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Pilot Scale-up Strategies for Biobased Acetal Monomers in High-performance Polymers

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The sustainable transformation of the chemical industry requires scalable processes to replace fossil-derived feedstocks with renewable alternatives that enable defossilization, circularity, and reduced environmental impact. Although many novel biobased molecules have been developed at the laboratory scale, few address the practical challenges of process scale-up and industrial implementation. Scaling these systems is essential to assess their processability, material properties, and economic feasibility under industrially relevant conditions.

Lignocellulosic biomass provides an abundant renewable carbon source, though its heterogeneity complicates efficient valorization. Aldehyde-assisted fractionation (AAF) offers a promising approach by stabilizing reactive intermediates through acetal formation, preserving oxygen functionality, and enhancing biomass utilization efficiency. This strategy has yielded two key monomer platforms: dimethylglyoxylate xylose (DMGX) derived from corncobs [1] and methyl glyoxylate glycerol (MGG) from biodiesel waste. Both enable the production of oxygen-rich polymers with advantages in mechanical strength, biodegradability, and recyclability, making them interesting candidates for sustainable high-performance plastics.

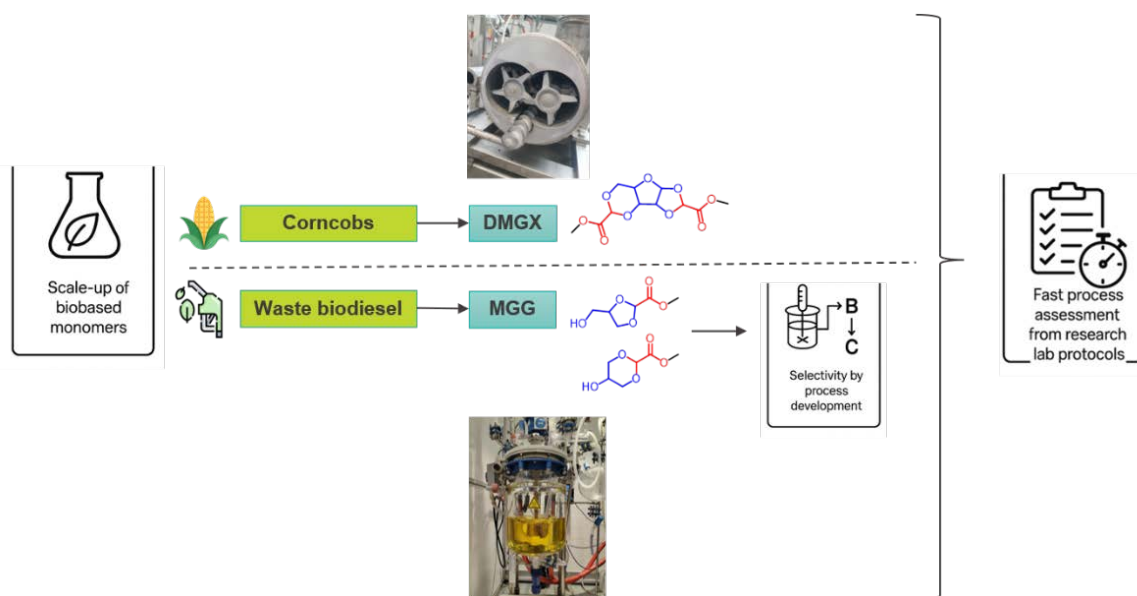


Figure 1. Overview of the pipeline from laboratory to pilot scale based on the DMGX and MGG platform chemicals.

Despite their promise, major barriers remain for scale-up, including the incompatibility of viscous, neat reaction mixtures with conventional batch reactors and the complexity of isomeric mixtures from natural feedstocks. Furthermore, early integration of techno-economic analysis (TEA) is critical to identify cost drivers and process bottlenecks, particularly regarding feedstock purity, solvent recovery, and purification strategies. Here we present our work to develop a scalable process pipeline from laboratory to pilot scale, using DMGX and MGG as case studies. At the HEIA pilot facility in Fribourg, monomers will be produced on a kilogram scale for downstream polymer processing while advancing process-intensification and isomer-selectivity strategies. Collectively, these efforts will deliver robust, scalable protocols for biomass-derived platform chemicals and accelerate their translation into industrially relevant bioplastics.

[1] L. Manker et al., *Nat.Chem.*, **2022**, 14, 976-984