Technology Readiness and Emerging Prospects of Coupled Catalytic Reactions for Sustainable Chemical Value Chains

Review Article

Author(s):
Preikschas, Phil (iD); Pérez-Ramírez, Javier

Technology Readiness and Emerging Prospects of Coupled Catalytic Reactions for Sustainable Chemical Value Chains

Phil Preikschas*[a] and Javier Pérez-Ramírez*[a]

Transitioning from both the direct and indirect use of fossil fuels to the renewable and sustainable resources of the near future demands a focal shift in catalysis research – from investigating catalytic reactions in isolation to developing coupled reactions for modern chemical value chains. In this Perspective, we discuss the status and emerging prospects of coupled catalytic reactions across various scales and provide key examples. Besides being a sustainable and essential alternative to current fossil-based processes, the coupling of catalytic reactions offers novel and scalable pathways to value-added chemicals. By emphasizing the specific requirements and challenges arising from coupled reactions, we aim to identify and underscore research needs that are critical to expedite their development and to fully unlock their potential for chemical and fuel production.

Introduction

Achieving climate neutrality demands a substantial transformation of the linear value chains of the chemical industry into an energy- and resource-efficient circular economy.[1–3] Unlike other energy-intensive sectors, emissions from the chemical industry are perceived as difficult to abate.[4] This reliance stems not only from the indirect use of fossil fuels for auxiliary energy but also from their direct use as a raw material. With over 96% of all manufactured goods being affected by chemistry,[4] around 8% of global greenhouse gas emissions are attributed to the chemical industry due to energy- and CO_2-intensive production processes.[5]

The current manufacture of over 30,000 chemical products relies on just ten fossil-based basic chemicals,[6] resulting in a tree-like structure of combined chemical processes (Figure 1). For an efficient use of resources and energy, these processes are operated in a highly integrated and interconnected manner, often at so-called Verbund sites.[7] In addition to improved efficiency and reduced environmental impact, this approach enables the instantaneous conversion of intermediates without further storage or transport to another chemical site. This is particularly important since the storage of many intermediates is energy intensive and, overall, challenging to maintain, as seen in the case of hydrogen, ethylene, or carbon monoxide.[8–12] Coupled catalytic reactions (CCRs; a list of acronyms and abbreviations is provided at the end of this Perspective) are thereby of utmost importance, especially in the context of a more decentralized energy and raw material landscape of the future chemical industry.[3] Moreover, since many intermediates are used directly at the point of production and consequently are not traded openly,[12] their market prices may not reflect their actual value, hindering an accurate techno-economic analysis (TEA). Thus, considering CCRs already at the catalyst development stage is crucial to identify the most valuable product.

Replacing fossil resources with renewable feedstocks cannot be realized solely by substituting existing processes with a sustainable alternative, as it requires the integration of CCRs throughout the entire value chain. For instance, the sustainable production of methanol, one of the most important bulk chemicals with a global production capacity of more than 110 $Mt\,a^{-1}$,[13] necessitates the replacement of both the hydrogen from steam methane reforming (SMR) and the fossil-based CO feedstock with ideally electrified processes.[14–17] Hence, the sustainable production of chemicals adds at least one additional catalytic reaction to existing value chains.

Multiple entry points exist and are under consideration to funnel renewable carbon resources into the existing structure of chemical production (Figure 1). Among these, synthesis gas (CO+H_2) and methane stand out due to advanced CO_2 utilization technologies for their production,[3] indicated by relatively high technology readiness levels (TRL) of 6–8 (Figure 2),[18,19] and their high demand due to various downstream processes, such as methanol,[13] higher alcohols,[20] or hydrocarbon production[21] (Figure 1). Although less developed (TRL < 6), methanol and ethylene production (150 $Mt\,a^{-1}$)[22] from CO_2 need to be highlighted, being key intermediates for several upgrading products and are directly accessible through catalytic hydrogenation or electrolysis.[23] Other considered entry points are only accessible by processes with high TRLs when combined with at least one other catalytic reaction (Figure 1), such as olefins and aromatics through reverse water-gas shift reaction (rWGS) with subsequent CO hydrogenation or CO_2 to methanol combined with methanol-to-olefins (MTO) or methanol-to-aromatics (MTA) processes.[24] It is noteworthy that no direct

[a] Dr. P. Preikschas, Prof. J. Pérez-Ramírez
Institute of Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich,
Vladimir-Prelog-Weg 1, 8093 Zurich (Switzerland)
E-mail: ppreikschas@ethz.ch
jpr@chem.ethz.ch

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routes based on technologies with high TRLs exist to produce olefine or aromatics from renewables (Figure 2 and Table 1).[19,25,26,39]

While numerous sustainable pathways involving two or more catalytic reactions are proposed, their coupling has only rarely been investigated and, in most cases, has not yet been demonstrated at relevant production scales, reflected in low TRLs of the combined chemical reactions.[40] One reason for the limited technology readiness is the research focus on catalytic reactions in isolation without considering the envisaged integration into a true chemical value chain. Particularly during catalyst development, the requirements of the integrated process are often neglected, resulting in performance assessment under reaction conditions optimized for the isolated and substantially different from those needed for the coupled reaction.

Nevertheless, the shift from fossil-based to renewable energy (heat, electricity) and raw materials (H_2O, N_2, CO_2, biogas, biomass, plastic waste) not only increases the complexity of chemical value chains but also presents unique challenges in the realm of process operation with implications for catalyst development. Future catalysts must be operational under fluctuating conditions and exhibit high compatibility with respect to conditions, reaction rates, and lifetime.

This Perspective examines the current status and future prospects of coupled reactions in catalysis research across various scales. By doing so, we will concentrate on the challenges and opportunities that emerge from incorporating sustainable alternatives into the chemical industry and highlight how novel pathways can be explored through an integration-oriented research approach. Lastly, we provide specific research needs to advance the development of CCRs, especially across different fields of catalysis, with emphasis on catalyst design and development.

Modes of Catalytic Coupling

As shown in Figure 1, sustainable and circular chemical value chains necessitate the coupling of at least two catalytic reactions. Typically, an entry point to the existing tree-like structure of the chemical industry is gained through an efficient reaction for small molecule activation (H_2O, N_2, CO_2, or methane).

This approach is strategically sound as it utilizes well-established chemical processes, which are now repurposed as upgrading components in sustainable production of sought-after chemicals (Figure 3a), such as formaldehyde,[28] urea,[29] ethylene oxide,[30] vinyl chloride,[31] or acetic acid[32] (Table 1). Especially in the power-to-x (PtX) concept, a sustainable technology for producing CO, such as rWGS or solid oxide electrolysis (SOE), is proposed to be combined with an effective downstream process, like Fischer-Tropsch synthesis (FTS) or higher alcohol synthesis (HAS).[21,27,41]

CCRs unfold across multiple scales, encompassing (i) the synergistic combination of processes, (ii) coupled catalytic materials, and (iii) the distinct interplay of separated active sites (Figure 4). Despite the apparent advantages of CCRs, various requirements must be considered, which are highly dependent on the individual length and time scales (Figure 3b). The main benefits of coupled reactions at all scales include the direct conversion of reaction intermediates without isolation, the accessibility of novel reaction pathways, and potentially lower purification and separation costs due to improved product selectivities. Moreover, the unique advantage at the process scale lies in the ability to integrate technologies across different fields, such as the inter-catalytic coupling of electrocatalysis with thermocatalysis or biocatalysis.

The most significant differences in the requirements specific to CCRs arise in catalyst design and development. At the reactor and catalyst scale, all materials or active sites must be functional under the same conditions (feed composition, temperature, pressure, potential, chemical environment), which might result in compromised productivity compared to isolated reactions. These requirements substantially complicate the identification of reactions suitable for an effective coupling, as the potential combinations are constrained by the intrinsic characteristics of the reactions of interest. At the same time, the combination of distinct catalytic systems for CCRs may give rise to previously unknown dynamic phenomena.

Coupling of Processes

The coupling of two or more thermocatalytic reactions is the most common form of intra-catalytic coupling at the process scale (Figure 4a) and already serves as the basis for highly integrated production routes in the contemporary chemical industry.[42,43] Established over 150 years ago with the first
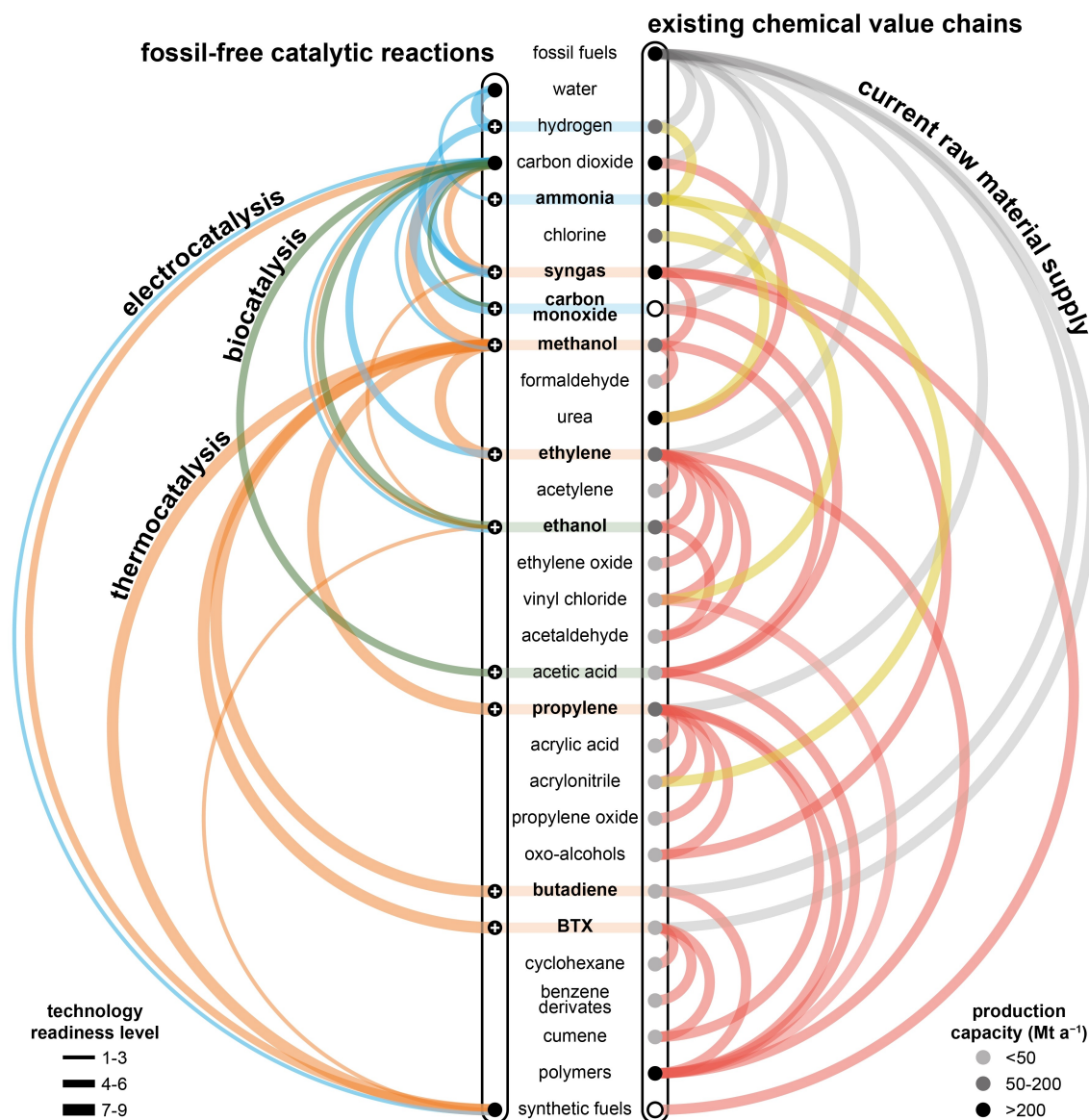
Phil Preikschas pursued his Ph.D. studies on heterogeneous catalysis, focusing on nano-structured synthesis and operando spectroscopy, at BasCat – UniCat BASF JointLab (Berlin). He then joined the group led by Prof. Javier Pérez-Ramírez at ETH Zurich as a postdoctoral researcher. His research focuses on the formation of valuable platform chemicals and fuels from renewable carbon feedstocks, with a particular emphasis on electro-catalytic CO_2 reduction.

Prof. Javier Pérez-Ramírez is Full Professor of Catalysis Engineering at ETH Zurich since 2010. His research pursues the nanoscale design of catalytic materials enabling the transition towards sustainable chemical and energy production. He directs NCCR Catalysis (www.nccr-catalysis.ch), a Swiss Centre of Competence in Research devoted to the development of carbon-neutral chemicals across the whole value chain through catalytic processes.

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Figure 1. The transition from fossil-based (gray) to sustainable raw materials through the coupling of electro- (blue), thermo- (orange), and biocatalytic (green) reactions to established inorganic (yellow) and organic (red) chemical value chains. Prospective entry points into existing chemical value chains are denoted with a plus sign (+). Technology readiness levels (TRLs) of fossil-free reactions are represented by different line widths, and production capacities of established processes by different dot shades. Hollow symbols denote unknown production capacities. BTX abbreviates benzene, toluene, and xylenes.
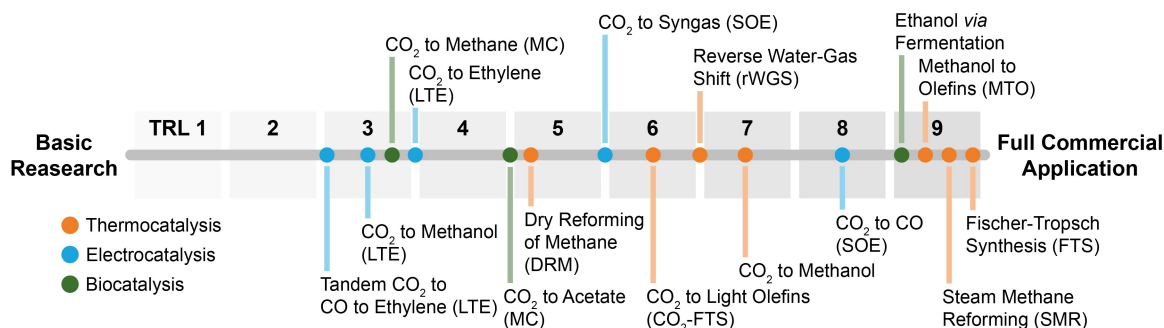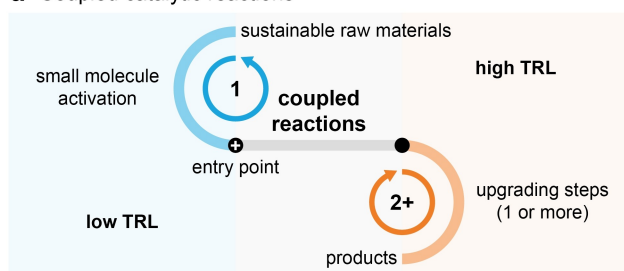

Figure 2. Technology readiness levels (TRL) of prospective thermo-, electro-, and biocatalytic coupling technologies. LTE, SOE, and MC abbreviate low-temperature electrolysis, solid oxide electrolysis, and microbial conversion, respectively.

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Table 1. Key catalytic reactions of current and future chemical value chains.

Product	Reaction or Process	TRL[a]	Production Capacity (Mt a^{-1})	Ref.[b]
Thermocatalysis				
hydrogen	cracking of crude oil, natural gas, or coal	9	69	9
ammonia	Haber-Bosch process	9	180	10
methane	CO_2 hydrogenation	7	–	17
synthesis gas	cracking of crude oil, natural gas, or coal	9	598	27
	reverse water-gas shift (rWGS)	6–7	–	17
	dry reforming of methane	5–6	–	17
carbon monoxide	cracking of crude oil, natural gas, or coal	9	–	-
methanol	CO hydrogenation	9	75	13
	CO_2 hydrogenation	7–8	–	17
formaldehyde	(oxidative) dehydrogenation or oxidation of methanol	9	46	28
	CO_2 hydrogenation	3		17
urea	Bosch-Meiser process	9	226	29
ethylene	thermal cracking	9	150	22
	methanol-to-olefins	9	–	-
	oxidative dehydrogenation	6–7	–	25
	CO_2 hydrogenation	5–7	–	25
acetylene	partial combustion of natural gas or calcium carbide conversion	9	0.7	6
ethanol	CO_2 hydrogenation	1–2	–	17
ethylene oxide	ethylene epoxidation	9	32	30
vinyl chloride	ethylene (oxo)chlorination	9	40	31
acetaldehyde	ethylene oxidation, ethanol dehydrogenation	9	3	6
acetic acid	methanol carbonylation, methanol oxidation	9	17	32
	synthesis from CH_4 and CO_2	3	–	17
propylene	thermal cracking, propane dehydrogenation	9	100	26
acrylic acid	propylene oxidation	9	4	6
	synthesis from ethylene and CO_2	3	–	17
acrylonitrile	propylene ammoxidation	9	6	6
propylene oxide	propylene oxidation	9	7	6
oxo-alcohols	hydroformylation	9	6	6
butadiene	thermal cracking	9	11	6
BTX	catalytic reforming or thermal cracking	9	36	6
MTBE[c]	etherification of methanol and isobutene	9	20	6
Electrocatalysis				
methanol	low-temperature CO_2 electrolysis	3	–	23
syngas	solid oxide CO_2 electrolysis	5–6	–	23
carbon monoxide	solid oxide CO_2 electrolysis	8	–	23
	low-temperature CO_2 electrolysis	5–6	–	23
formic acid	low-temperature CO_2 electrolysis	3–5	–	23
ethylene	low-temperature CO_2 electrolysis	3–4	–	23
ethanol	low-temperature CO_2 electrolysis	1–2	–	17
Biocatalysis/Biological Approaches				
methane	microbial conversion of CO_2	3–4	–	17
carbon monoxide	microbial conversion of CO_2	3	–	33

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Table 1. continued				
Product	Reaction or Process	TRL[a]	Production Capacity (Mt a^{-1})	Ref.[b]
ethanol	sugar fermentation	9	86	34
	syngas fermentation	9	–	35
	microbial conversion of CO_2	6	–	36
acetate	microbial conversion of CO_2	4–5	–	37
acrylamide	acrylonitrile hydration	9	0.2	6
lactic acid	carbohydrates fermentation	9	0.04	38
[a] TRL: technology readiness level. [b] Reference for either TRL or production capacity if TRL = 9. [c] MTBE: methyl *tert*-butyl ether.				

Figure 3. (a) Sustainable chemical value chains through the coupling of catalytic reactions across different length scales. (b) Benefits and drawbacks of coupled processes, catalytic materials, and active sites.
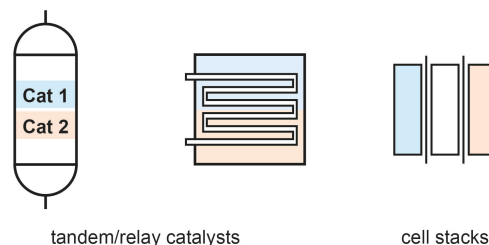

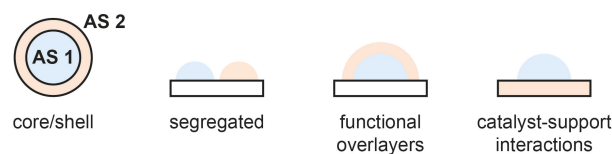**Figure 4.** Schematic representations of coupled (a) catalytic processes, (b) catalytic materials, and (c) active sites.

Verbund site,[44] the integrated operation of heterogeneous catalysts continues to drive the development of highly innovative processes, such as the co-production of methanol and ammonia.[45] Given the urgent need for defossilization, coupling of existing technologies is essential for a rapid transformation of the chemical industry. This approach remains necessary until direct routes, such as CO_2 hydrogenation to higher alcohols, lower olefins, or fuels, become competitive.

Identifying suitable catalytic reactions for coupling requires a thorough and comprehensive evaluation of environmental and economic impacts based on life-cycle assessment (LCA) and TEA.[46] When these criteria are unavailable for a particular chemical product, an initial selection can be made based on key catalytic reactions (Table 1), which involves assessing production capacities and considering the TRL of a catalytic process. Moreover, this guideline can facilitate the identification of promising yet underdeveloped technologies and assist in understanding how fossil-based reactions, subject to current research, can be operated sustainably. For instance, research efforts in CO hydrogenation, which depends on fossil-based synthesis gas from natural gas or coal, are often justified by the potential use of a sustainable synthesis gas source. Initially, this argument holds merit because LCA and TEA studies render this reaction based on renewable resources economically feasible

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and environmentally beneficial.[3] However, without an experimental proof of concept, this approach overlooks several aspects critical to catalyst development, such as varying feed compositions and levels of impurities depending on the syngas source,[47] fluctuation in the raw material and energy supply from renewables,[48] and challenges associated to non-continuous operation due to decentralization.[49] All these aspects need to be taken into account, as combining two technologies with high TRLs does not necessarily result in a production-ready combined process. Thus, considering the scale-transcending effects of prospective sustainable value chains is crucial when conducting (atomic-level) catalyst development.

Similar concepts also hold promise in biocatalysis and especially in electrocatalysis, which is well-suited for the activation of small molecules,[23,28] as indicated by the relatively high TRLs of 8 and 5–6 for CO_2 electroreduction to CO or co-electrolysis to syngas, respectively (Table 1). Despite the clear advantages of electrocatalytic processes, such as the enhanced scalability and the ability to operate under varying loads,[49] the coupling of two or more electrocatalytic reactions has been less intensively explored. The less intensive research on intra-catalytic coupling of electrochemical reactions is partly ascribed to their restriction in the formation of primarily small molecules, which ultimately means that most of the sustainable chemical value chains cannot be fully addressed by electrocatalytic reactions alone (Figure 1). With the recent discovery of novel electrocatalytic systems using nickel-based catalysts,[50,51] multi-carbon products with more than two carbon atoms are achievable. This development highlights the potential for electrocatalysis to extend across entire value chains of sustainable chemicals. Also in the case of biocatalysis or biological conversion technologies, the combination of two processes is utilized to increase production rates, *e.g.*, the two-stage fermentation of synthesis gas to ethanol using acetic acid as an intermediate.[35,52,53]

Given the advantages of electrocatalysis in small molecule activation, it is apparent that integrating it with thermo- or biocatalysis can further advance the sustainable production of chemicals and fuels (Figure 4a). Considering the projected demand for fossil-free hydrogen in chemical production, the vital role of electrocatalysis in the defossilization is thus emphasized. The inter-catalytic coupling of electro- and thermocatalytic processes has already been demonstrated at the production scale by integrating water electrolysis into chemical processes.[49] Other promising reactions include the formation of CO, either in the pure form or as synthesis gas, as highlighted by the high production capacities and increased TRLs (Figure 2 and Table 1).

While it remains a subject of debate whether thermo-, electrocatalytic, or bio-based generation of syngas is the most efficient and environmentally friendly way,[54] it is apparent that multiple technologies are required to meet our current and future demands. Similarly, given the various syngas-upgrading processes and the diverse accompanying requirements, versatile syngas production routes are needed, *e.g.*, rWGS, biomass or plastic waste gasification.

Furthermore, the effective coupling of electro- and thermo-catalysis to produce more complex products has recently been demonstrated at the laboratory scale, underscoring the potential of inter-catalytic coupling, *e.g.*, the formation of lactone monomer,[55] butane,[56] or oxygenates (Figure 5a).[57]

A similar concept based on the electrocatalytic acetate formation coupled to microbial acetate conversion is gaining growing interest and shows great promise in the production of higher-value products, such as acetoin or 2,3-butandiol.[58] Another promising strategy is the microbial electrosynthesis (MES), in which a microbial conversion is driven by electricity using electrochemical cells. This technology has potential for sustainable formation of oxygenated products from CO_2, *e.g.*, acetate,[37] ethanol,[36] carbon monoxide,[33] or methane.[59] Despite the promising progress in the combination of electro- and biocatalysis, it is important to highlight that the TRLs remain relatively low and significant progress, especially in increasing production capacities, is needed for a practical and competitive application.[35,60]
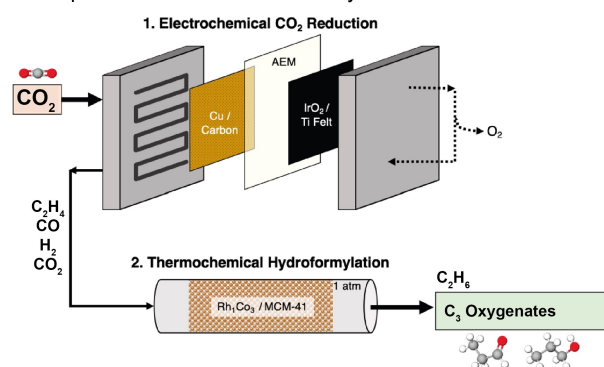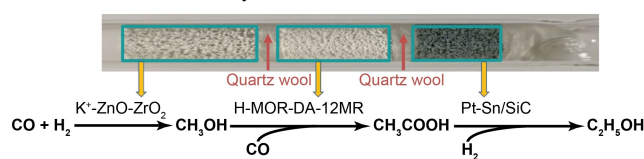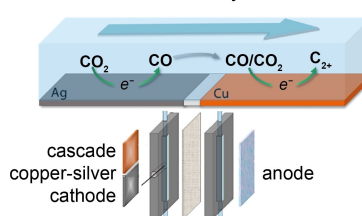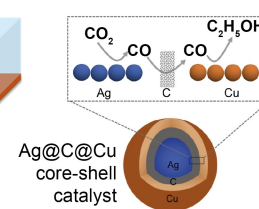

Figure 5. Key examples of coupled catalytic reaction across different scales. (a) Formation of C_3 oxygenates through coupling of CO_2 electrolysis and hydroformylation. Adapted with permission from Ref. [49], ACS. (b) Ethanol synthesis over a triple tandem system. Adapted from Ref. [54] under CC BY 4.0 license. (c) Sequential cascade electrocatalytic CO_2 reduction to C_{2+} oxygenates. Adapted with permission from Ref. [55], ACS. (d) Electro-ocatalytic ethanol formation over a Ag@C@Cu core-shell catalyst. Adapted with permission from Ref. [65], Cell Press.

From Coupled Catalysts to Active Sites

Once catalysts are operational under the same reaction conditions, they can be coupled through relay/tandem catalysis or as electrocatalytic cell stacks (Figure 4b).[61–63] This approach is especially attractive as it reduces both capital and operational costs since two or more reactions are operated in a single reactor, minimizing the need for separation or purification of intermediates. The use of tandem catalysts was demonstrated for several thermo- and electrocatalytic processes but has not yet been commercialized, e.g., methanol to liquid fuels,[64] ethanol synthesis (Figure 5b),[65] or CO to ethylene.[66] Moreover, tandem systems are also attracting growing interest in the electrocatalytic synthesis of more complex chemicals, such as the formation of C_{2+} oxygenates over a silver-copper tandem electrode (Figure 5c).[67] The combination of an efficient CO-forming catalyst with an additional electrocatalytic reaction provides promising prospects, as adsorbed CO is considered the key intermediate[68,69] in C–C (acetate[70]) and C–N coupling reactions (urea,[29,71] amines,[72,73] or amides[74]).

Tandem catalysis is particularly useful in gaining an in-depth understanding of complex, multicomponent materials, where several surface reactions co-occur at different active sites. By decoupling these surface reactions through the combination of catalytic materials with defined functionalities, complex reaction networks can be elucidated. Thus, precise structure-function relationships can be determined regardless of the reaction's complexity, which is especially relevant for studying the formation of complex compounds such as multicarbon products or chemicals with C–N moieties. Moreover, employing tandem catalysis does not require specialized equipment and, therefore, has the potential to greatly enhance our understanding of CCRs in the short term.

Once structure-function relationships and reaction networks on tandem catalysts are derived, novel direct routes can be established through an information-guided reverse engineering approach. This approach allows the tailored design of multifunctional catalysts through the incorporation of all required active sites in a single catalyst (Figure 4c), such as core/shell structures,[75,76] catalyst-support interactions,[77] or functional overlayers.[78] For example, the electrocatalytic synthesis of

ethanol from CO_2 was realized with a silver-copper core-shell catalyst (Figure 5d).[76] Despite the appeal of designing single catalysts with multiple active sites for novel direct routes, it is important to note that reaction mechanisms on these systems are often not explicitly validated, and further progress in both experimental validation and theoretical understanding is essential for enhancing the mechanistic understanding of these complex, multicomponent catalysts.

Research Needs

As CCRs extend from atomic-level active sites to processes with global impacts, a multidisciplinary research approach is needed to drive progress (Figure 6). While reaching high TRLs for combined processes presents an enormous challenge in reaction and process engineering, a focus on integration-oriented catalyst development could greatly assist in the establishment of sustainable production routes. To this end, catalysis research must shift from focusing solely on isolated catalyst performance to considering how catalytic systems can be efficiently integrated into actual chemical value chains, including future renewable feedstocks, such as CO_2, biomass, or plastic waste.[79] This integration-driven approach, which utilizes comprehensive LCA and TEA to take environmental and economic impacts into account at an early stage, must include the assessment of productivity under relevant reaction conditions that align with the requirements of the intended coupled process.

Additionally, gaining a deeper understanding of the reaction mechanisms and kinetics of coupled reactions is crucial for optimizing catalytic systems further. In this regard, tandem catalysis should be recognized not only as a strategy of process operation but also as a powerful tool for unravelling complex reaction networks and potentially identifying novel direct routes. A deeper fundamental knowledge of catalyst dynamics and stability under realistic and ideally fluctuating conditions needs to be derived by using *in situ* and *operando* characterization techniques and computational simulations, which are currently underutilized in studies on CCRs and particularly on coupled actives sites, for which clear structure-function relation-

Figure 6. Research needs for developing and establishing coupled catalytic reactions for future chemical value chains.

ships are often not established. Understanding all these fundamental aspects is vital for improving the interaction between multiple catalytic materials or active sites and developing practically relevant catalytic systems.

Summary

The coupling of catalytic reactions across chemical value chains is inevitable and pivotal for the urgently needed transition of the chemical industry towards sustainability. However, present technology readiness levels of coupled processes are currently low due to significant challenges in reaction and process engineering associated with the use of renewable resources. Equally important is the development of novel catalytic materials specifically designed to meet the unique requirements of coupled reactions. This Perspective offers insights into coupled catalytic reactions (CCRs) for novel and scalable pathways to value-added chemicals. An integration-oriented approach to catalyst development is suggested to transcend scales, which is crucial for the accelerated implementation of sustainable processes and the establishment of novel direct routes through tandem catalysis or the coupling of distinct active sites. By leveraging this understanding, we can establish the foundation for modern chemical value chains that align with the energy and raw material landscapes of the near future.

List of Acronyms and Abbreviations

BTX   benzene, toluene and xylenes
CCR   coupled catalytic reaction
DRM   dry reforming of methane
FTS   Fischer-Tropsch synthesis
HAS   higher alcohol synthesis
LCA   life-cycle assessment
LTE   low-temperature electrolysis
MC   microbial conversion
MES   microbial electrosynthesis
MTA   methanol-to-aromatics
MTBE   methyl *tert*-butyl ether
MTO   methanol-to-olefins
PtX   power-to-x
rWGS   reverse water-gas shift reaction
SMR   steam methane reforming
SOE   solid oxide electrolysis
TEA   techno-economic analysis
TRL   technology readiness level

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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PERSPECTIVE

The transition from fossil fuels to sustainable resources of the near future demands a shift in catalysis research – from investigating reactions in isolation to developing coupled catalytic reactions. This Perspective discusses the status and emerging prospects of coupled catalytic reactions across various scales, from active sites to processes.
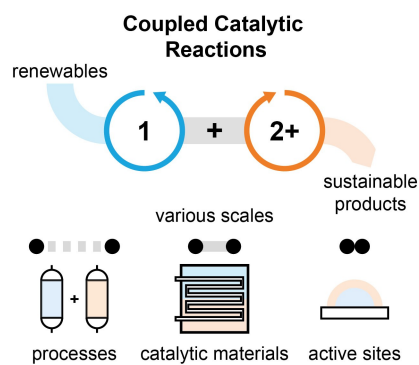
Dr. P. Preikschas*, Prof. J. Pérez-Ramírez*

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Technology Readiness and Emerging Prospects of Coupled Catalytic Reactions for Sustainable Chemical Value Chains