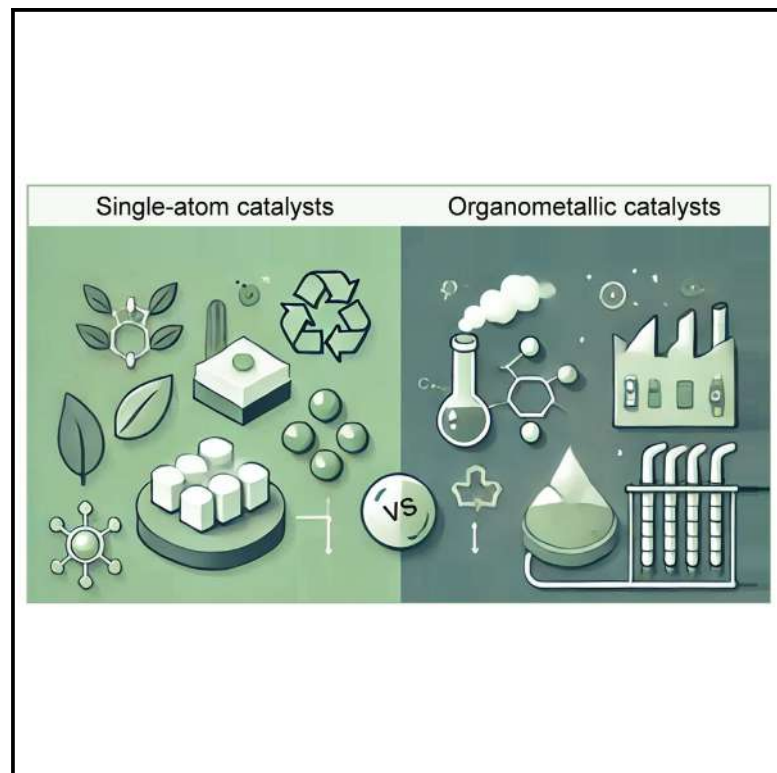


Sustainability assessment of single-atom catalysts in the transition to greener chemical processes

Graphical abstract



Authors

Mark A. Bajada, Maxim Tschulkow, Gianvito Vilé

Correspondence

gianvito.vile@polimi.it

In brief

This study compares the environmental and economic impacts of homogeneous, heterogeneous, and single-atom catalysts for ester synthesis, under thermal, photocatalytic, and electrocatalytic conditions, highlighting that heterogeneous, Ni-based single-atom catalysts provide a more sustainable alternative to traditional catalysts. The findings contribute to advancing sustainable manufacturing in fine chemical production.

Highlights

- SACs offer greener alternatives to traditional systems with lower GHG emissions
- Earth-abundant SACs are preferred, reducing reliance on critical and rare metals
- SACs enhance catalytic efficiency with minimal waste in chemical synthesis
- Photocatalytic methods exploiting SACs offer sustainable, cost-effective solutions

Article

Sustainability assessment of single-atom catalysts in the transition to greener chemical processes

Mark A. Bajada,^{1,4} Maxim Tschulkow,^{2,3,4} and Gianvito Vilé^{1,5,*}

¹Department of Chemistry, Materials, and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

²Department of Engineering Management, University of Antwerp, Prinsstraat 13, 2000 Antwerp, Belgium

³Flanders Make@UAntwerp, 2000 Antwerp, Belgium

⁴These authors contributed equally

⁵Lead contact

*Correspondence: gianvito.vile@polimi.it

<https://doi.org/10.1016/j.crsus.2024.100286>

SCIENCE FOR SOCIETY Sustainability in synthetic chemistry is crucial for reducing environmental impacts and promoting a greener future. Our study provides a comprehensive analysis of how single-atom catalysts minimize greenhouse gas emissions, resource consumption, and waste generation in fine chemical manufacturing. In particular, among the broad spectrum of transition metal catalysts, we demonstrate that catalysts made from earth-abundant materials, such as nickel, outperform those based on rare and expensive metals like palladium or iridium, enabling more sustainable and cost-effective chemical production. These catalysts are also recyclable and operate under moderate conditions, resulting in fewer harmful emissions, reduced energy consumption, and lower costs for everyday products—from medicines and personal care items to food additives. Furthermore, the study highlights that using renewable energy sources to power these processes directly supports global efforts to reduce reliance on fossil fuels. Together, these advancements pave the way for greener manufacturing practices that make essential products more affordable while minimizing ecological impacts, ensuring these benefits are accessible to all.

SUMMARY

Fine chemical manufacturing is vital to the global economy, yet it faces growing pressure to address the environmental challenges inherent in its processes and products. In this study, we conducted a comprehensive analysis of various catalytic methodologies employed in the synthesis of fine chemicals by using the coupling of aryl halides and carboxylic acids to yield esters as a representative case. We compared the greenhouse gas emissions and criticality factors associated with the fabrication of various catalytic entities alongside the economic implications of different synthetic routes to yield the targeted ester compound. Our findings reveal key trends and guiding principles for the eco-design of single-atom catalyzed chemical processes, as well as the challenges and opportunities within this space. We emphasize the critical importance of integrating renewable energy sources for long-term sustainability and advocate for the adoption of heterogeneous catalysts over traditional homogeneous systems.

INTRODUCTION

Chemical manufacturing ranks among the largest industries worldwide, boasting an annual revenue of around €4.3 trillion.¹ This is paired to an analogously high CO₂ emission rate, totaling to approximately 935 million metric tons of CO₂ and accounting for around 2% of global emissions.² The products this industry creates are deeply embedded in the world's largest value chains, affecting the consumer goods, materials production, and pharmaceutical sectors, among various other domains critical to

the global economy. Meanwhile, with the drastic anthropogenically induced environmental changes, the industry itself has been subject to several fundamental shifts, including the requirements for lower-carbon products and better incorporation of circular materials along the supply chain. Catalysis emerges as a key enabling technology for driving innovation and sustainability in chemical synthesis, and, to diversify the chemical synthetic toolbox, it is mandatory to discover and develop new, more efficient catalysts that are (1) activated by green and more renewable forms of energy (such as photons or renewable electricity

rather than fossil-fuel-derived heat) and (2) deemed more viable from a resource-economical perspective (e.g., relying on reduced usage of precious metals or their entire replacement while also facilitating easier recovery and reusability in subsequent synthetic processes).

Catalysts are often classified as homogeneous, which exist in the same phase as the reactants, or heterogeneous, typically in solid form. Homogeneous organometallic complexes, consisting of a metal ion bound to a certain number of ligands, which comprise the primary coordination sphere,³ have long stood as the preferred catalytic systems in fine chemical synthesis, where the stereochemistry and purity of the obtained compounds are critical. These catalysts exhibit remarkable efficiency and selectivity in catalyzing a diverse range of chemical transformations, including cross-coupling reactions,⁴ C–H bond functionalization,⁵ olefin polymerization,⁶ and metathesis,⁷ among others. Rational modulation of the proximal ligand groups provides chemists with a handle to alter the interaction of the metal center with a particular substrate, thus imparting stereo- and site selectivity.⁸ Ligand substituents distal to metal centers, comprising the secondary coordination sphere of the metal, provide complex non-covalent effects, such as electrostatic, hydrophobic, steric, and hydrogen bonding interactions, which further impact catalyst reactivity and selectivity.^{9–12} Despite their effectiveness, homogeneous catalysts complicate post-reaction separation and purification processes (typically necessitating several steps), thereby increasing overall product costs and limiting the recyclability of the catalytic components.¹³ Additionally, the catalyst may be more prone to degradation and leaching, while downstream waste containing spent catalysts may raise significant environmental concerns owing to the prevalent use of heavy metals in the preparation of such organometallic complexes. Some catalysts might have limited solubility in the desired reaction medium or incorporate ligands that require intricate and laborious synthetic protocols.¹⁴

Over the past decades, academic and industrial research endeavors have predominantly concentrated on enhancing the recyclability and separation efficiency of catalysts by transitioning from homogeneous to heterogeneous catalysis. Heterogeneous catalysis, however, does present several challenges that limit its efficiency and application. These challenges include issues with mass transfer limitations and lower selectivity for the target compound compared with their homogeneous counterparts. Another significant limitation is the deactivation of the catalyst over time due to sintering, poisoning, or fouling, which can reduce the catalyst's effectiveness and longevity. Furthermore, the heterogeneous nature of these catalysts can result in non-uniform active sites, contributing to inconsistent catalytic activity.

The recent emergence of “single-atom catalysis” on the catalytic spectrum can be viewed as a bridging concept between conventional homogeneous and heterogeneous systems.^{15,16} Here, individual metal atoms are generally confined by means of a heterogeneous support system with high surface area and abundant anchoring sites to prevent aggregation.¹⁷ In this context, the term “confining” means that the single metal atoms can be stabilized by the local (unsaturated) coordinating environment of the scaffold. These sites facilitate the binding of reaction intermediates, thereby aiding and enhancing the reaction

pathway.¹⁸ Moreover, single-atom catalysts (SACs) represent the ideal paradigm of site isolation, thus approaching the limit of heterogeneous catalysis in terms of economy and optimal use of the metal phase.¹⁹ The application of these alternative and attractive catalysts, particularly activated by light or electricity, has found recent use in synthesizing a variety of fine chemicals.^{15,20} However, to facilitate the investment and integration of such potential and alternative atom- and step-economic catalytic technologies, it is crucial for the scientific community to employ a holistic approach and assess devised catalytic systems designed for a given reaction or classes of reactions. Such evaluations are pivotal for both the academic and industrial communities to gauge their suitability—particularly in terms of sustainability—for broader-scale implementation and intensified applications.

Integrating a comprehensive sustainability analysis into the development and implementation of various catalytic processes is crucial for ensuring long-term viability. This trend aligns with the expanding emphasis on green economy, now permeating various domains across the multidisciplinary sphere of the chemical industry, and is driving a drastic re-evaluation within the fine chemical sector, which has been historically characterized by high environmental impact factors (*E* factors),²¹ as a consequence of the widespread use of organic solvents, stoichiometric reagents in place of catalytic systems, and the limited recyclability of homogeneous catalysts employed. The general directives and guiding principles for improving the sustainability of fine chemical processes therefore include consideration of the mode of catalyst activation (be it thermal, photo, or electro activation), the incorporation of heterogeneous rather than homogeneous catalytic systems to improve recyclability and reusability (particularly, of a single-atom nature to optimize metal usage and number of active catalytic sites), and additionally the substitution of precious metals and expensive ligands with more earth-abundant and cost-effective alternatives.

Despite the importance of such an exercise, comparative life cycle assessment (LCA) studies for SACs and analogous systems are rare.^{22,23} To date, only one article that specifically evaluates the environmental impact using various indicators (chiefly the global warming potential [GWP], human health, ecosystem quality, and resource scarcity) has been published.²⁴ In this article though, the authors focus solely on thermally activated palladium-based single-atom heterogeneous and the corresponding homogeneous catalytic systems for the Sonogashira coupling reaction, without broadening their scope to other catalytic and activation methods to fulfill the same transformation. The gap in the literature for such LCA investigations of catalytic systems partially arises from insufficient information *vis-à-vis* catalytic systems before pilot-scale demonstrations and commercialization, particularly regarding available data for the synthesis and preparation of the catalyst. The complexity of the overall catalytic mixture (especially if several additives or ligating agents are needed, as is often the case with molecular [homogeneous] catalytic systems) also hampers the formulation of a thorough LCA model.^{24–27} Nevertheless, comparing systems that share a similar technology readiness level (TRL) can reveal important trends and information, aiding in the identification of methods that demonstrate the lowest environmental

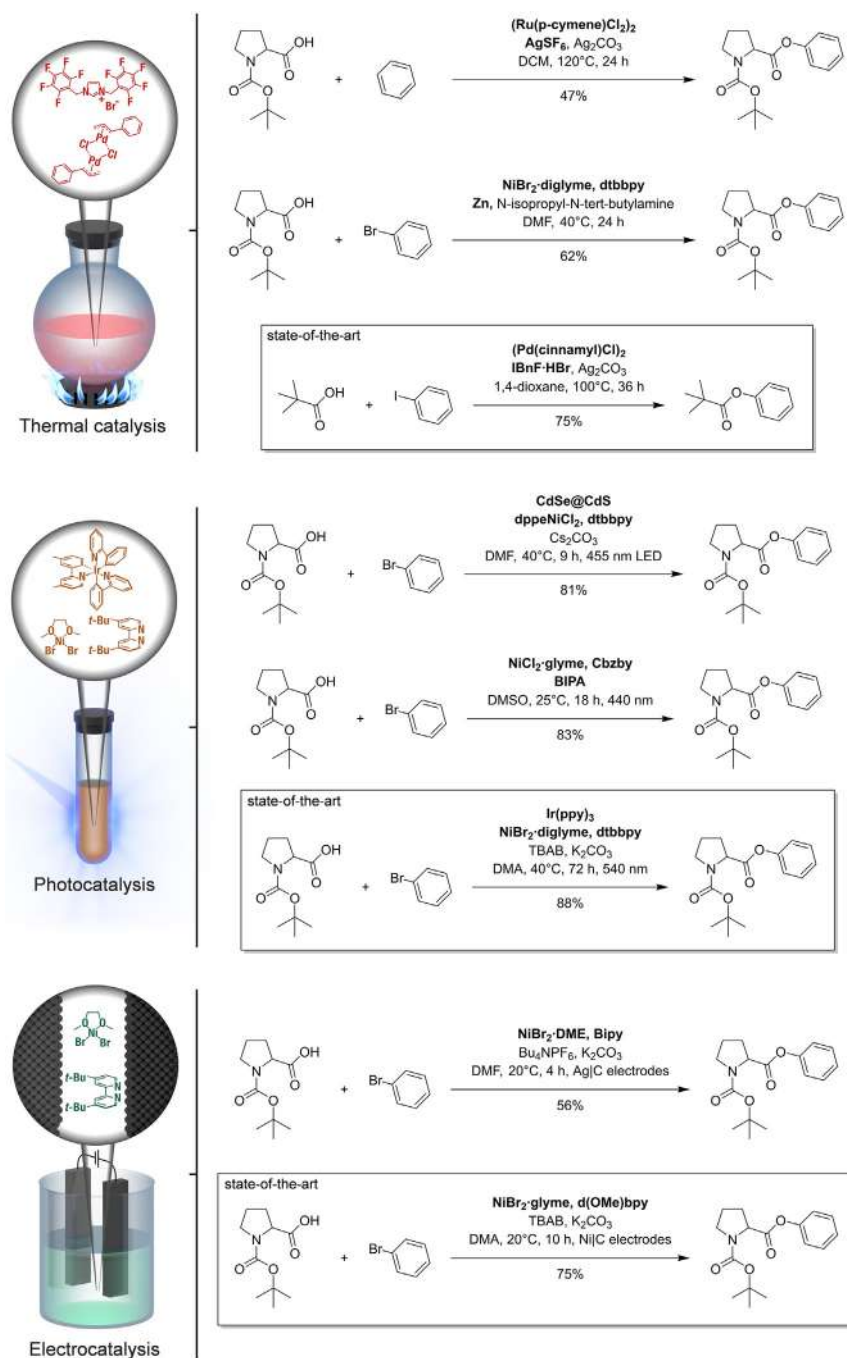


Figure 1. Model C–O coupling reaction, and representative catalytic systems

The figure shows the coupling of carboxylic acids and organohalides using thermal catalysis (top), photocatalytic (middle), and electrocatalytic (bottom) methods. For each method, the state-of-the-art approach and literature precedents are reported.

case studies of comparable TRL were considered, each encompassing a varied homogeneous catalytic system activated by a distinct mode: a conventional thermal pathway and the more emerging photo- and electro-activation routes. Their performance was comparatively investigated and analyzed. The key catalytic features and corresponding chemical structures of such systems are illustrated in Figure 1. For these cases, we evaluated the GWP and the criticality of raw material inputs required for catalyst component synthesis, along with the system costs for producing 1 kg of the C–O-coupled product, in order to better gauge system sustainability and economics for the present (2024) and future (2035) scenarios. After this investigation, we also analyzed the changes in the GWP metric resulting from the transition from a homogeneous photocatalytic to a semi-heterogeneous, and ultimately to a single-atom heterogeneous material.

RESULTS

GHG emissions in homogeneous catalyst production

In order to model the three studies that employ homogeneous catalysts, we used a retrosynthetic technique to break down the respective catalyst components into simpler constituents and building blocks, tracing each to its simplest form, which has corresponding greenhouse gas (GHG)-related information tabulated within commercial databases (see methods and Table S1). The functional unit was set to

be the production of 1 kg of the respective catalytic component per system in the years 2024 and 2035, using a cradle-to-gate approach.

For the year 2024, the synthesis of the photocatalytic complex emits the most GHG emissions, followed by the thermal catalytic system. Examining the breakdown of the corresponding components illustrated in the Sankey diagrams in Figure 2, it is clear that the presence of platinum group metals (PGMs) in the catalyst mixture leads to a significant rise in GHG emissions, with Ir (in the photocatalytic component Ir(ppy)₃) and Pd (in the thermal

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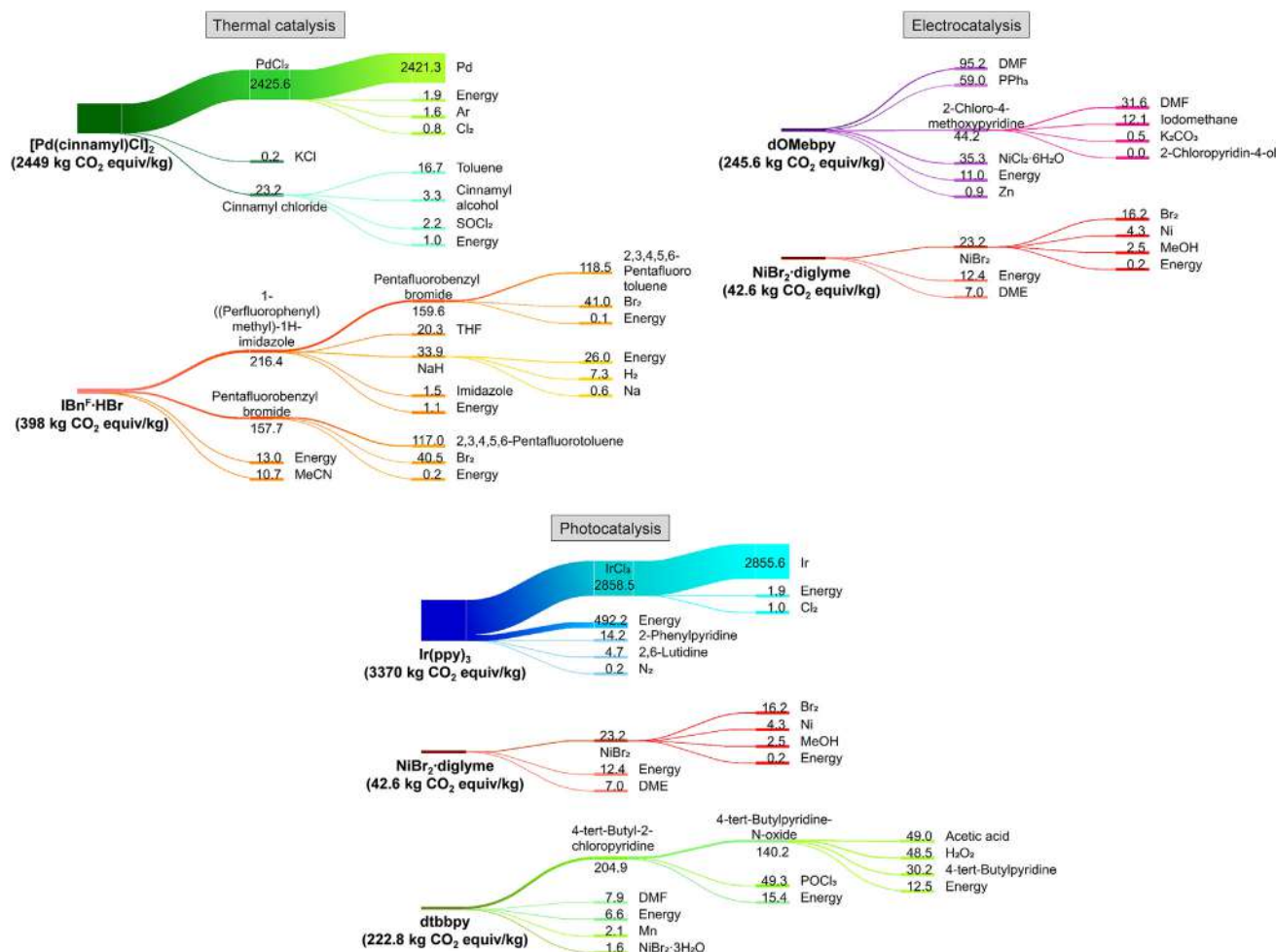


Figure 2. Global warming impact (kg CO₂ equiv/kg catalyst component) of three homogeneous catalytic systems (thermal catalysis, photocatalysis, and electrocatalysis) for the year 2024, using a retrosynthetic approach to analyze each chemical component

catalytic component [Pd(cinnamyl)Cl]₂) accounting for 84.7% and for 98.9% of the complexes' total carbon footprint, respectively. It is of interest to note that the Ir- and Pd-containing complexes exhibit GHG emissions that are at least an order of magnitude higher than those associated with purely organic-based ligands. For Pd and Ir a cumulative energy demand of 72,700 and 216,000 MJ equiv/kg is required, respectively. In both cases, the energy demand is similar for PGMs, with around 40% attributed to mining, 17% to refining (which includes pre-treatment processes like magnetic, gravity, and mechanical separation), and finally 40% to the production stage (involving pyrometallurgical and hydrometallurgical processes to acquire pure products).^{28,29} This highlights a strong correlation between GHG emissions and the energy required to extract and refine precious metals present in the catalytic components.

Projections to the year 2035 provide some key insight into the possible future trends in catalyst production *vis-à-vis* their GWP impact. Mainly, GHG emissions per kg of catalyst component are expected to decrease substantially for all three case studies (Figure S1). While the continued use of PGMs, along with their

associated mining and refining processes, contributes to GHG emissions, the overall impact of catalyst production is expected to be mitigated by the adoption of cleaner energy sources and higher industrial electrification affiliated with materials preparation.^{30,31} Moreover, advancements in both catalyst manufacturing and precious metal recovery techniques are expected to lead to a more efficient use of PGMs. Such transformations are outlined in several international energy policies, where, for instance, the EU's renewable energy policy RES-2035 targets a 100% renewable energy rate by 2035.³² This transition is expected to result in an approximate 92% decrease in GHG emissions from the European electricity mix, while the GHG emissions for the global electricity mix are expected to decrease by 76% based on analogous extrapolations. However, it is important to note that the main GHG-emitting elements in the aforementioned case studies, specifically Pd and Ir, are primarily sourced and processed in Russia and South Africa^{33,34}—regions that rely heavily on natural gas and coal, respectively. While both countries are projected to modernize their energy sectors and increase the share of renewables and other less carbon-intensive

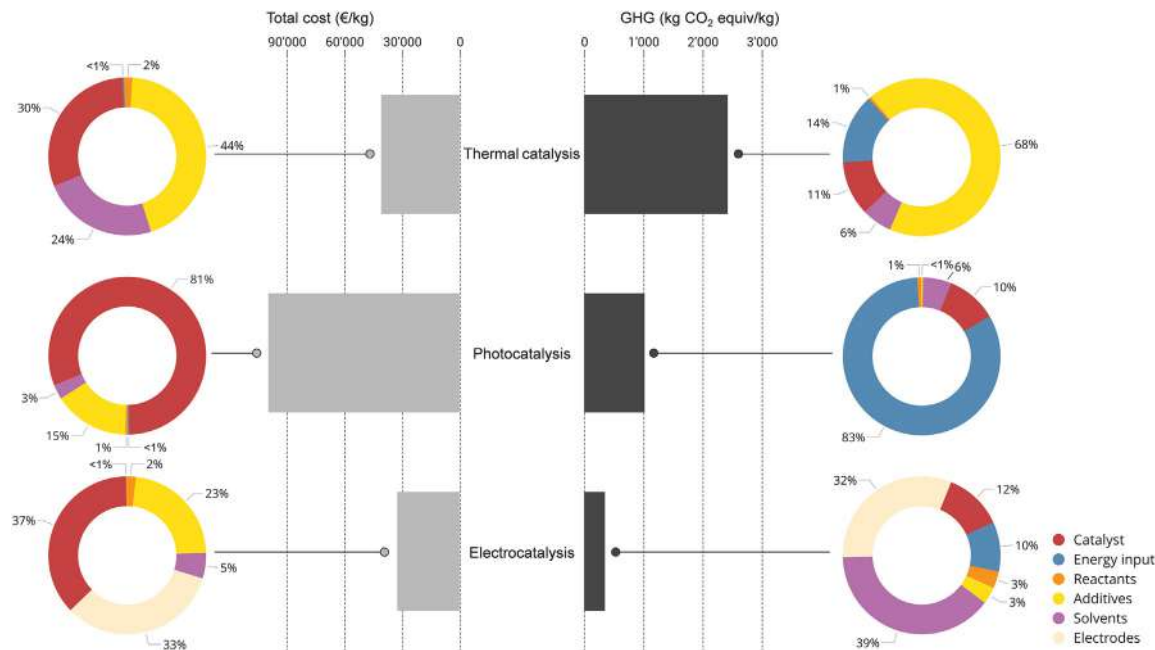


Figure 3. Cost and GHG emissions (along with the respective breakdown) attributed to the formation of the C–O-coupled product for the three homogeneous case studies (2024)

energy sources in their electricity mixes, specific target dates for these transitions have not been explicitly defined. Developing catalyst structures that minimize or eliminate the use of precious metals will remain an important factor to consider in further reducing GHG emissions in fine chemical synthesis over the next decade (Figure S1).

GHG emissions and techno-economic analysis in using homogeneous catalysts for fine chemical synthesis

The homogeneous catalytic systems discussed above are utilized in the C–O coupling transformation, as depicted in Figure 1. Therefore, besides investigating the GHG emissions from the catalytic components in the three studies, we also computed the GHG emissions and conducted a techno-economic assessment of the C–O-coupled product across the various catalytic routes. Figure 3 summarizes the results and provides a more detailed breakdown of both the costs and GHG emissions associated with the three homogeneous catalytic processes. GHG emissions were noted to be highest for the thermal catalytic pathway, approaching 2,500 kg CO₂ equiv/kg of the C–O-coupled product. Upon closer investigation of the GHG emissions breakdown, however, it can be observed that the “additives” segment (representing the need for additional chemical constituents to facilitate the reaction that are not the primary reactants or catalysts) accounts for 68% of the total (Figure 3; Table S8). For example, this is due to the use of Ag₂CO₃ as an excess reagent in the proposed reaction mixture by the authors. The extraction and refinement of silver are emissions-intensive processes that correspondingly impact the overall GWP of the thermal catalytic route. Total GHG emissions progressively decrease for the photo- and electrocatalytic systems, with the latter achieving a reduction in the GHG emissions of almost

85% relative to the thermal system. In the photocatalytic case, the highest contributor to the total GHG emissions is the “energy input” parameter. In this scenario, the authors of the work made use of a generic photoreactor vial and an unoptimized visible light irradiation setup, thus probably consuming more energy than was required to conduct the reaction at the desired rate.³⁵ This highlights the importance of the various impacts associated with the overall catalytic reaction environment. Simply switching to light-driven chemistry will not necessarily lead to a reduction in the GHG emissions of the synthesized product unless the external quantum efficiency (probed by varying reactor geometry, incident wavelength, and visible light irradiance) and the electrical-to-optical power efficiency of the light source are both fine-tuned.^{36,37}

In the referenced electrocatalytic method,³⁸ a Ni-foam cathode and a graphite plate anode are necessary, which together contribute 32% to the total GHG emissions. Literature sources indicate that these materials generally exhibit stable electrode performance over multiple reaction cycles,³⁹ although this stability can be influenced by factors such as physical wear, chemical degradation, or fouling. Nonetheless, assuming a conservative reusability factor of 10, with negligible degradation and thus no efficiency loss, the overall GHG emissions associated with the synthesis of the C–O-coupled product via the electrocatalytic route could potentially be reduced by 28% (tallying to 252 kg CO₂ equiv/kg).

The catalytic components themselves, being homogeneous in nature in all three cases, are difficult and costly to recover and purify and thus are typically utilized in a “single-use” fashion.⁴⁰ This thereby prevents assessing the possible reduction in GHG emissions through catalyst reuse and recycle methods, unlike for the electrode materials described above.

Box 1. Concept of sustainability in synthetic chemistry

Sustainability is difficult to define as a single term, but, in the context of synthetic chemistry, it should encompass the key notion of minimizing the overall carbon footprint of the chemical transformation. This implies that a sustainable chemical process to be devised should incorporate earth-abundant catalytic components, make use of renewable energy inputs, minimize waste streams (*vis-à-vis* catalyst manufacturing and process intensification), and feature reusable or recyclable system components. Additional aspects that support this overarching directive are the importance of system efficiency (i.e., rate of product formation, catalyst lifetime, moderate operating conditions), environmental compatibility (i.e., minimization of toxic or harmful emissions into surrounding environmental compartments), and economic viability (i.e., improvements in resource and system efficiency must outweigh investment and operating costs).

This shift from homogeneous to heterogeneous catalysis is indeed one of the main drivers of sustainability (see Box 1). Heterogeneous catalysts offer significant advantages in terms of recovery and recyclability, while homogeneous catalysts are usually challenging to separate, isolate, and purify from reaction mixtures. This ability to recycle catalysts and reuse them in new reactions helps to reduce both system costs and environmental impact.

Finally, for comparative purposes, the same model reactants (for both the carboxylic acid and the aryl halide) were used in all three cases. Generally, these reactants contributed minimally to the overall GHG emissions, accounting for only 1% to 3% of the total. This is important in the context of substrate scope analysis, particularly because fine chemical industries employ the same reaction protocols to produce variously substituted compounds. It highlights that the environmental impact is predominantly influenced by the catalyst and reaction conditions rather than the reactants themselves. Consequently, when assessing the sustainability of different substrates for a given reaction, the focus should be on factors such as catalyst efficiency, energy consumption, and waste generation. Overall, when considering these three relatively low TRL technologies, the electrocatalytic route appears to produce the lowest GHG emissions per kg of the C–O-coupled product, both from an overall and detailed emissions standpoint. Future scenarios (for 2035) follow the trends previously discussed, primarily due to the increased penetration of renewable energy into the electricity market (Table S9).

From a techno-economic viewpoint, the highest costs for producing 1 kg of the C–O-coupled product are associated with the photocatalytic route, followed by the thermal catalytic and electrocatalytic systems. This primarily stems from the large and proportionally high (81%) cost of the catalyst components required in the photo-assisted reaction protocol. Both the photo and thermal systems incorporate the use of precious metals (Ir and Pd, respectively). Notwithstanding the improved catalyst-to-product ratio in the photo and thermal reactors for the precious metal component (0.027 versus 0.080 kg precious metal per kg product), the higher expense of Ir (161,050 €/kg for Ir versus 32,875 €/kg for Pd, Figures S5 and S6) offsets this advantage, resulting in a greater overall cost per kg of the C–O-coupled product, as illustrated in Figure 3.

Despite the difference in the absolute cost of the electrical energy input required to operate the three reactor types, the fractional share for the energy cost remains just below 1% in all cases. This may appear to be somewhat counterintuitive given the correspondingly larger segments on the GHG emissions donut charts that are attributed to “energy,” particularly for the photocatalytic case (Figure 3). This result, however, stems from the fact that electricity is relatively cheap due to low production costs (e.g., nuclear power) and highly subsidized fossil-based energy. In 2022, the total amount of subsidized fossil-based energy globally reached more than €1 trillion.⁴¹ In the first half of 2023, fossil fuels accounted for approximately 33% of the EU’s, 60% of the United States’, and 70% of China’s electricity generation.⁴² However, the continual decline of fossil fuels and the shift to expand renewable energy sources are anticipated in all three markets. It is important to note that while the increasing share in renewable energy holds the promise of cleaner, potentially cheaper energy in the long term, it is likely to result in an increase in electricity prices in the short to mid-term. Such short- to mid-term increases are primarily caused by investment and infrastructure costs required for the transition (including wind turbines, solar panels, energy storage systems, and extensive upgrades to the grid), carbon pricing, and market instability as the energy market transitions away from fossil fuels, relying more solely on renewables.

Regarding the other sectors affecting the total cost of the C–O-coupled product, the Ag₂CO₃ additive and the solvent in the thermal catalysis route contribute significantly to the overall cost, while reactant costs are fairly low (1%–2%) across all three cases. Finally, it is important to comment on the large increase in price of the critical metals that feature in the case studies herein. Particularly, prices for Pd, Ir, and Ni are expected to rise by 165%, 140%, and 107%, respectively, by 2035. For other materials, assuming an average annual inflation rate of 2%⁴³ over the next decade, we anticipate a 24% increase in the respective price by 2035. Consequently, these projections suggest a conservative overall cost increase for 1 kg of the C–O-coupled product by 2035: of 38% for the thermal catalytic process, 50% for the photocatalytic process, and 27% for the electrocatalytic process.

Criticality

Criticality comprehensively assesses resources by considering socioeconomic, environmental, and geopolitical factors that affect the availability and use of materials.^{44,45} It serves as a risk assessment tool, aiding in anticipating potential challenges in resource supply and demand across industries.⁴⁶ Existing methods, such as the critical raw materials (CRMs) assessments by the European Commission, typically rely on fixed temporal and spatial reference systems,³³ meaning that they provide only static snapshots of the current balance between supply and demand and may overlook potential future changes or geopolitical conflicts that could impact material availability.⁴⁷ Nonetheless, the European Commission’s CRM model sheds important insight on material criticality due to its structured framework for evaluating resource vulnerability and is a relevant tool to consider when conducting an analysis and screening of promising competing catalytic technologies.

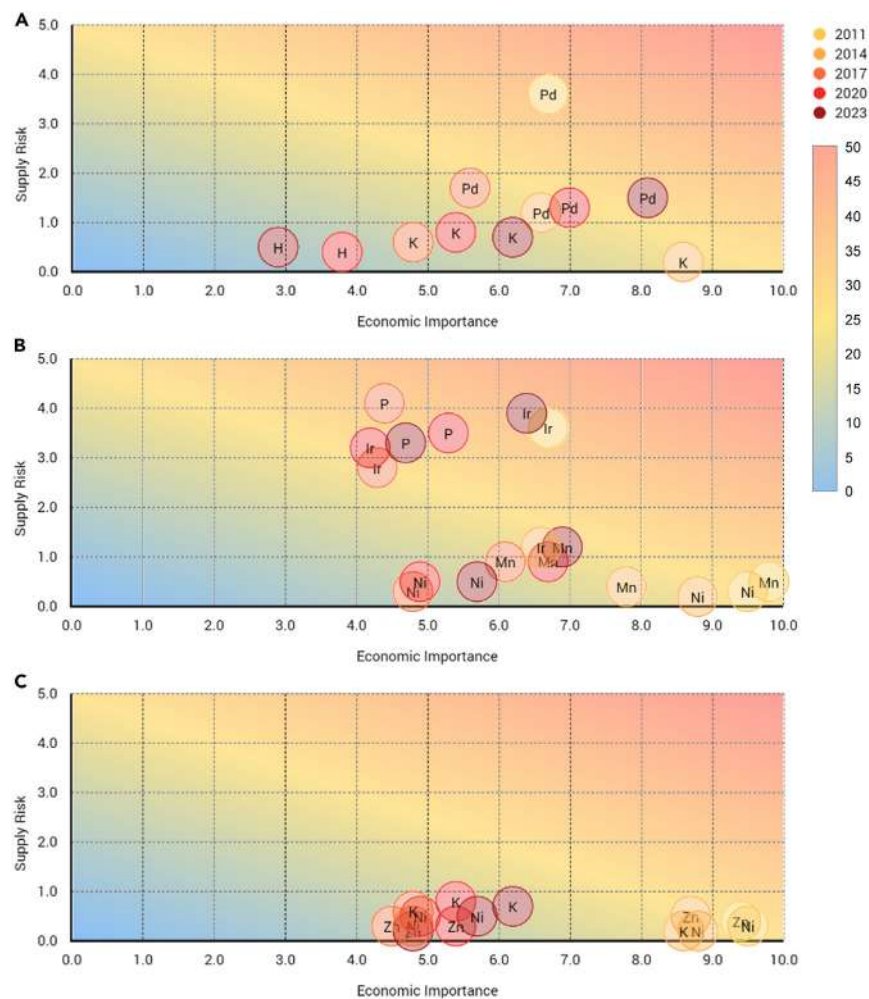


Figure 4. CRM assessment of the three homogeneous studies for 2024

Materials are considered critical if the supply risk ($SR \geq 1.0$) and the economic importance ($EI \geq 2.8$) thresholds are crossed. Ni is classified as a CRM due to its strategic economic importance, although crossing only the EI threshold.

consequence of the multiple variables that affect this function, which typically include economic fluctuations, technological advancements, political instability, and environmental regulations, among others. Nonetheless, to address this challenge, we provide a conservative outlook of how the criticality might develop by 2035. This projection was performed by extrapolating historical trends from data provided by the European Commission.³³ We further contextualize these trends by discussing current insights derived from the literature, offering a comprehensive outlook on the anticipated developments.

For instance, by 2035, criticality for Pd is expected to intensify, with anticipated EI and SR scores of 9.3 and 9.8, respectively. Pd is vital in the automotive catalytic industry (83% of global demand) and the chemical sector (6%). Although Pd demand may decrease due to the rise of electric vehicles⁵¹ this decline could be potentially offset by an increased demand for hybrid cars (incorporating combustion engines) and anticipated growth in the chemical industry.^{51,52} The

The CRM model rates materials based on supply risk (SR) and economic importance (EI) metrics on a 0 to 10 scale, setting the threshold at 1.0 for SR and 2.8 for EI. Materials that exceed both of these thresholds are deemed critical. Specific cases do apply, however; for instance, although the global production of Ni is sufficiently diversified, ensuring low SR, its fundamental importance, particularly in electrification, merits inclusion on the CRM list as a strategic raw material around the world, especially for the EU,³³ United States,⁴⁸ and Chinese economies.⁴⁹ In our investigation, and based on the CRM model, the photocatalytic system is considered to be the most critical, containing three such materials: Ir, Ni, and P. The thermal catalytic and electrocatalytic systems feature one critical material each, Pd and Ni, respectively (Figure 4). In 2023, Pd had an EI value of 8.1 and an SR value of 1.5, while corresponding values for Ir were 6.4 and 3.9. In 2023, global Pd production reached 210 t, with Russia as the leading supplier, contributing 44%, followed by South Africa at 34%. Together, these two countries accounted for 78% of the world's Pd production. In the case of Ir, South Africa dominated the global market in 2022, producing 90% of the total 6.8 t.⁵⁰

As indicated in Figure 4, criticality trends exhibited by industrially relevant materials tend to be quite difficult to predict, as a

estimate for global iridium demand is expected to reach 20 t/year by 2040 (SSP2, Middle of the road scenario),⁵³ compared with a production of 6.8 t/year in 2022,⁵⁰ with the importance of Ir closely linked to emerging green technologies, particularly for H₂ production, and is a key raw ingredient for electrocatalyst manufacturing. Efficiency gains and recyclability of Ir can help reduce supply pressure, but the low recycling material rates of 14%, a share that contributes to the total inputs of new raw materials,²⁸ cast doubt on achieving full recyclability before 2040.⁵⁴ Other sources further argue that Ir demand for a global H₂ economy would exceed the current annual production by a factor of 11 and current reserves by a factor of 1.7.⁵⁵ Hence, the current literature supports our conservative forecast for 2035, estimating a sharp increase in criticality to an EI value of 8.1 by 2026 and an SR value of 10 (finite limit) by 2030. The expected EI value for Ni is projected to reach the upper limit of the criticality matrix (10) by 2030, whereas the SR value is anticipated to increase to 1.5 by 2035. Despite the widespread availability and more scattered global production of Ni (3.7 million t/year in 2024⁵⁶), competition for Ni is strong and will most likely intensify in the near future.⁵⁷ Ni's critical applications in steel production and the automotive and battery industries underscore its

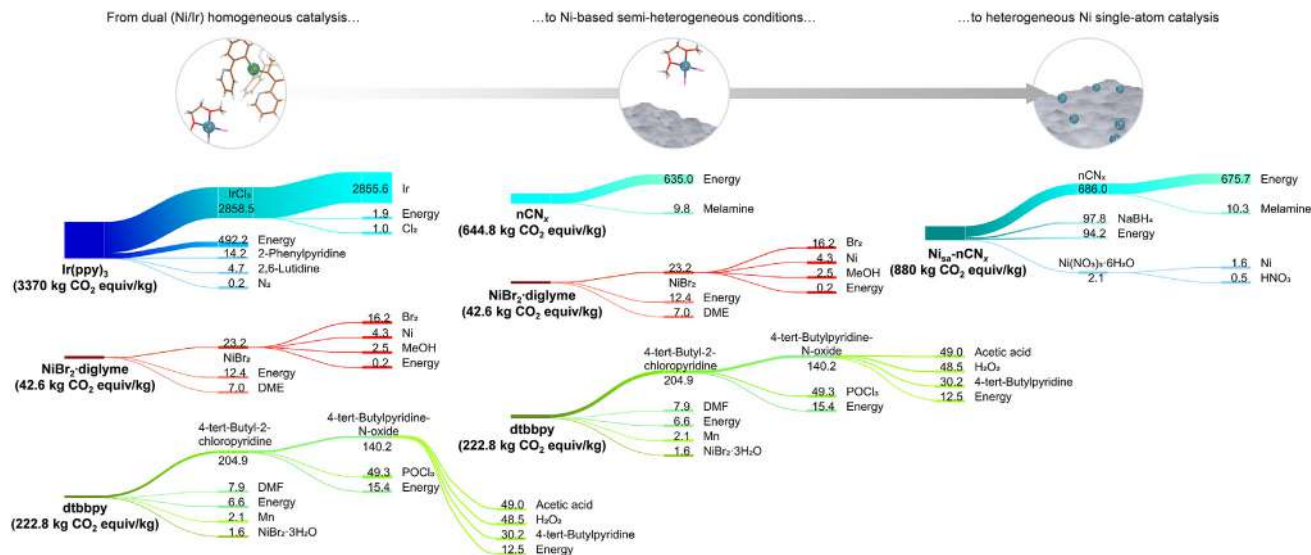


Figure 5. Global warming impact (kg CO₂ equiv/kg catalyst component) for the semi-heterogeneous and heterogeneous SAC systems (2024)
A similar retrosynthetic breakdown was adopted, as applied for the three previously discussed homogeneous studies.

vital role in advancing clean energy and storage solutions.³³ The clean technologies share for total nickel demand is projected to grow over 30% under a business-as-usual scenario and to 60% in a trajectory aligned with the goals of the Paris Agreement by 2040, compared with 10% in 2022.⁵⁸ By that point, the demand from the battery sector is expected to surpass that of stainless steel, becoming the largest consumer of Ni,⁵⁸ supporting our forecast that the SR value will rise from 0.5 in 2023 to 1.5 in 2035. While our EI-value forecast is more conservative, predicting that the EI limit will be reached by 2030, this diverges from broader literature findings. Therefore, based on our analysis and existing literature, we estimate that the EI value will likely range between 6 and 8 by 2035.

GHG emissions for transitioning to heterogeneous catalytic systems

With growing interest in the catalysis sector to design and engineer heterogeneous materials that can match or surpass the efficiency and performance of their homogeneous analogs, we proceeded to investigate the GHG emissions resulting from the transition to partially and fully heterogeneous catalytic systems. For this reason, we looked at photoactivation as a means of catalyst activation and compared the GHG emissions associated with the aforementioned homogeneous case to those of a semi-heterogeneous and finally a fully heterogeneous (single-atom) catalytic system (Figures 1, 2, and 5).

Fully heterogeneous SACs are proving to be highly active for both energy-related and organic synthetic reactions and can be made using a variety of methods, often classified as the “bottom-up” or “top-down” approach. Bottom-up procedures exploit chemical reactions among atoms, ions, and molecules to “construct” a catalyst with atomically isolated sites. Methods such as wet chemistry, atomic layer deposition, chemical vapor deposition, or electrochemical synthesis can be used for this purpose.⁵⁹ Alternatively, in top-down techniques, larger

particles or bulk materials are broken down into single atoms through the application of a high-energy process. Mechanochemical and photochemical methods, laser ablation, or pyrolysis are among the methods that can be used to achieve this.⁶⁰ Applications of SACs range from energy-related electrochemical processes, such as electrocatalytic CO₂ reduction,⁶¹ to reactions more typically utilized in fine chemical synthesis, including thermally driven Suzuki C–C coupling reactions,⁶² metallaphotoredox C–O coupling avenues,⁶³ chemoselective hydrogenations,⁶⁴ and the aziridinations of alkenes,⁶⁵ among numerous others. Readers interested in a more detailed exploration of these topics are encouraged to consult comprehensive reviews specifically dedicated to these subjects.^{20,66}

First considering the semi-heterogeneous case (Figure 1B), where the Ir photocatalyst is essentially substituted for carbon nitride, a metal-free, polymeric photocatalytic material that is easily synthesized from abundant and inexpensive starting reagents.⁶⁷ The Ni complex and corresponding dipyriddy-based ligands are used in both the homogeneous and semi-heterogeneous system and are required for the overall catalytic cycle. The modification of the photocatalyst component alone accounts for a drop in GHG emissions of just over 80% (3,370 kg CO₂ equiv/kg of Ir(ppy)₃ compared with 645 kg CO₂ equiv/kg of the nanosheet-based carbon nitride material [nCN_x]).

The main driver for the decrease in GHG emissions is the removal of the Ir element in the heterogeneous photocatalyst. The energy input is the key contributor to total GHG emissions, with the starting material (melamine) contributing insignificantly (Figure 5). While the disproportionate weighting on energy may raise concerns, it actually signals a more positive outcome—as the energy and hence electricity mix begins to incorporate a greater proportion of renewables, the reduction in GHG emissions associated with the energy input will have a significant impact on the GHG emissions for nCN_x photocatalyst synthesis.

This is clearly illustrated in the prospective Sankey diagram for the semi-heterogeneous system (Figure S2).

Shifting to the fully heterogeneous SAC, in which case the “Ni component” is present as surface-bound single-atom sites within the polymeric carbon nitride framework, rather than a separate homogeneous entity in the system. Our calculations yield a GHG emissions value of 880 kg CO₂ equiv/kg of the Ni single-atom-supported nanosheet carbon nitride material (denoted as Ni_{SA}-nCN_x in the Sankey diagram, Figure 5). The transition from the nCN_x to the Ni_{SA}-nCN_x material results in a 36% increase in the GHG emissions, which is attributed to the additional fabrication steps required to incorporate the Ni single atoms into the carbon nitride scaffold. The additional steps in the fabrication of the nickel SAC feature the use of a reducing agent (NaBH₄ in this case) and the combined energy required to power the reactor—these are the major contributors to the increase in the GHG value versus the bare nCN_x material. A minor contribution originates from the nickel salt precursor (see Figure 5; Table S2). Although this represents a significant increase, the actual total GHG emissions of the semi-heterogeneous system (on a kg-by-kg basis, factoring in all three components) amounts to 910 kg CO₂ equiv/kg, which is even higher than that for the nickel SAC. Furthermore, the inherently heterogeneous nature of the nickel SAC, which has demonstrated sustained catalytic activity across multiple recycling studies,⁶³ suggests additional GHG emissions reduction. By adopting a conservative recycling rate of 10, it is projected that the total GHG emissions could be lowered by approximately an order of magnitude (after accounting for GHG penalties tied to the separation and filtration of the material).

A sensitivity analysis for different Ni loadings of the SAC was performed and benchmarked against the loading value adopted from the literature (7.5 wt % Ni).⁶³ However, both the higher and lower loadings of Ni that were selected (i.e., 0.5, 1.0, and 10 wt %) had a negligible effect on the total GHG emissions (\pm 0.2% of the benchmark value; Table S10). This is related to the relatively low GHG emissions of the Ni salt used in synthesizing the SAC versus the much higher GHG emissions associated with the precious metal salts, such as those of Ir and Pd, used in the fabrication of the respective homogeneous catalytic components (cf. Figure 1). Finally, we assessed the GHG emissions of a similar Ni SAC material that is synthesized in a slightly modified approach to the benchmark case shown in Figure 5. This simplified procedure, referred to as a thermal co-polymerization route, resulted in 608 kg CO₂ equiv/kg of the modified Ni SAC, thus highlighting that a further reduction in emissions is possible through the process of method simplification and optimization (Figure S3).

DISCUSSION

Emerging technologies in the early laboratory/experimental stage, possessing a low TRL (2–4), encounter uncertainty due to limited data availability and scale-up validation.⁶⁸ During this stage, the primary goal is to conduct a proof-of-concept investigation and gather initial data to support the proposed hypothesis. The reaction protocols—including the precise amounts and types of catalysts, solvents, and additives used, as well as energy input—are

typically not optimized. This lack of optimization can lead to unnecessarily high costs and increased GHG emissions from both in-built processes (such as catalyst preparation) and operational procedures (such as C–O product formation via the chosen catalyzed route). Typically, it takes usually 10 to 15 years to progress from this stage to commercialization,^{69,70} although this timeline can vary drastically, depending on the technology and industry sector. As a result, estimating the true economic and environmental impacts upon commercialization is often a non-trivial process, and comparing early-stage technologies with optimized commercial alternatives can be misleading.⁷¹

Simulating the scale-up process itself, from laboratory to commercial scale, is therefore essential to identify economic and environmental outcomes, pinpoint hotspots and bottlenecks,⁷² and guide R&D efforts to address such concerns during the earlier design stages.⁷³ This would transition the emerging technology through multiple iterative learning and optimization routines.⁷⁴ During this process, the system is adjusted to the near-commercial application, which involves additional units (e.g., separation and purification), increasing the absolute costs and GHG emissions. Simultaneously, such metrics typically decrease as a result of process and materials and energy utilization. Economies of scale further decrease costs and GHG emissions by requiring fewer resources per product. Hence, a significant cost reduction of between 40% to 60% can be expected primarily driven by learning effects and economies of scale.⁷⁵ Additional literature findings demonstrate that scaling up from a laboratory to a commercial stage significantly reduces GHG emissions by an estimated 90%, making them potentially competitive with existing commercial solutions.⁷⁶

Reductions in cost (including both capital expenditures, or CAPEX, and operating expenditures, or OPEX) can further be achieved through learning effects by extrapolating trends and commercialization pathways from similar technologies.⁷⁷ Of course, cost savings and minimization of associated GHG emissions do not stop at the commercial breakthrough of the technology but are also the result of further optimization and thorough R&D efforts. In our study, we considered catalytic systems that are based on a similar laboratory/experimental level, assessing and comparing data that is related to the techno-chemical functionality rather than on the optimization of scaling up such processes.

The key outcomes from our overall study are summarized in Figure 6, wherein our investigation highlights the necessity of holistically evaluating catalytic systems of similar TRL while considering environmental, economic, and performance criteria. This approach thus serves as a guiding tool to determine which catalytic systems offer the most sustainable route for further development, process intensification, and commercial scalability. Notably, the analysis indicates that while the homogeneous electrocatalytic system may initially appear to be the most sustainable, after considering the ease of recyclability of the heterogeneous catalyst, the latter single-atom catalytic technology emerges as the more sustainable option. In terms of metals, Ni, despite its classification as a critical material by the EU, United States, and China, proves to be a preferable choice over Pd and Ir, which both suffer from high costs, GHG emissions, and criticality issues. As we advance in comparative

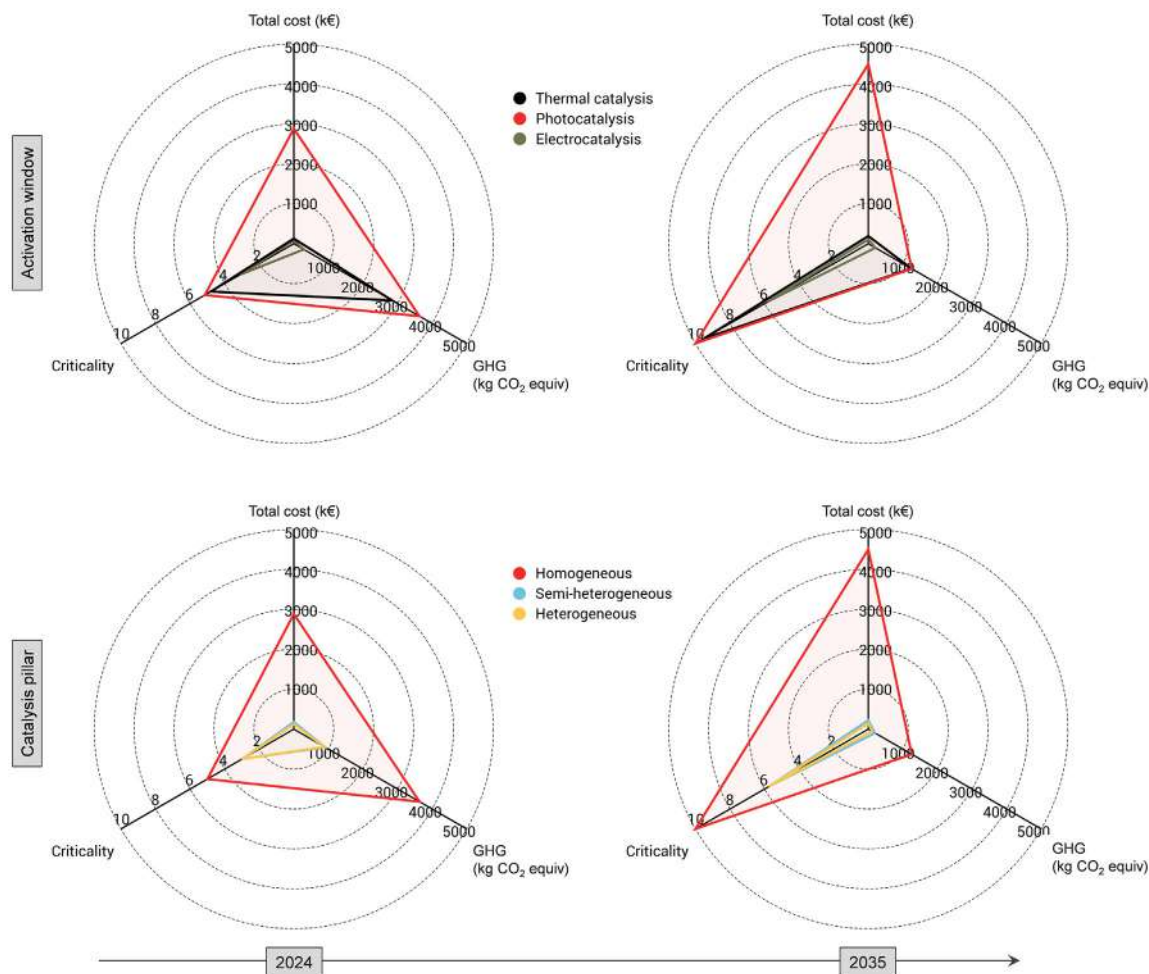


Figure 6. Summarized comparative sustainability assessment, considering costs, GHG emissions, and criticality of strategic raw materials, of the catalytic systems analyzed for the formation of the C–O-coupled products

Total costs and GHG emissions of each catalytic system were done on a kg-by-kg basis of the respective components, while criticality, defined as the equally weighted average of supply risk and economic importance, was determined by the most critical element within the system. On top, we analyze the "activation window," focusing exclusively on homogeneous catalytic methods. The figure illustrates that homogeneous electrocatalysis is the most sustainable approach compared to thermal and photocatalytic methods and will remain so within the next decade. The photocatalytic method is then further elaborated under the "catalysis pillar" in the bottom, assessing the sustainability of this method when homogeneous, semi-heterogeneous, and fully heterogeneous catalysts (exploiting SACs) are used. The figure demonstrates that, through single-atom catalysis design, the photocatalytic route has the potential to be competitive, leading to drastic cost, GHG emission, and criticality reductions.

LCA modeling for catalytic systems within the fine chemicals sector, focus will be placed on better understanding and defining the scaling effects of these nascent technologies more clearly for a more accurate estimation of potential economic and environmental impacts on a more industrially relevant level.

METHODS

LCA

The GHG emissions of the catalytic systems and C–O-coupled products in the present (2024) scenario were assessed using a stoichiometric level 3-based LCA approach, considering molar ratios, heat requirements, and yields.⁷⁸ The GWP (GWP100) metric with a 100-year time horizon, measured in kg CO₂ equiv,

was employed, as outlined in the 6th Intergovernmental Panel on Climate Change (IPCC) assessment report.⁷⁹ We consider a cradle-to-gate approach encompassing emissions associated with the main life cycle stages: material exploitation, acquisition, and production, excluding usage and disposal stages. The functional unit is defined as 1 kg of the targeted components (catalyst, end product) at the end stage of the production process, produced in the European Union. A retrosynthetic analysis was employed to deconstruct the catalyst components into more fundamental building blocks and associated energy requirements. We utilized the Reaxys platform to access comprehensive chemical data and literature references, which supported the validation of the proposed retrosynthetic pathways (see Table S1). Background life cycle inventories were then retrieved

from Ecoinvent 3.9.1 cut-off and Carbon Minds databases. Suitable proxies were adopted in place of any chemicals that were unavailable in either database.

For the prospective LCA targeting 2035, the Python tool *Premise*⁸⁰ was used for prospective LCA, specifically to project the Ecoinvent 3.9.1 database into the future. It incorporates scenarios from the integrated assessment model “REMIND”⁸¹ to modify the Ecoinvent database. This adaptation reflects projected energy policy trajectories, includes emerging technologies, and adjusts market shares and technology efficiencies. The Impact Assessment Methodologies (IAMs) use shared socioeconomic pathways (SSPs) and representative concentration pathways (RCPs) to create detailed scenarios that facilitate our understanding of potential future states of the world under different assumptions about GHG emissions and socioeconomic conditions.⁸² In the opted IAM for the prospective LCA, we considered the “middle of the road” SSP.⁸³

Techno-economic assessment

A techno-economic assessment on the three homogeneous catalytic systems (thermal, photo, and electro activation; TRL 2–4) was conducted to compare the production cost of 1 kg of the C–O-coupled product. This first involved a market study in order to understand the techno-chemical processes of the individual systems and their cost structure. Second, the mass and energy inputs of the processes were defined (see [Table S11](#)) in accordance with the cited literature, in which the C–O-coupled product was synthesized in mg amounts on a low TRL setup (laboratory stage, TRL 2–3).^{35,38,84} The numbers were scaled to 1 kg of the product, mimicking a fine chemical production scale. For the pricing of catalysts, we utilized commercial rates available from Merck’s marketplace. The costs for $\text{IBN}^{\text{F}}\text{-HBr}$ and $\text{Ni}_{\text{SA-nCN}_x}$ were the only two that were not defined. In these instances, the aforementioned retrosynthetic analysis was also used to gauge an estimate of the production cost for 1 kg of the compound or material in question. OPEX, such as reactants, solvents, catalysts, and additives, were considered ([Tables S13](#) and [S14](#)), while energy requirements were estimated based on the retrosynthetic analysis ([Table S1](#)). Given that equipment in laboratory settings is typically shared across various experiments and multiple iterations, accurately assigning costs to any single project is challenging. Consequently, to facilitate a fair economic comparison, CAPEX on equipment was not included in this cost model. To project the future costs of critical materials and electricity, an autoregressive analysis was conducted ([Equation S1](#)) using historical monthly price data from 2015 to 2024 as inputs (see [Figures S4–S8](#)). Particularly for electricity, the price shock caused by the Ukraine war (2022–2024) was omitted. For the remaining inputs, an average inflation rate of 2% over 11 years was considered.⁴³

Energy consumption

To determine the energy consumption during the retrosynthetic analysis, we employed thermodynamic data from the literature to calculate the necessary heat requirements. We applied various methods for calculating heat and/or electricity consumption, tailored to the specific needs of each synthetic stage (see [supplemental information](#) for further details). These methods included the use of a flow-based tubular furnace and a muffle

furnace (particularly relevant for gas-solid interactions that need to be conducted under a specific gaseous atmosphere or air, respectively) and a semi-sealed vessel on a heated surface for liquid-based reactions. Electrical power was considered for electrochemical processes.

Criticality assessment

Analyzing the criticality of essential raw materials in the catalytic systems studied is essential for predicting future challenges related to cost and availability. We utilized the European Commission’s CRM assessments, which measure SRs and EI on a scale from 0 to 10, setting criticality thresholds at an $\text{SR} \geq 1.0$ and an $\text{EI} \geq 2.8$.³³ To forecast how these criticality levels might evolve by 2035, we conducted a regression analysis using historical data from 2011 to 2023, sourced from the European Commission. Additionally, a comprehensive literature review was performed to validate our projections.

RESOURCE AVAILABILITY

Lead contact

Requests for further information and resources should be directed to and will be fulfilled by the lead contact, Prof. Dr. Gianvito Vilé (gianvito.vile@polimi.it).

Materials availability

This study did not generate new unique reagents.

Data and code availability

All the data supporting the findings of this study are available within the article and its [supplemental information](#) and also from the corresponding author upon reasonable request. This paper does not report original code.

ACKNOWLEDGMENTS

This work was supported by the European Commission’s Horizon Europe research and innovation actions, with M.A.B. receiving funding through the SusPharma project (grant agreement no. 101057430) and M.T. receiving funding through the ALIGNED project (grant agreement no. 101059430). G.V. thanks the European Research Council (SAC_2.0, grant agreement no. 101075832) for funding. The authors extend their acknowledgments to Dr. Philippe Nimmegeers and Prof. Dr. Steven Van Passel (University of Antwerp) for initial discussions.

AUTHOR CONTRIBUTIONS

Conceptualization, M.A.B. and G.V.; methodology, M.A.B. and M.T.; formal analysis, M.A.B. and M.T.; investigation, M.A.B. and M.T.; resources, M.T.; writing – original draft, M.A.B., M.T., and G.V.; writing – review & editing, M.A.B., M.T., and G.V.; visualization, M.T. and G.V.; funding acquisition, G.V.; supervision, G.V.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.crsus.2024.100286>.

Received: August 1, 2024

Revised: October 20, 2024

Accepted: November 21, 2024

Published: December 27, 2024

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