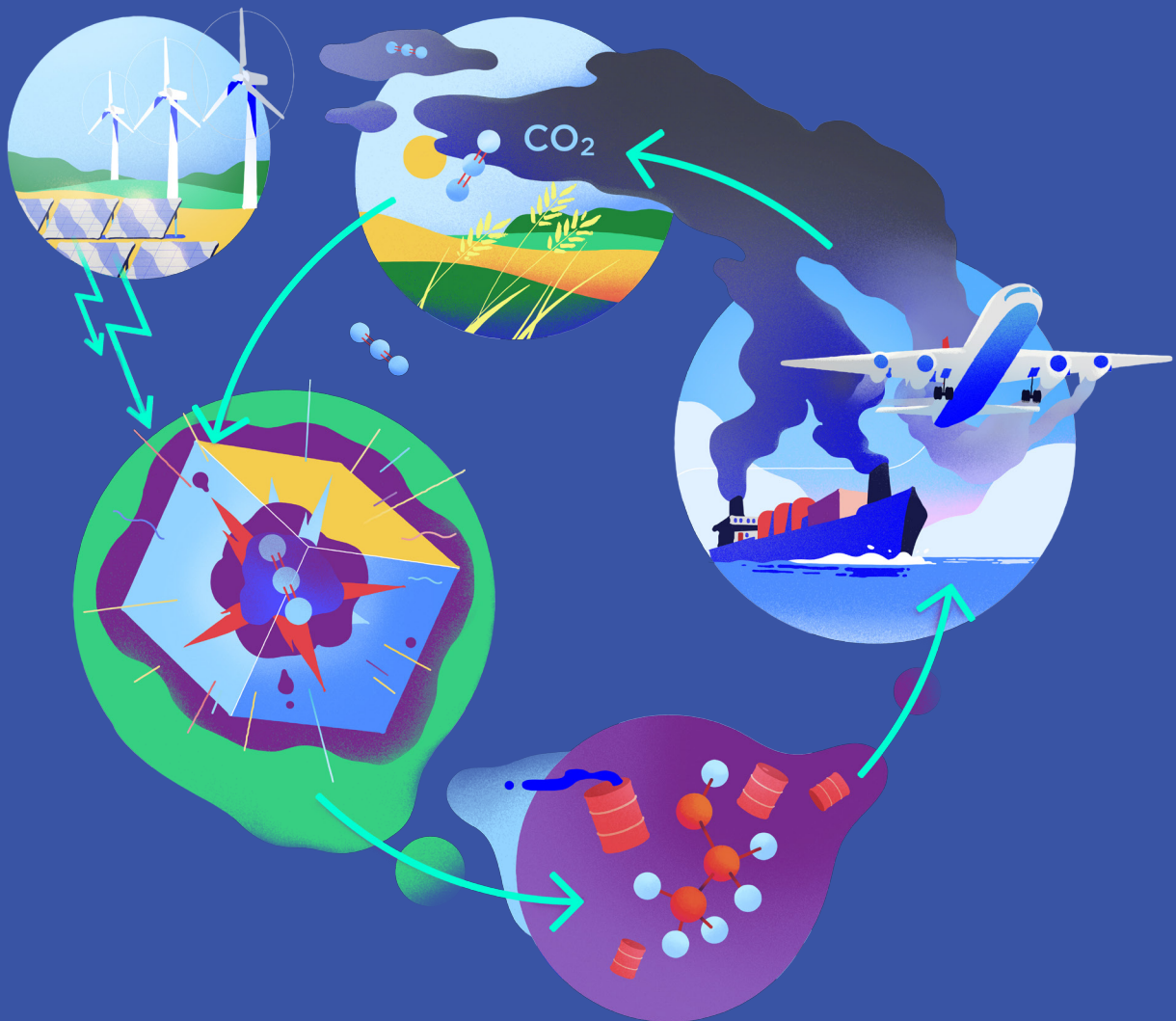


Research needs

towards sustainable production of fuels and chemicals



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Executive Summary

To mitigate climate change, we must further develop the sustainable alternatives to fossil resources to meet our energy and chemical needs. Electricity from solar cells and wind turbines is gradually becoming economically competitive, but economically-viable technologies for the storage of electricity remain critically lacking. Battery technologies are part of the solution, but they are not readily amenable to many activities currently supported by fossil fuels, including large parts of the transport sector (e.g. air and long-distance transportation), energy storage to overcome medium and long term temporal variations, and the transmission of large quantities of energy from one region to another. Synthetic fuels offer a promising alternative to fossil fuels as they have the highest energy density of all energy storage media; can be stored cheaply over long periods of time; and fit into a vast, existing infrastructure for storage, transmission, and use. Beyond their importance as an energy source, fossil resources also form the basis of our current chemical industry, which uses more than 10% of all fossil resources in Europe. Replacing fossil resources with sustainably produced synthetic fuels and chemicals would allow us to close the carbon cycle and eliminate net CO₂ emissions, providing the tools to combat climate change.

To efficiently convert electricity into sustainable fuels and chemicals, the development of radically new electrochemical and thermochemical catalytic processes that are energy-efficient, selective, and composed of Earth-abundant and non-critical elements is key. The core scientific challenges associated with the realization of such systems lie in molecular and interfacial catalysis. Catalysts for these processes exist, but are limited by their poor efficiency, low product selectivity, high cost, and rarity, making current sustainable processes too expensive to compete with fossil-based ones. Additional technological challenges are associated with the scale-up and integration of sustainable processes, given the enormous size of our energy needs. Furthermore, there are also many social challenges associated with the reshaping of the energy landscape.

Major ongoing scientific developments are making new, highly-effective catalysts achievable. These include theoretical methods with predictive power, advanced catalyst synthesis with atom-scale precision, and operando characterization methods. These approaches can be integrated and combined with new machine learning methodology and artificial intelligence (AI) to enable radically accelerated catalyst and chemical process discovery. However, reaching the net 80 to 95 percent

reduction of EU emissions called for by the Paris Agreement by year 2050 will require swift and targeted efforts toward sustainable fuels and chemicals in the immediate future. Such advances necessitate a large-scale, coordinated approach relying on experts from diverse fields and integrating fundamental discovery with industrial scale-up and social adoption. Towards this end, the present scientific roadmap addresses the main scientific and technological challenges that must be overcome to enable the sustainable production of fuels and chemicals. It is based on input from more than 150 of the top European academic and industrial researchers in the field. A three-day workshop with experts from chemistry, physics, engineering, and the economic and social sciences was the basis for defining the current status, challenges, and foremost research needs of twelve areas that are key to the transition to sustainable fuel and chemical production. These twelve areas fall broadly into three levels of grand challenges: (i) the development and discovery of new catalysts and processes, (ii) scale-up and integration of new processes, and (iii) the engagement of all societal stakeholders.

Central to the production of renewable fuels and chemicals is electrochemical water splitting, which produces molecular hydrogen (H_2) to be used as a feedstock or fuel. A promising water splitting technology for coupling to renewable electricity utilizes an acidic membrane, necessitating the use of iridium to catalyze the oxygen evolution reaction (OER) due to its stability. Because of the high cost and low abundance of iridium, there is an urgent need to reduce the amount of iridium used by discovering an alternative catalyst with comparable activity and stability. Alkaline electrolyzers can use cheaper catalysts but lack a suitably conductive and stable alkaline membrane. All known OER catalysts have significant overpotentials and could be improved.

Two other important electrochemical reactions involve the reduction of CO_2 and N_2 to produce hydrocarbons, oxygenates, and ammonia. However, neither of these reduction reactions have active or selective enough catalysts to be economically viable. Specifically, for CO_2 reduction, making (longer) hydrocarbon or alcohol products, compatible with the current energy sector and chemical industry, requires very large overpotentials. For N_2 reduction, both activity and selectivity are significantly worse than nitrogenase enzymes and produce quantities of ammonia that are often below detection limits of conventional techniques. For both reactions significantly more active and selective catalysts are needed.

Currently, thermal processes are much more developed at scale than electrochemical processes, and they will continue to be important as we transition to a fossil-free future. The thermal catalytic reactions explored include N_2 reduction, CO_2 reduction, and syngas (mixtures of H_2 , CO , and possibly CO_2) chemistries. Generally, these industrial processes run at steady-state using hydrogen derived from natural gas, so an overarching challenge is to make these processes compatible with renewable H_2 feedstocks. This shift will likely require decentralized and/or intermittent operation at lower temperatures and pressures, necessitating the development of more active and selective catalysts.

In general, development of new catalysts, heterogeneous as well as homogenous, for both

thermal and electrochemical processes will benefit greatly from improved operando characterization techniques, theoretical tools for modeling systems under realistic conditions, and multi-scale modeling. Applying AI techniques to catalyst design has the potential to accelerate these efforts, but hinges on more systematic and extensive sharing of reliable data. Furthermore, biological processes can also be optimized for all of the aforementioned reactions, but the development of a robust systems engineering framework towards the rational design of modular biological and bioinspired catalysts is a key aim.

Many of the aforementioned chemistries are fledgling and will face additional technological challenges related to their scale-up and integration. Even the processes for more established chemistries, e.g. thermal syngas chemistries and N_2 reduction, will need to be reoptimized to fit into a renewable energy framework (e.g. intermittent and decentralized operation). General challenges here include the development of modular and robust reactor concepts that facilitate operation under dynamic, transient, and intermittent conditions. Accelerating scale-up from benchtop to pilot-scale requires increased communication between research institutions and industry, and further scale-up would benefit from instruments, such as testbeds, that facilitate high-risk prototype testing by sharing the risk among public and private stakeholders. Furthermore, technologies that utilize CO_2 as a feedstock must ultimately be integrated with a CO_2 source via a CO_2 capture process. Challenges here include the design and implementation of a CO_2 network infrastructure, process optimization that accounts for incompatibility between CO_2 source and sink (e.g. steady-state power plant point-source vs. intermittent electrochemical CO_2 reduction), and the development of improved CO_2 capture technologies.

Finally, the critical role that society will play in the transition to renewable energies cannot be understated. In particular, industrial actors can hybridize existing processes to be compatible with electricity from renewable sources, lead in the development of fully integrated demonstration projects at relevant scales, and strengthen academic collaborations. To facilitate the transition to sustainable fuel and chemical production at an industrial scale, regulatory action must be taken by the legislature to encourage proper life cycle analysis practices and to make “green” hydrogen more cost-competitive in the short term (e.g. by imposing a CO_2 tax, enforcing renewable blending quotas, or gradually lowering the CO_2 emissions quotas of individual sectors over time). It is critical to find an effective, efficient, and fair governance structure for the transition to a sustainable future. Research questions include how to trigger and secure investments, prevent carbon leakage, regulate emissions, encourage social acceptance, and involve consumers and other stakeholders, including (non-) governmental bodies, effectively.

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Introduction

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Climate change makes it imperative that we discover alternatives to fossil resources for our energy and chemical needs. To avoid a 2 °C increase in average global temperature, the Paris Agreement has called for a net 80 to 95 percent reduction of EU emissions by 2050. Furthermore, the technologies developed to meet this goal should align with and contribute to the Sustainable Development Goals put forward by the United Nations, such as ending poverty, ending hunger, providing clean and affordable energy to everyone, promoting sustainable industrialization, fostering innovation, and building resilient infrastructure. The production of fuels and chemicals from renewable sources has the potential not only to reduce CO₂ emissions and meet emissions quotas, but also to do so sustainably and equitably.

While electricity from solar cells and wind turbines is gradually becoming economically competitive [2], we must discover ways of storing and transmitting the energy from these intermittent sources to mitigate our dependence on fossil fuels and curb further climate change. Battery technology offers part of a solution, but it is not readily amenable to many activities currently supported by fossil fuels. Such applications include large parts of the transport sector (e.g. air and long-distance transportation), energy storage to overcome seasonal variations, and the transmission of large quantities of energy from one region to another. Synthetic fuels offer a promising alternative to fossil fuels as they have the highest energy density of all energy storage media (Figure 1), can be stored cheaply

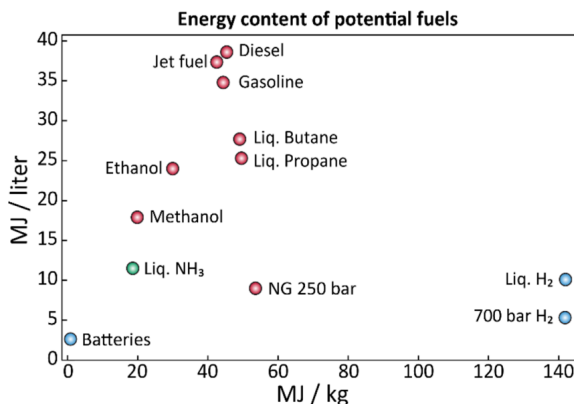


Figure 1: Volumetric and gravimetric energy densities of different energy storage media. Reproduced from reference [1].

over long periods of time, and fit into a vast, existing infrastructure for storage, transmission, and use. Replacing fossil fuels with sustainably produced synthetic fuels would allow us to close the carbon cycle and eliminate net CO₂ emissions (Figure 2), providing the tools to combat climate change and to make nations more energy-independent.

Eliminating the need for fossil fuels as an energy source is not enough, however. Fossil resources also form the basis of our current chemical industry. Polymers, adhesives, and lightweight carbon composites, just to mention a few products, all consist of carbon backbones. The chemical industry uses more than 10% of all fossil resources in Europe [3, 4]. Therefore, replacing the fossil feedstocks currently used in the chemical industry with sustainably produced base chemicals would play a significant role in decreasing net CO₂ emissions. Capturing and storing underground the CO₂ produced by current processes can also serve to decrease these emissions but is not the focus of this work [5].

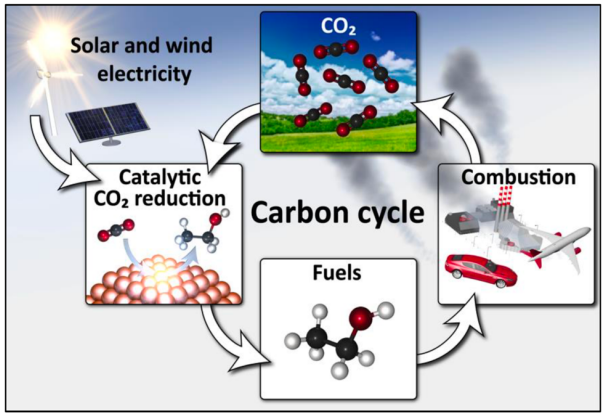


Figure 2: A sustainable carbon cycle. CO₂ from the atmosphere is reduced to a fuel, which stores energy for later use in a combustion process, which again releases CO₂ to the atmosphere. Therefore, the cycle is carbon-neutral. The critical, missing technology is efficient reduction of CO₂ using sustainable energy. Such a process requires both CO₂ sequestration (by plants or absorbers) and chemical transformation into larger carbon chains (fuels). A similar cycle exists for nitrogen. Graphics courtesy of Jakob Kibsgaard, DTU.

A system in which renewable sources are used as primary input and products are recycled at their end of life is referred to as a “circular economy.” The conversion of abundant molecules (in particular, water, CO₂, and N₂) into fuels and base chemicals (e.g. H₂, methanol, light olefins, aromatics, and ammonia) using renewable electricity and electrocatalysis, photocatalysis, or thermal catalysis is an essential component in any such sustainable energy and chemical production system, as illustrated in Figure 3. The use of non-edible biomass as a carbon source to produce important chemicals and fuels represents another interesting avenue, but it is beyond the scope of this work. There is today technology (electrolysis combined with traditional thermal catalysis) that can produce fuels and base chemicals from renewable electricity. But currently no existing technology can do it in an adequately efficient way to be economically competitive with fossil resource-based processes [6]. In addition, the distributed nature of electricity production from solar panels and wind turbines calls for distributed energy storage, which is also technologically challenging.

To solve these challenges, the discovery and development of radically new processes, materials, and technologies is key. In order for the conversion of electricity into fuels and chemicals to be economically viable, these processes must be energy-efficient, selective towards desired products, and based on Earth-abundant and non-critical elements. The core scientific challenges for these systems lie in molecular and interfacial catalysis. Additional technological challenges are associated

with the scale-up and integration of such processes, given the enormous size of our energy needs. In spite of decades of research, we still do not have the catalysts or processes for the production of fuels and chemicals from electricity in place today.

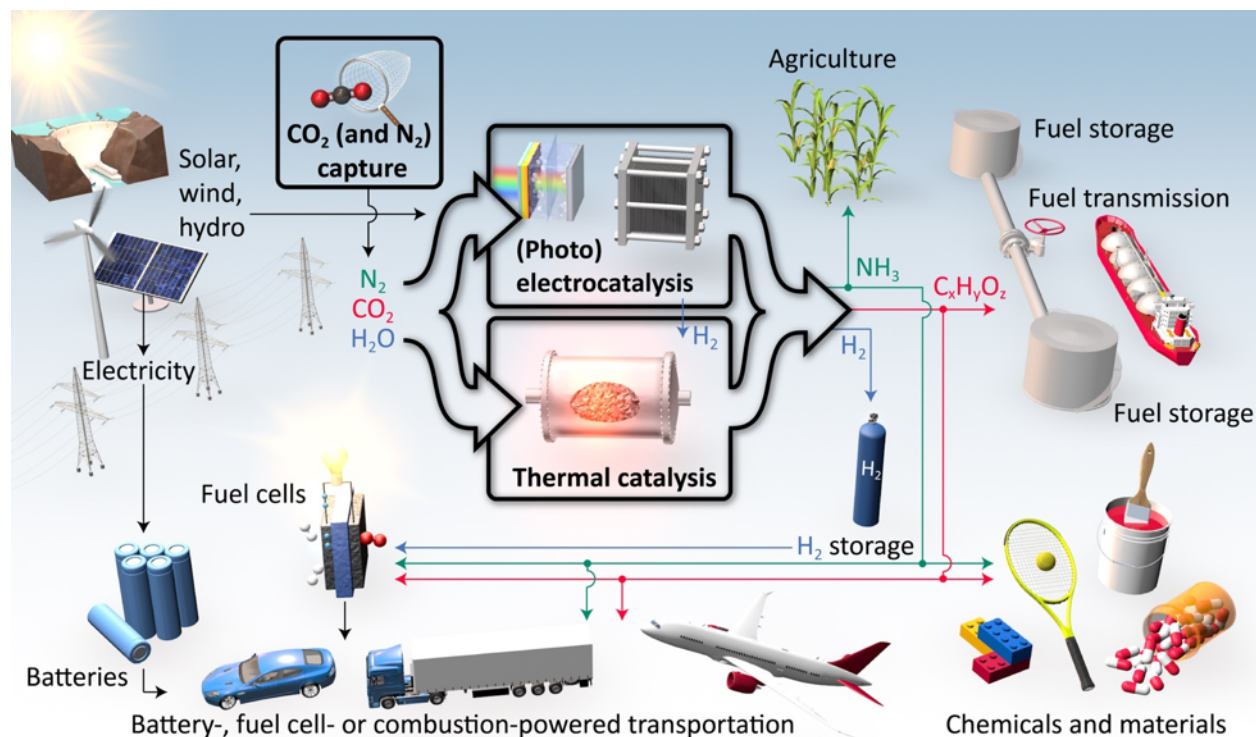


Figure 3: Illustration of a sustainable energy system. Several components are industrially well-developed at the moment. A green (grey in black and white) background is used to highlight the areas addressed in the present document in which current technologies are not economically viable. Key processes are electrochemical water splitting and thermal and electrochemical CO_2 and N_2 reduction. Graphics courtesy of Jakob Kibsgaard, DTU. An earlier version of this figure appeared in [7].

The present research needs report, or scientific roadmap, addresses the main scientific and technological challenges that must be overcome to enable the sustainable production of fuels and chemicals.¹ It is based on input from more than 150 of the top academic and industrial researchers in the field from Europe and beyond. A three-day workshop with experts from chemistry, physics, engineering, and the economic and social sciences was the basis for defining the current status, challenges, and foremost research needs of twelve areas that are key to the transition to sustainable fuel and chemical production.

The document begins by examining three key front-end catalytic reactions that are among the most challenging targets in chemistry: water splitting, CO_2 reduction, and N_2 reduction. Water splitting is considered electrochemically, whereas electrochemical and thermocatalytic routes

¹The present report builds upon and provides an updated European perspective on similar reports from the US Department of Energy: Basic research needs, catalysis for energy (2007), Sustainable ammonia synthesis (2016), Basic research needs for catalysis science to transform energy (2017). It also adds scientific content to previous European reports on the subject [8].

are considered for CO₂ and N₂ reduction as well as downstream processes to form fuels and chemicals. All types of catalysis, including heterogeneous, homogeneous, and bio-catalytic processes, are considered. The potential for data-driven approaches and Artificial Intelligence (AI) to accelerate catalyst discovery is also explored. Having considered the technological challenges of these key reactions, challenges associated with the scale-up and integration of new processes are examined. Finally, the role of society in the transition to sustainability with regard to the economy and industry is considered. In many Sections, concrete goals and objectives are suggested in areas the authors believe are ripe for development and potentially even demonstrator-scale deployment. Importantly, many Sections identify common cross-cutting goals as being key to the further development of the Section’s respective technologies and chemistries. These cross-cutting goals are related to developments in: (i) *in situ* and operando characterization techniques, (ii) theory tools for modeling realistic catalysts, (iii) multiscale modeling, and (iv) new reactor concepts, especially related to intermittent and decentralized operation. In the following Overview Section, we offer a brief introduction to each Section and its relevance to sustainable fuels and chemicals.

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Overview

The development and discovery of new catalysts and processes

Section 1 covers the various water electrolysis technologies that have been investigated to date, from the very mature alkaline water electrolysis to the nascent alkaline membrane water electrolysis. While the former is an established technology deployed on the hundreds of MW scale, it is not readily compatible with intermittent electricity sources. Membrane electrolysis devices are more favorable for renewable applications but suffer from either unsustainable iridium usage as an electrocatalyst or poor membrane conductivity/stability. Furthermore, suboptimal catalysts are the source of energy inefficiency in all systems. Future research efforts should be devoted to discovery of new catalysts with lower losses and decreasing the iridium usage in membrane electrolysis systems either through replacement with an alternative catalyst or through the discovery of a suitably conductive support material. Such efforts rely on advancing fundamental understanding of electrocatalytic water oxidation with advanced operando techniques and computational methods. Finally, there are also many opportunities to improve device performance by optimizing cell components beyond the electrodes (e.g. membranes, transport layers, overall cell design).

The direct electrochemical reduction of CO₂ to fuels and chemicals is explored in **Section 2**. The most efficient processes that have been demonstrated in this field are the generation of two electron products, namely CO and formic acid. CO is a particularly important target product for the chemical industry, as it is widely employed in several large-scale industrial processes. The formation of further reduced products such as multicarbon alcohols and hydrocarbons has proven more difficult, and new, better catalysts are needed. This requires advancements in fundamental understanding of the mechanism and role of the electrochemical interface via advanced operando techniques and computational methods. Additionally, future research efforts should be devoted to optimizing device performance through new cell designs that can operate at realistic current densities.

Where **Section 2** explores electrochemical routes towards the reduction of CO₂ to fuels and chemicals, **Section 3** explores thermochemical routes to this end. Technologies exist for the thermochemical reduction of CO₂ to a multitude of products, including methanol, syngas, methane, and bulk and fine chemicals. However, these processes largely require high temperatures (due

to the absence of highly active catalysts), high pressures (due to the resultant unfavorable thermodynamics), and thus most often require centralized production units to be economical. The main challenges associated with sustainable thermochemical CO₂ reduction are related to plant decentralization, energy intermittency, and the development of earth-abundant, sustainable catalyst materials. While several technologies are already in place at the demonstrator-plant level, more active, stable/water-resistant, and earth-abundant catalysts are needed for economic viability. The successful development of such catalysts is dependent on continued research in targeted catalyst synthesis, theoretical methods, and operando characterization. Furthermore, entirely new chemistries are needed to convert CO₂ to more complex molecules (e.g. those that involve C-C coupling). For more developed chemistries, new reaction and reactor concepts and plant design developments will be needed, especially to support the transition to de-localized production.

In addition to being directly reduced, CO₂ can also be reduced in a multistep pathway, in which it is first converted to CO, or included in higher ratios in syngas feeds. In **Section 4**, the adaptation of the established thermocatalytic conversion of syngas (CO, CO₂, and H₂) to sustainable fuels and chemicals is explored. Syngas chemistry is a pillar of the petrochemical and synthetic fuel industries, but the high investment costs associated with the generation of syngas mean that production at large scale is currently required for economic operation. Towards the development of syngas chemistries for the sustainable production of fuels and chemicals, novel processes are needed that achieve high selectivity under low temperatures and pressures. In particular, robust design principles and structure-property relationships are needed to determine what controls activity and selectivity under variable conditions, which will rely on developments in microkinetic modeling and operando characterization. Furthermore, flexible-size, robust, and modular reactor concepts need to be developed for operation under changing, transient, and intermittent conditions.

Besides carbon-based chemicals, nitrogen-based chemicals are also of great importance to our society. **Section 5** covers two distinct routes to sustainable ammonia synthesis for use as fertilizer or fuel: thermal and electrochemical reduction of N₂. The thermal route is currently used to provide fertilizer that supports the world’s population but consumes a colossal >1% of global fossil fuel production. Switching to a sustainably produced H₂ feedstock (e.g. from water electrolysis) would essentially solve this problem, but the currently implemented thermal catalytic process is not amenable to an intermittent H₂ source or decentralized, small/medium scale operation. Therefore, future research is required to address the implications of intermittent operation, which may include the development of new ammonia synthesis catalysts that operate at lower temperature and pressure. The electrochemical reduction of N₂ represents an alternative, but current catalysts are prohibitively inefficient. Critical research needs include the discovery of new electrode and electrolyte materials and design of efficient processes. A preliminary goal is to establish and adopt standards and protocols for product detection.

While the preceding Sections largely focus on heterogeneous (electro-)catalytic reactions,

Section 6 focuses on homogeneous catalysis. These catalytic processes, enabled by molecular organometallic or organic compounds as active species, are also a vital technology in today’s petrochemical value chain and have potential to be key actors in the transition to a sustainable future. In particular, homogeneous chemistries allow for precisely controlled and diverse molecular connectivities, which will be crucial in the development of entirely new chemistries for the production of complex, value-added products and functional chemicals from readily-available starting materials like CO₂, H₂O, and N₂. Current technologies based on homogeneous catalysts have been optimized to facilitate the utilization of fossil resources (oil, natural gas, and coal) in centralized processes, using, for instance, CO as an intermediate. Opportunities for the transition to the sustainable production of fuels and chemicals include (i) adapting these current processes to consume renewable feedstocks (using primarily CO₂ and green H₂ or electricity) or (ii) developing alternative conversion routes that directly transform renewable feedstocks to value-added products, requiring multi-electron redox processes and sequential bond-breaking/bond-forming events. Data-driven approaches enabling increasing integration of experiment and theory are expected to play a significant role in the discovery of new, ground-breaking catalysts for such reactions.

Section 7 demonstrates how biological systems can be used as sources of inspiration to sustainably convert solar energy to fuels and chemicals. In addition to providing important chemistry and engineering lessons that may be broadly translated in all areas of catalysis, the evolved photosynthetic pathways of biological systems can provide inspiration for artificial photosynthesis. Several technologies involving photosynthetic microbial cell factories are already in place at the demonstrator-plant level, and biohybrid systems are finding success at the R&D level, but integrated devices are largely missing. Advances are needed in both fundamental understanding and device development to achieve real technological solutions. In particular, developing a systems engineering framework to help rationally design modular biological and bioinspired catalysts is a key aim. Furthermore, both synthetic biology toolboxes and bioreactor designs must continue to be improved for photosynthetic microbial cell factories to move beyond demonstrator level. Advances are needed in designing strong electron sinks targeting a range of useful products, enhancing photosynthetic efficiency by suppressing unproductive pathways and design systems for secretion of products.

Artificial intelligence (AI) and computational methods have the potential to rapidly accelerate the transition to sustainably produced fuels and chemicals in a number of ways, from the atomic level (e.g. facilitating materials discovery) to the systems level (e.g. optimizing plant operating conditions and schedules). **Section 8** investigates the role of data and AI in the discovery of new materials, primarily catalysts. The efficient use of AI tools relies on the availability of large amounts of appropriately described data. Thus, encouraging the catalysis community to openly share scientific data is essential and may be facilitated by the creation of a new catalysis database with support for computational and experimental data. This is particularly challenging

owing to the complex and heterogeneous nature of the techniques involved in experimental catalysis research, and thus the definition of suitable metadata is a significant challenge. Beyond the sharing of data, it is also important that such data also be reliable. For computational data, this means benchmarking to higher-level methods and considering multi-scale techniques under realistic operating conditions. For experimental data, this means establishing standards and protocols for catalyst characterization and test conditions. Improving the data climate in the field of catalysis research will accelerate the impact of AI, but additional research into the application of AI itself is also important, particularly for identifying statistically exceptional data points, creating models with superior speed/accuracy compared to first-principles calculations, and using active learning to guide experiments and simulations.

Scale-up and integration of new processes

While some of the aforementioned electrochemical processes have demonstrated promising results, electrochemical production processes for most products are not yet developed and implemented at a scale, that can sustain the global need for chemicals and fuels. Thus, the scale-up of electrochemical processes is critical to meet EU goals for the transition away from fossil resources and is the subject of **Section 9**. Accelerating scale-up at low technology readiness levels requires increased communication between research institutions and industry, identifying technically and economically feasible technologies in the perspective of large-scale deployment and thus guiding the progress towards pilot-scale demonstration. The scale-up of pilot-scale processes to the industrial scale requires evaluation of technical, economic, and social feasibility. In particular, the use of testbeds may be particularly effective in facilitating high-risk prototype testing and demonstrations by sharing the risk among public and private stakeholders and thus mitigating reluctance to scale-up in an uncertain economic environment.

Any chemical conversion technology that utilizes CO₂ (as explored in Sections 2, 3, and 4) must couple to a CO₂ source via a CO₂ capture process. Section 10 examines the linkages between CO₂ sources (e.g. industrial and power plants, ambient air), CO₂ capture processes (e.g. amine scrubbing, adsorption), and CO₂ utilization (as in the aforementioned processes, thus providing a temporary CO₂ sink) or CO₂ sequestration underground (providing a permanent sink). It analyses the different technology chains that provide societal services via fuels and chemicals (heat and power, propulsion, consumer products) using either captured CO₂ or fossil carbon as feedstock. Then, it establishes that their sustainability, i.e. their compliance with the net-zero-CO₂-emissions constraint (by 2040-50) defined by the IPCC, must be assessed via a detailed systems analysis considering energy efficiency, carbon cycle, resource utilization, and cost. Challenges that must be overcome to realize systems at scale include the design and implementation of a CO₂ network infrastructure, process optimization that accounts for incompatibility between CO₂ source and sink

(e.g. steady-state power plant point-source vs. intermittent electrochemical CO₂ reduction), and the development of improved CO₂ capture technologies, particularly to efficiently capture CO₂ from air using managed biomass growth or direct air capture.

The role of society

While previous Sections focus largely on technological developments required of specific chemistries, these are only one important piece to the puzzle. In **Section 11**, industry’s critical role in the transition to a sustainable future is explored. Increasingly, stakeholders are demanding companies develop and execute their strategies to be consistent with sustainability targets, and many companies are converging on water splitting as an alternative to hydrogen production from fossil fuels. While water splitting technologies are already feasible at the MW scale, this “green” hydrogen is more expensive than its fossil-derived alternative. To facilitate the transition to sustainable fuel and chemical production at an industrial scale, regulatory action must be encouraged and proper life cycle analysis practices established. In the short term, existing processes can be hybridized to be compatible with electricity from renewable sources and fund the development of fully-integrated demonstration projects at relevant scales. Furthermore, collaborations with academia can be strengthened, with a focus on the exploration of both breakthrough technologies (e.g. N₂ and CO₂ reduction) as well as optimization of processes like water splitting.

In **Section 12**, the political and economic considerations that will be key to the successful transition to a circular economy are explored. This Section assumes a technologically-neutral approach, flexible to new innovations and future challenges as they arise. Three important dimensions of the transition are considered: i) integration of sustainable systems into current industry and consumer standards; ii) involvement of a wide spectrum of stakeholders; and iii) intelligent tools and protocol development, status monitoring, and identification of appropriate actions. The emergent research questions are structured along the lines of relevant actors and levels of political decision making, leading to a three-dimensional research hierarchy, from the global to the national and local levels. It is critical to find an effective, efficient, and fair governance structure for the transition to a sustainable future. Research questions include how to trigger and secure investments, prevent carbon leakage, regulate emissions, encourage social acceptance, and involve consumers and other stakeholders effectively. Specifically, fossil-based volumes will need to be reduced, sustainable primary and recycled materials integrated, and downcycling minimized. Effectively managing a circular economy will also entail new business models, intensified customer integration, and appropriate regulations.

Section 1

Water splitting and sustainable H₂ production

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1.1 Importance of subject

Securing the provision of the required energy and materials to a growing number of people on Earth with minimal environmental impact requires the sustainable production of fuels and chemicals. This implies closing the technological cycles of key elements such as carbon, nitrogen, hydrogen, and oxygen. Closing the hydrogen cycle through large-scale production of molecular hydrogen is of particular importance to provide the required chemically reducing equivalents to close the other cycles, particularly the carbon cycle. Hydrogen itself is an energy storage molecule and reactive chemical intermediate that enables a large variety of indispensable chemical transformations to more complex energy storage molecules or industrial chemicals and materials (see Sections 3, 4, and 5).

Under the premise of the availability of cheap renewable electricity, the electrolytic production of hydrogen from water is an attractive route. While the earth's surface water is technically not the only possible feedstock for this process, it is the best choice since its global abundance is commensurate with the scale of hydrogen required for the sustainable production of fuels and chemicals.

Electrolytic hydrogen production and its various uses are key enablers of a new type of energy and chemical industry system, characterized by a close coupling of previously separate technology sectors such as transport, chemicals, electricity, and energy storage. Distributed production of hydrogen is potentially useful for the refueling of light, medium, and heavy road vehicles; trains;

and small planes. Medium-sized hydrogen production systems will supply fossil-free feedstocks to industrial chemical plants (e.g. ammonia and syngas), while large scale electrolytic hydrogen production will be mainly used for energy storage purposes, i.e. to balance excess electricity by combining with re-electrification via fuel cells or injection into the gas grid.

1.2 State of the art and scientific challenges

Today’s water electrolyzer technology comprises four distinct approaches, each of which will be discussed in the following. Alkaline water electrolysis (AWE) is the oldest and most mature technology, beginning at the end of the 19th century. It developed on the industrial scale in the 1920s with unit capacities of up to 50 MW, plant capacities of 100s of MW, and demonstrated 30+ year unit durability [1]. Conventional AWE systems are also relatively cheap, utilizing Ni-based electrodes, KOH solutions, and inexpensive meshes as contact elements. However, they suffer from large ohmic losses, gas crossover (preventing operation at elevated pressure), and poor startup/shutdown dynamics, making them suboptimal for coupling to renewable energy sources in a sustainable fuels and chemicals future. Polymer electrolyte membrane water electrolysis (PEMWE) was originally developed in the 1950s for the regeneration of life support media (oxygen, water, carbon) in space and submarine vessels. The replacement of aqueous electrolyte with a relatively thin solid ion exchange membrane largely solves the three challenges faced by AWE systems noted above, enabling higher current densities, higher pressures, and intermittent operation. PEMWEs have been recently deployed and developed to the MW stack scale with reported durability of more than 10,000 hours. However, further scale-up to the level necessitated by global consumption of fuels and chemicals, is currently not possible due to the technology’s reliance on scarce materials, namely iridium and platinum, which are used as electrocatalysts to accelerate the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), respectively.

The sluggish kinetics of the OER constitute a particularly significant loss in energy efficiency to the overall process, and iridium-oxide is the best known OER catalyst with long-term stability in the very corrosive acidic environment imposed by the proton conducting membrane. Because there is no known catalyst support with sufficient conductivity and stability, either unsupported iridium catalysts or large amounts of iridium on a non-conductive support are currently used, which results in very high catalyst loading. Consequently, PEMWE cells require of the order of 0.5g Ir/kW [2]. Iridium is an extremely rare material with an annual production of only a few tons per year. Assuming one ton per year is available for PEMWE implementation corresponds to an annual growth of only 2 GW, which is well short of the hundreds of GW/year necessary to have global impact. To reach this goal, the utilization of iridium needs to be improved to 0.01 g/kW, a factor of 50 better than today’s technology (Figure 1.1).

Platinum, which is the catalyst used for HER at the PEMWE cathode, is also quite rare but

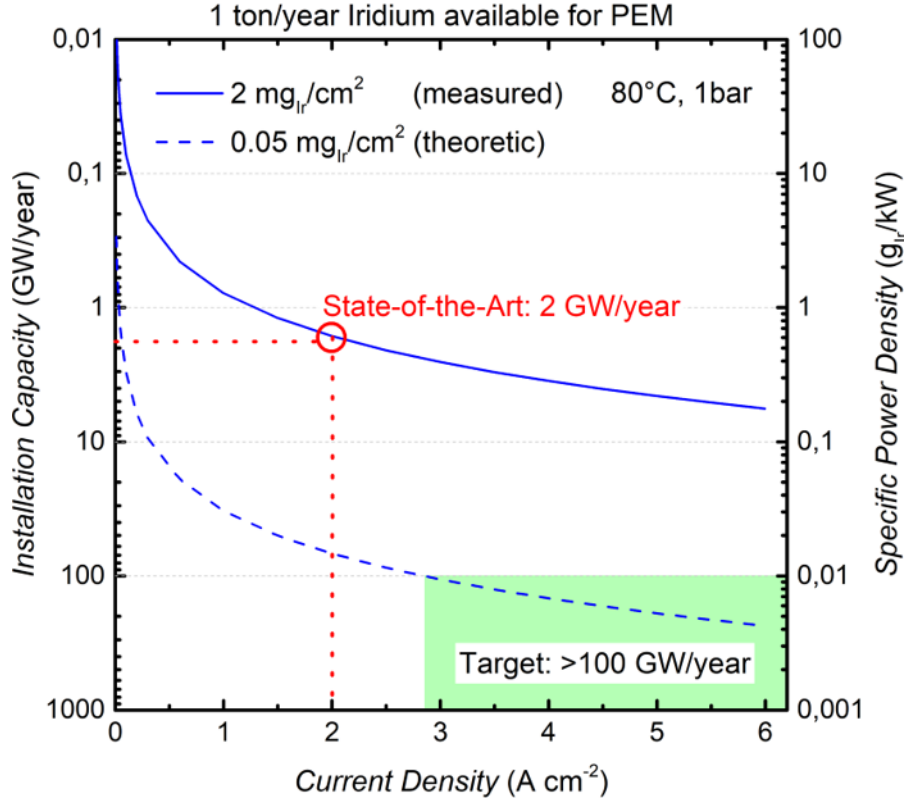


Figure 1.1: Iridium specific power density and the related installation capacity for PEMWE (assuming one ton of iridium available per year for PEMWE) comparing state of the art technology (loading of 2 mg Ir/cm²) the needed improvement in iridium utilization to reach the target of 100 GW/year [2].

is still produced at a rate two orders of magnitude higher than that of iridium. Additionally, due to its exceptional catalytic activity and superior utilization, only 0.01 g Pt/kW is necessary, which then corresponds to one ton of platinum consumption per year for 100 GW/year of PEMWE growth [2]. Thus, while it is desirable to replace platinum at the PEMWE cathode with something less expensive, *the current usage of iridium at the PEMWE anode is a fundamental obstacle limiting the growth of PEMWE technology.*

Anion exchange membrane water electrolysis (AEMWE) is a promising new development that attempt to combine the advantages of both AWE and PEMWE. The inherently alkaline membrane is less corrosive and allows for the replacement of iridium with nickel-based catalysts similar to those used for AWE. These devices have shown promise to achieve practical current densities but suffer from membrane and ionomer instability. They are currently available commercially, although only at the kW scale with a 10 Nm³/h productivity per module. *The primary challenge with AEMWE technology is develop a suitable anion exchange membrane with ohmic resistance, gas permeability, and long-term stability simliar to that of the membrane used for PEMWE.* Additionally, the use of expensive porous transport layers (PTL) and/or complex flow field designs increases both PEMWE and AEMWE system cost relative to AWE.

The fourth approach to water electrolysis operates at higher temperatures using solid oxide electrolysis cells (SOEC). The SOEC technology is based on the use of a dense ceramic electrolyte that conducts oxygen anions from the cathode where hydrogen is generated to the anode where oxygen is generated. Owing to the low conductivity of such ceramics at low temperature, SOEC are operated at high temperatures of ~ 800 °C. The use of high temperature benefits both the chemical kinetics and thermodynamics, which results in improved efficiency, but also leads to accelerated degradation. SOEC also suffer from mechanical stress placed on the dense ceramics by the pressure differential. The following report will focus primarily on the three low-temperature technologies (AWE, PEMWE, and AEMWE) and the reader is directed to Section 9 for more discussion on SOEC systems.

Figure 1.2 compares practical characteristics of AWE, PEMWE, and SOEC technologies with a spider map (AEMWE technology is not included owing to its early stage of development). While the membrane technologies, PEMWE and AEMWE, are considered to be better suited to the transition to an energy system based on intermittent, renewable electricity, none of the above water electrolysis technologies in their current form meet the requirements for sustainable hydrogen production at scale required for sustainable fuel and chemical production [1].

1.3 Future research needs

Based on the challenges facing current water electrolysis technologies outlined above, we have defined the following three key research needs that require attention in the near future.

1.3.1 Decreasing iridium usage in PEMWE anodes

As discussed above, decreasing the usage of iridium at the PEMWE anode by a factor of 50 is a critical requirement for the technology to make an impact at the global scale. Shown in Figure 1.3 are two distinct research directions that can address this challenge:

- Discovery of a new OER catalyst with improved intrinsic activity and comparable stability

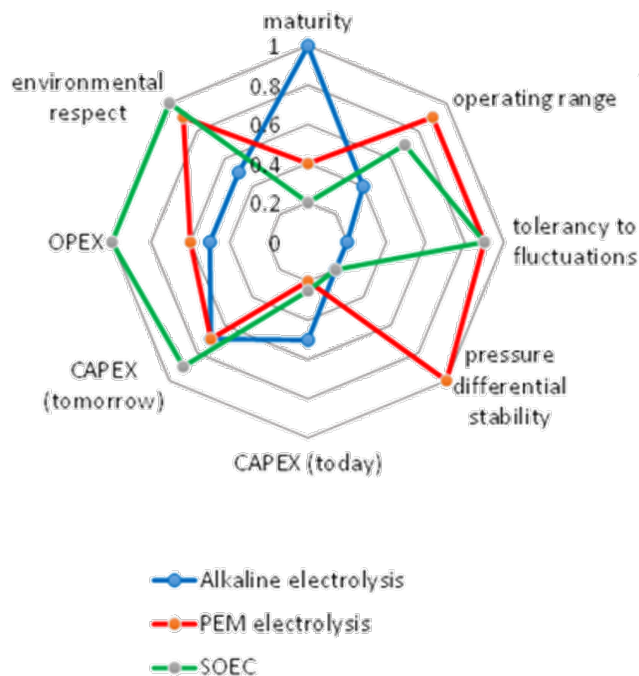


Figure 1.2: Spider map for the three mature water electrolyzer technologies (AWE, PEMWE and SOEC); taken from Section 9.

compared to iridium. This could be achieved by an acid-stable mixed metal oxide, carbide, sulfide, nitride or by substitution with inert metals.

- Better utilization of the catalyst material, which may be obtained by discovery of a new stable and conductive support material (e.g. transition metal nitrides)

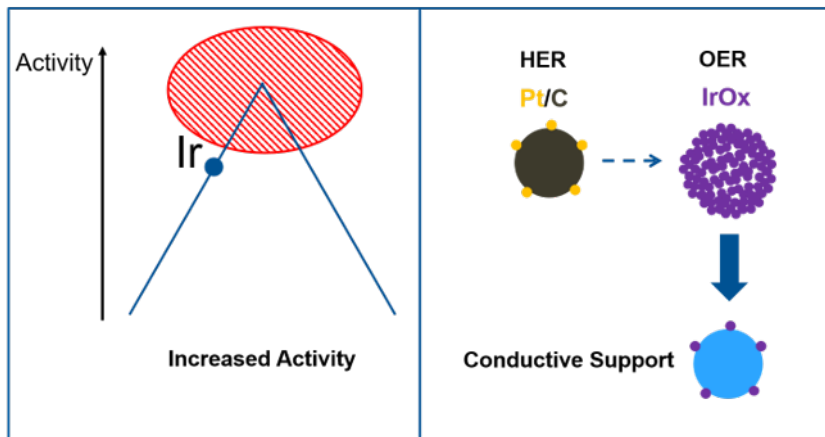


Figure 1.3: Two main research directions for reducing the usage of iridium catalysts: better intrinsic activity and better utilization through the use of a stable and conductive support.

1.3.2 Advancing fundamental understanding of OER electrocatalysis

To surpass the current state of the art materials in terms of both activity and stability, we need in-depth experimental and theoretical insight into the mechanistic pathways and properties of the electrochemical interface under operating conditions. For this, *in situ*/operando measurements are essential to bridge the methodological gap that exists for current computational methods to describe electrocatalysts under realistic conditions. This calls for covering a wide materials spectrum ranging from model systems, such as single-crystalline electrodes, to device-implementable catalyst materials. This also calls for extensive development of new methods including

- ***Photon-based spectroscopies and electron-based spectroscopies and microscopies:*** surface-sensitive techniques with time and space resolution to resolve the catalytic intermediates under reaction conditions
- ***Computational methods:*** more realistic representation of the electrochemical interface and data-driven approaches to discover new materials (see Section 8)
- ***Evaluation of real electrochemically active surface areas (ECSA):*** new chemical probes/approaches that quantify the number of electrochemically active sites. This is especially challenging for oxides and non-metallic materials in general, but it is essential to accurately assess intrinsic catalytic activity.

1.3.3 Optimizing electrolyzer components besides the electrode

The majority of research efforts in water electrolysis today focus on electrode materials, especially the electrocatalyst. Below are other important research directions that should be pursued to improve the overall of current and future devices.

- ***Developing an AEM membrane:*** AEMWE systems represent an improvement over PEMWE systems in that they do not require acid-stable catalysts such as iridium-oxide. However, the current state of the art anion conducting membranes are inferior to proton conducting membranes in terms of conductivity, gas permeability, and, in particular, stability. These challenges may be met by developing: i) ultra-thin membranes, ii) new ion conduction mechanisms inside solids/membranes, iii) mechanical/chemical stabilization based on new chemical backbones/side chains. Additionally, novel approaches to interface engineering should be explored, including the use of new liquid electrolytes as well as solid electrolytes operating at elevated temperatures (100-400 °C) with a water vapor feed.
- ***New porous transport layer and bipolar plate components and design concepts:*** PTLs consist of a thin micro-porous layer (MPL) directly adjacent to a macro porous layer. With the MPL facing the electrode layer to ensure its function as a current collector, PTLs on the anode and cathode control charge and mass transport (water, oxygen, hydrogen) between the membrane electrode assembly (MEA) and the bipolar plates in PEMWE and AEMWE. PTLs on the anode of electrolyzers are typically made of expensive titanium materials, which form insulating oxides over time, leading to increased ohmic losses. This is why, today, PTLs have to be protected by expensive noble-metal Pt and Ir coatings. A similar problem exists for the bipolar plates. This explains why bipolar plates and PTLs are responsible for the bulk of today's electrolyzer stack cost. To meet these challenges, novel inexpensive ultra-thin MPL, PTL and Bipolar Plate materials with high electrical conductivity, high corrosion stability, and good mechanical stability must be developed. New PTL morphologies may include meshes, fleeces, or layered expanded metal alloys could be used to realize flow-field less plate designs. In addition, tailored noble-metal free anti-corrosion coatings are needed to prevent surface oxidation of the PTL bulk material [3]. In addition to the cost and ohmic resistance challenges of today's bipolar plates and PTLs, the formation of gas bubbles on the electrode surface limits the over efficiency of electrolyzer cells. In order to lower the local bubble formation at the catalyst surface, future MPL/PTL design must be designed with a balance between hydrophobicity and hydrophilicity . Promising approaches include expanded porous Teflon sheets (GoreTex) adjacent to electrode layers which allow for the gas to penetrate, yet prevent liquid water from crossing thereby preventing bubble formation at the catalyst [4].

- ***Harmonization of test protocols and experimental best practices:*** Development of accelerated stress tests specific for different cell components and establishing standards for measuring electrochemical surface area and reporting surface specific activity.
- ***Computational multiscale modeling of membrane electrode assembly structure:*** Current modeling efforts are primarily focused on atomistically describing the electrochemical interface. Multiscale modeling of the entire electrochemical cell will aid in the rational design of new cell and stack architectures, which is especially important when scaling up new technologies (see Section 9).
- ***Exploring self-healing materials and mechanisms:*** to break the activity/stability compromise for OER catalysts, the notion of self-healing materials needs to be explored on a more fundamental level using techniques that follow corrosion and degradation at the atomic scale. This could be done with the use of identical-location electron microscopy or by coupling ICP-MS with gas detection techniques to estimate the faradic efficiency for a given catalyst.

1.4 Specific research goals

Table 1.1 lists important performance metrics for current state of the art AWE and PEMWE technologies as well as targets that should be achieved in the next ten years.

1.5 Conclusion

Two mature low temperature water electrolysis technologies currently exist, AWE and PEMWE. To make these technologies viable on a global scale, their advantages must be combined. For AWE, the primary advantage is the usage of cheap materials thanks to the alkaline environment. For PEMWE, the primary advantages are higher current densities and superior performance under dynamic loads. These advantages can all be realized in a single device by either developing a suitable anion conducting membrane or by reducing or replacing iridium usage in acidic environments (Figure 1.4). Both of these strategies rely on improved fundamental understanding of material structure-property relationships obtained via *in situ*/operando experiments and first principles simulation. Even the best known OER catalysts to date have non-negligible overpotentials, and furthering fundamental understanding may also lead to the discovery of OER catalysts with improved activity. While the majority of research efforts in water electrolysis today focus on electrode materials, we have identified other important research directions that should be pursued to improve overall performance of current and future devices.

Table 1.1: Summary of performance metrics that are currently attainable and targeted by 2030 for AWE and PEMWE technologies. Data from reference [5].

No	Parameter	Unit	State of the art		Targets
			AWE	PEMWE	2030
System and Stack					
1	Electricity consumption @nominal capacity	kWh/kg	51	53	43
2	System Capital cost	€/(kg/d) €/kW	1,600 750	1325 600	<720 <400
3	Cell voltage @nominal capacity	V	1.9	2.0	1.6
4	Hydrogen Cost	€/kg	5-10	5-10	<2
5	Stack cost	€/cm ² €/kW	1 1000	1.3 325	0.5 160
6	Catalyst Mass Activity @ 1.6 V _{cell} ~1.5 V _{IR free}	A/g	8-20	1 300	63 000
7	Geometric Catalyst Loading	mg _{metal} / cm ²	-	2.000 (Ir) 0.500 (Pt)	< 0.03 (Ir) 0.05 (Pt)
8	Membrane Resistance	Ohm cm ²	0.83	0.25	< 0.05
9	H ₂ crossover permeability	mA / (cm ² bar _{H2})	20 (500 microns)	1 (50 microns)	0,1 (< 50 microns)
Stack					
7	Degradation	% / 1000 h	0.13	0.250	0.1
8	Current density @nominal capacity	A/cm ²	0.5 @ 2.0 V _{cell}	2.0 @ 2.0 V _{cell}	2.0 @ 1.6 V _{cell}
9	Use of critical raw materials as catalysts	mg/W	0,73 (Co)	0,5 (Ir, Pt)	0.01 (Ir, Pt)

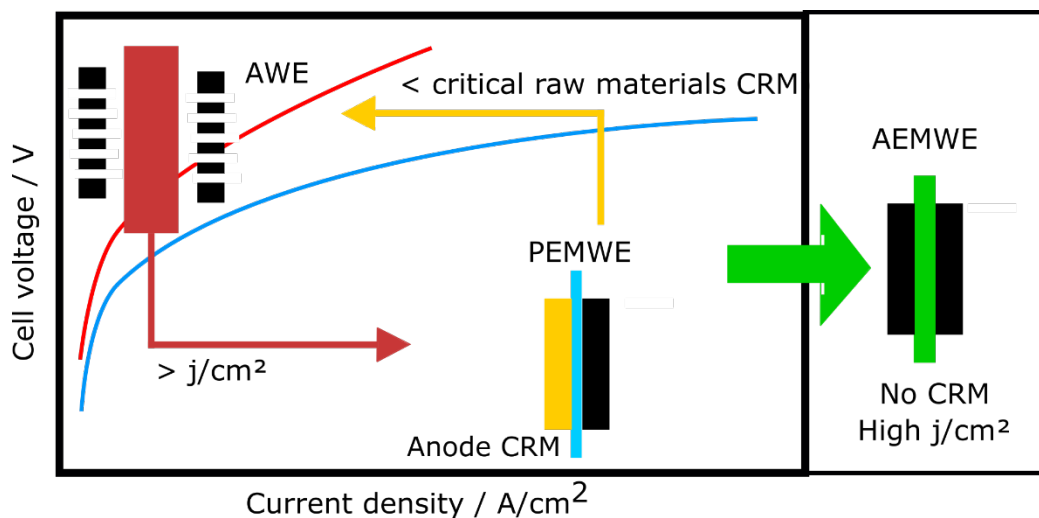


Figure 1.4: Foreseen improvement for low temperature water electrolysis technologies by reducing the amount of critical materials used in PEMWE and/or by increasing the current density for alkaline electrolyzer through the use of anion conducting membrane.

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Section 2

Electrochemical CO₂ reduction

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2.1 Importance of subject

The electrochemical conversion of CO₂ to fuels and chemicals via renewable electricity is an attractive and sustainable alternative to the mass utilization of fossil resources. Such a process has the potential to drive the transition towards a new green economy based on a cyclic CO₂-neutral production and utilization of fuels and chemicals (Figure 2.1). At the center of this cycle is the electrochemical CO₂ reduction reaction (CO₂RR), which mimics photosynthesis

but uses artificial materials and processes that allow for a more efficient large-scale implementation. This reaction provides a pathway for using intermittent, renewable electricity to produce fuels and chemicals. Operating at ambient temperatures and pressures, it is highly modular and easily scaled up through stacking, making it attractive for decentralized operation. Furthermore, CO₂RR can be combined with a suitable non-sacrificial oxidation processes (“paired electrolysis”), so that further valuable products can be produced.

The role of CO₂RR in the bigger picture of a sustainable fuels and chemicals economy is illustrated in Figure 2.2. As shown, valuable multi-carbon fuels/chemicals can be produced either directly via CO₂RR or by first generating chemical feedstocks via CO₂RR (e.g. CO and formic acid) that are then fed into other electrochemical or thermal catalytic processes. There are thus important cross-cutting aspects relating CO₂RR to its thermal counterpart (Section 3), syngas conversion

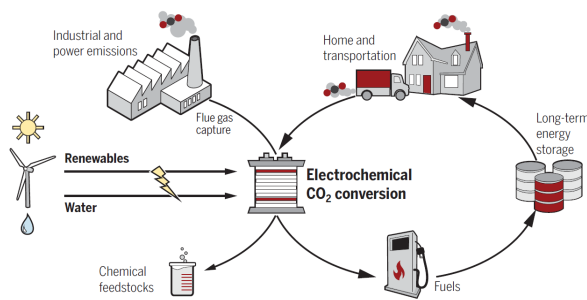


Figure 2.1: Electrochemical CO₂RR powered by renewable sources. Reproduced with permission from [1].

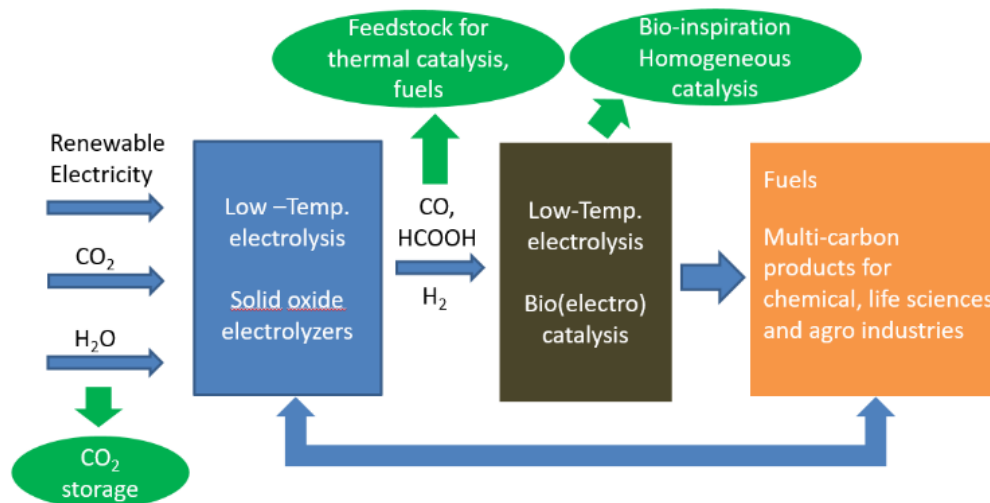


Figure 2.2: Role of CO₂RR in the grand scheme of sustainable fuels and chemicals.

(Section 4), water electrolysis (Section 1), CO₂ capture (Section 10), bio-inspired catalysis (Section 7), and homogeneous catalysis (Section 6).

2.2 State of the art and scientific challenges

The most common CO₂RR products are two-electron products, namely CO and formic acid, and can be generated by several molecular and heterogeneous catalysts (e.g. silver for CO production) at high rates and faradaic efficiencies. CO is a particularly important target product for the chemical industry, as it is widely employed in several large-scale industrial processes, such as the Fischer-Tropsch synthesis of liquid fuels, the production of methanol, the Monsanto/Cativa acetic acid synthesis, and the hydroformylation of olefins to aldehydes and alcohols (see Sections 3, 4, and 6). Moreover, electrochemical CO₂-to-CO has also attracted growing interest for applications in organic synthesis, where CO produced *in situ* may be used for a wide variety of carbonylation reactions [2].

The formation of further reduced products, such as multicarbon alcohols and hydrocarbons (C₂₊), is even more attractive due to their higher energy content and importance as chemical feedstocks. Ethylene is a particularly attractive target molecule since it is essential for the industrial production of plastics, detergents, and agricultural products, and state of the art systems have demonstrated impressive energy efficiency and reaction rates for ethylene production, but long-term stability needs to be significantly improved. Copper-based heterogeneous materials are the only catalysts reported so far that can catalyze the electrochemical conversion of CO₂ to C₂ hydrocarbons and oxygenates with non-negligible selectivity. However, the selectivity is still too low and the overpotential too high for practical applications. In addition, the catalyst surface has been shown

to restructure under reaction conditions, negatively impacting performance over time. Studies of nanostructured catalysts have identified particle size, shape, roughness, defect density, and metal composition as the main factors that govern CO₂RR activity and selectivity (Figure 2.3) [3–5]. Environmental conditions (e.g. local pH, electrolyte, electric fields) have also been found to play a crucial role in determining the CO₂RR selectivity [5], but understanding many of these effects from a mechanistic perspective remains a challenge.

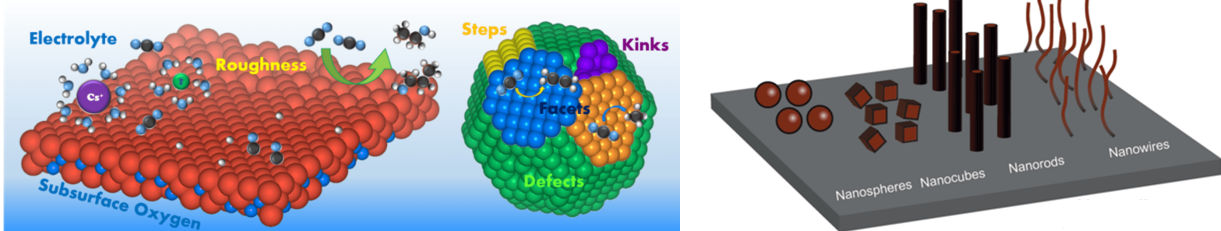


Figure 2.3: Schematic of the parameters influencing the activity and selectivity of CO₂RR catalysts. Reproduced with permission from [3] and [5].

Most current CO₂RR studies are performed in H-type cells with CO₂ dissolved in an aqueous electrolyte, which means the upper bound of the reaction rate is limited by the low solubility of CO₂ regardless of catalyst performance. The field has begun moving closer to practical applications by studying complex electrode assemblies and cell designs that employ gas-diffusion electrodes and allow operation at industrially relevant current densities ($>100 \text{ mA/cm}^2$) [6]. The first multi-stack CO₂ electrolysis cell has also been recently demonstrated [7].

2.3 Future research needs

For CO₂RR to become competitive with the fossil fuel-derived industry, its energy efficiency, reaction rate, selectivity, and long-term stability should be comparable to water electrolysis. A longer-term goal is to advance these metrics for CO₂RR to those of the thermal catalytic conversion processes considered in Sections 3 and 4. To reach these goals, the development of novel catalysts, suitable and stable membranes, electrolytes, gas-diffusion layers, and electrolysis cell architectures are key challenges. To this end, we propose five critical research areas that deserve attention in the near future.

2.3.1 Improving catalyst activity, selectivity, and stability

Sufficient enhancements in energy efficiency require operating at significantly lower CO₂RR overpotentials than the state of the art. For C₁ products, cascade cell operation having CO as intermediate product would require achieving catalyst efficiencies of up to 70%. Different approaches can be un-

dertaken in order to develop more active and selective CO₂RR electrocatalysts, including tuning the catalyst surface morphology, surface composition, and interaction with the electrolyte. Hybrid approaches combining heterogeneous and molecular catalysts may be especially interesting for improving selectivity.

An important aspect of improving selectivity towards carbon products requires quenching the hydrogen evolution reaction (HER), which concurrently takes place under CO₂RR conditions. Additionally, the selective production of any single multi-carbon product is rarely achieved. Overcoming these challenges necessitates a better understanding of the roles of pH gradients near the electrode surface, mass transport, local buffering capacity, electrode charge, and local mesoscale electrode architecture on the overall performance of porous, high surface area electrodes. If sufficiently selective catalysts for particular products remain elusive, the integration of efficient separation technologies may be needed.

Towards improving stability, a deeper understanding of the dynamic evolution of electrode structure and surface composition at the atomic-scale is necessary. Control of catalyst structure for thousands of hours of CO₂RR operation is already an immense challenge that will only be enhanced once intermittent operation due to renewable energy sources is considered. In general, the stability of electrode surfaces under large cathodic overpotentials (“cathodic corrosion”) is relatively unexplored and needs to be addressed at a more fundamental level, combining theory and experiment (Figure 2.4).

2.3.2 Advancing fundamental understanding of CO₂RR: *in situ* techniques

Many of the major challenges in this field arise from the general lack of fundamental understanding of the reaction mechanism for the most active and complex catalysts, hindering the design of improved electrode/electrolyte systems. To rationally design an efficient catalyst, one must be able to evaluate candidates under realistic reaction conditions. Along these lines, the development of improved *in situ* and operando microscopic and spectroscopic characterization techniques is

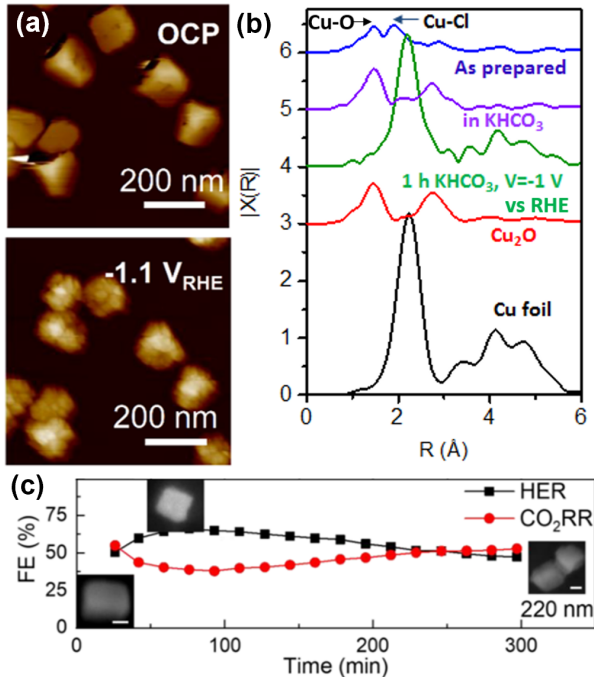


Figure 2.4: (a) Operando EC-AFM images of Cu cubes acquired in 0.1 M KHCO₃ at open circuit potential (OCP) and at -1.1 V vs RHE for 1 min. (b) EXAFS data of these samples acquired in air, in the electrolyte under OCP and operando after 1 h CO₂RR at -1 V vs RHE. (c) Temporal evolution of the faradic efficiency for CO₂RR and HER of Cu Cubes (-1 V vs RHE). Adapted with permission from [8].

highly desirable. Ideally, these techniques would be compatible with industrially relevant reaction conditions (high current densities, high pH, light illumination, gas-diffusion electrode). These techniques would not only shed light on questions related to the reaction mechanism through the identification of reaction intermediates such as those illustrated in Figure 2.5, but they would also provide a route to correlate activity and selectivity with material structure and composition [8–10].

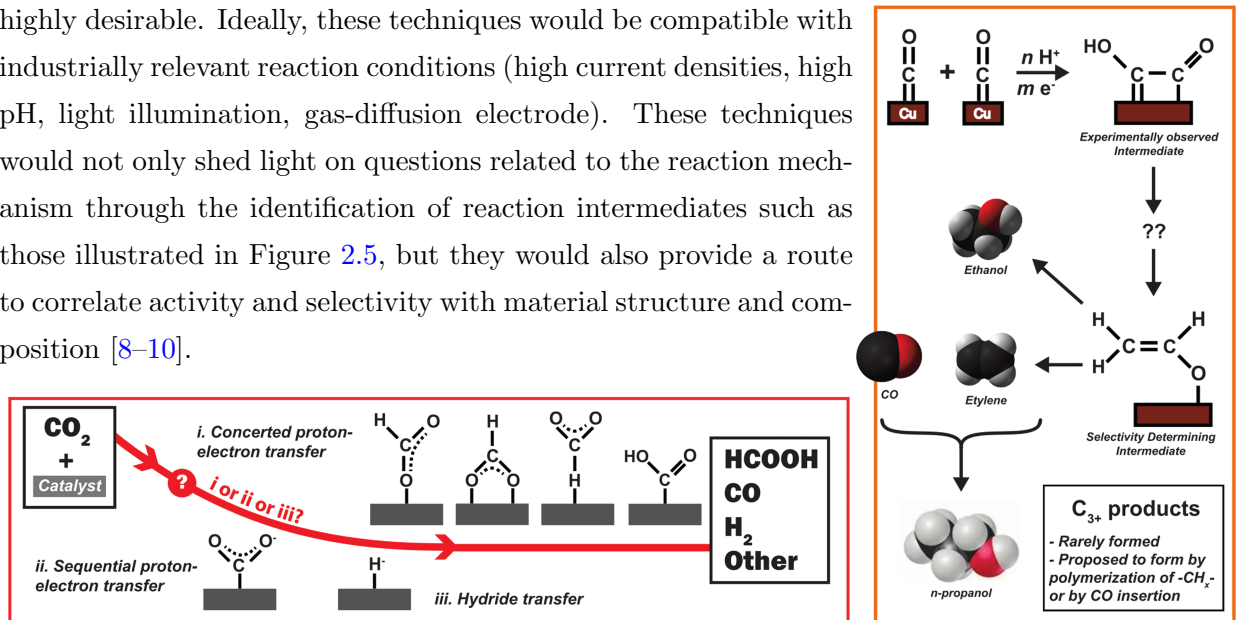


Figure 2.5: Key reaction mechanism questions in CO₂RR. Reproduced with permission from [5].

Simultaneously, fundamental understanding of the CO₂RR under relevant process conditions will be aided by the design of well-defined and well-characterized electrode architectures (e.g. prepared by colloidal or solvothermal routes, electrochemistry or nano-lithography) for optimal control over the interplay between surface electrocatalysis and chemical potential gradients existing in the electrolyte.

2.3.3 Advancing fundamental understanding of CO₂RR: theoretical methods

A core cross-cutting goal is the advancement of existing theoretical methods in concert with the *in situ* and operando experimental techniques described above. Advances are needed in the realistic *ab initio* modeling of electrode-electrolyte interfaces (including explicit solvent, electrolyte ions, and electrolyte-driven surface reconstructions) as well as in the coupling of atomic-scale mechanistic insights to reaction kinetics and mass transport phenomena at longer length scales with the ultimate goal of elucidating critical activity and selectivity descriptors for high-value products (Figure 2.6).

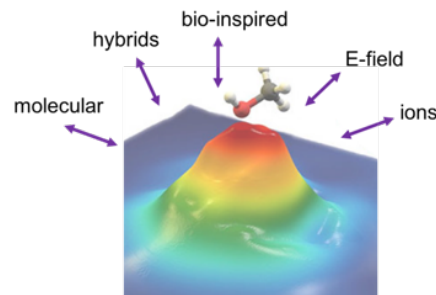


Figure 2.6: Descriptor-based approach to catalyst discovery. Adapted with permission from [11].

Mass and heat transport phenomena and water management should be explored with larger-scale, continuum models of porous electrodes and full cell and stack-level models. Validation of theoretical models will crucially depend on high-quality experimental data on well-characterized systems

and on the dedicated and synergetic collaboration between theoretical and experimental groups. Theoretical models should also be used to consider less conventional areas and process conditions, e.g. exploring novel electrode materials beyond copper and silver.

2.3.4 Optimizing device performance and scale-up

As discussed above, flow cells with gas diffusion electrodes that operate at practically relevant current densities (>100 mA/cm²) have started to emerge. As electrode assemblies that can sustain higher current densities become available, they should be tested in larger scale electrolyzers (up to 1 kW) using standardized and commonly agreed upon protocols. This should result in system-wide stable components with larger electrolyzer areas, possibly including stack configurations. Consideration of cell components other than the catalyst (e.g. membrane, electrolyte, cell architecture) is also essential. In particular, stable anion exchange membranes with affinity to CO₂ are still lacking. Simultaneously optimizing every piece of the CO₂RR process will require effective cooperation among catalysis design, interfacial electrochemistry, materials science, and chemical engineering, and thorough consideration and integration of upstream (CO₂ capture, see Section 10) and downstream processes (product separation and conversion of e.g. CO or formic acid by thermal catalysis or microbial electrochemistry to higher-value products). For example, most preliminary CO₂RR applications and studies rely on the availability of concentrated CO₂ from industrial point-sources and the assumption of clean CO₂ streams. A future challenge would be efficient operation using mixed gaseous streams or CO₂ from direct air capture. Dynamic and intermittent operation of catalysts and systems will be another crucial aspect for the successful implementation of this technology. Further discussion on such system design issues are given in Sections 9 and 10.

2.3.5 Exploring novel systems and reaction conditions

To accelerate progress in the field, new ideas should be pursued, such as operation at high pressures (including supercritical CO₂), at intermediate to high temperatures, and in non-aqueous solvents and unconventional electrolytes and with novel membrane architectures. There are exciting opportunities to learn and gain inspiration from mechanistic insights obtained in neighboring fields (e.g. thermal heterogeneous catalysis, enzymatic and microbial catalysis, homogeneous/molecular catalysis) and to explore hybrid catalytic approaches.

2.4 Specific research goals

Table 2.1 summarizes practical goals for the CO₂RR community moving forward. In the next 5 years, significant progress should be made on the development of CO₂ electrocatalysts and electrolyzers for CO and formic acid production, culminating in devices that operate at relevant current

Table 2.1: Roadmap for CO₂RR.

	State-of-the-art	5 years	10 years
Catalysts	Ag, Cu, Fe- and Co-based molecular catalysts	Metallic, non-metallic, molecular, bio & hybrid	
Current density	100-300 mAcm ⁻²	500 mAcm ⁻²	1000 mAcm ⁻²
Stable cell V	3.0 V	2.5 V	2.0 - 2.2 V
Faradaic Efficiency	95% for CO & HCOOH 60-70% C ₂ H ₄	100% for CO & HCOOH	Other products with reasonable FE
Single-pass Efficiency	10-30 %	40%	60%
Stability	> 100 h	> 1000 h	> 10000 h
Practical Deliverables		EU test beds with realistic feedstocks, EU labs for testing & benchmarking 1KW electrolyzers	Pilot plant industrial electrolyzers for CO, HCOOH and C ₂ H ₄ (10,000 t/year), Pilot scale plants for value-added products (halides, H ₂ O ₂ , organics) & intermittent electricity supply

densities (>100 mA/cm²) with high Faradaic efficiency and good stability (>100 hours). Simultaneously, “niche” applications for CO₂RR to higher-value products should be identified. For instance, CO₂RR might be combined with other conversions (paired electrolysis to produce value-added products at the anode at reduced energy cost, cascade and tandem systems, thermal catalysis, organic synthesis, microbial electrocatalysis).

In the long term (5-10 years and beyond), emphasis should be placed on the synthesis of high-density fuels and other high-value chemicals (Figure 2.7) at commercially relevant current densities (500-1000 mA/cm²) [12]. Consideration should be given to integrating electrochemical CO₂ reduction processes with industrial processes (e.g. Fischer-Tropsch), microbial “upgrading”, separation, and other downstream operations as well as the integration with upstream CO₂ capture.

To achieve these practical goals, benchmarks will need to be defined for each component of the cell, e.g. catalyst, membrane, ionomer, electrolyte, gas-diffusion layer, and cell frame. Life-cycle analysis of these components should be performed, and product separation and materials recycling should be considered.

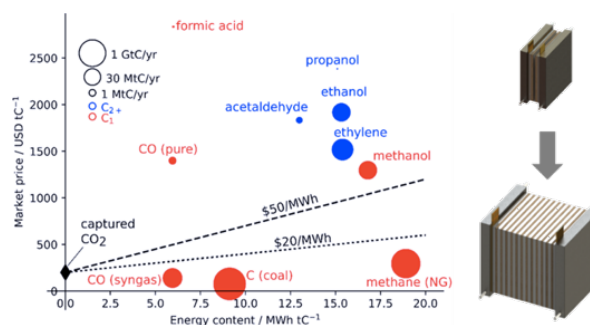


Figure 2.7: High density fuel targets and illustration of cell scale-up. Adapted with permission from [12].

2.5 Conclusion

Electrochemical CO₂ reduction is a key technology in the transition to a CO₂-neutral energy cycle. Impressive advances have been made in recent years in the understanding and formulation of electrocatalysts with suitable activities and selectivities, and the field is moving towards implementing and testing these catalysts in real systems with realistic current densities. However, challenges lie in the fundamental understanding of the reaction mechanism, which is essential for the rational design of the next generation of catalysts. Achieving these elusive fundamental insights will require the synergistic coupling of *in situ*/operando characterization with multi-scale modeling of the electrode/electrolyte interface. Optimizing the long-term stability of electrodes and other cell components will be another crucial scientific and technical challenge to be addressed. Exciting opportunities lie in the interplay between electrochemical CO₂ reduction and related scientific fields and technologies, including organic chemistry, inorganic chemistry, biochemistry and biotechnology, polymer and membrane science, chemical engineering, and process technology.

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Section 3

Thermal CO₂ reduction

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3.1 Importance of subject

Here, we examine the possibility of reducing the CO₂ burden in the atmosphere by considering new, thermally-catalyzed approaches to utilize captured CO₂ directly (Section 10) by making fuels and chemicals. The thermodynamic stability of CO₂ can be overcome when reacted with hydrogen (which should be provided by renewable energy powered water electrolysis (Section 1) and suitable catalysts, rendering accessible a multitude of options for CO₂ conversion (Figure 3.1). All such options are suitable routes for the chemical recycling of CO₂ in the context of carbon capture and utilization (CCU) concepts (reference to carbon cycle in introduction). In particular, many of these chemical transformations produce non-fossil (i.e. renewable) fuels and can thus contribute substantially to chemical storage of volatile renewable energy. Considering the large scale required of energy storage technologies as well as their technical feasibility, we have chosen to focus on the following CO₂ conversion technologies: CO₂ to methanol, CO₂ to synthesis gas, CO₂ to methane, and CO₂ to bulk and fine chemicals.

3.2 State of the art and scientific challenges

There already exist technologies for each of the aforementioned chemical conversions of CO₂. However, these processes largely require high temperatures and pressures and thus centralized production to be economical. The development of technologies that require lower temperatures and pressures would facilitate decentralized production and thus greater compatibility with electrochemical hydrogen feedstocks. Some of these existing hydrogenation technologies, e.g. those involving synthesis gas chemistry (Section 4), serve as a feasible starting platform for new CCU processes.

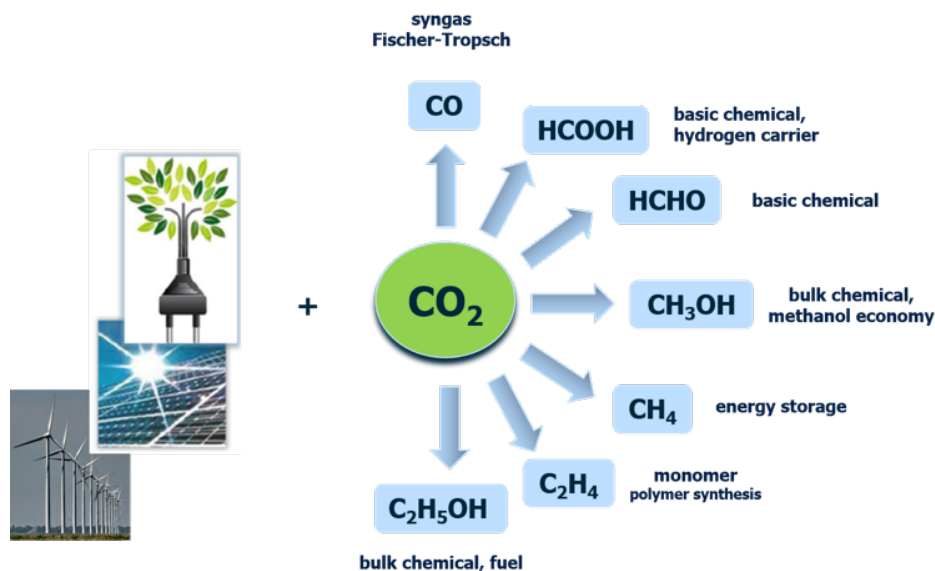


Figure 3.1: Overview of promising options for thermo-catalytic conversion of CO₂ if combined with hydrogen as a renewable reductant.

However, even these developed technologies will be required to face the challenges associated with renewable energy feedstocks. Besides decentralization in small units, these include intermittent operation and use of abundant catalyst materials. The state of the art and challenges associated with renewable conversion of CO₂ to methanol, synthesis gas, methane, and bulk and fine chemicals are covered below in more detail.

3.2.1 CO₂-to-Methanol

Methanol is an important commodity chemical with great potential as a fuel or hydrogen carrier and thus a preferred target of CO₂ hydrogenation [1]. Today methanol is synthesized industrially from CO₂-containing CO/H₂ synthesis gas originating from fossil sources using catalysts based on copper, zinc oxide and alumina. As it is known that CO₂ is converted much faster than CO in this process for the current industrial catalyst, it may be argued that a large-scale, mature industrial CO₂ conversion process already exists (i.e. $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$, $\Delta H^\circ = -49.8$ kJ/mol). In fact, CO₂ to methanol synthesis has already been developed to the level needed for the realization of certain demonstrator plants. In particular, a plant is operational in Iceland, and a plant developed in Germany as an Horizon 2020 project is newly operational [2] and planned to be scaled-up in China (Figure 3.2).

Unfortunately, this technology is not ready to be used to meet our future energy goal of decentralized conversion of CO-free CO₂/H₂ feeds from CCU (Section 12). Because the methanol synthesis reaction from CO₂ is subject to the strong equilibrium limitations imposed by the 220-250 °C required by current catalysts, the process requires high pressures of synthesis gas (50-100

bars). Additionally, the coupled product, water (or related adsorbed oxygen species at the catalyst surface), kinetically inhibits the catalyst’s activity. The latter is mediated in the industrially employed CO_2 -containing CO/H_2 synthesis gas feeds by CO functioning as a scavenger for water and surface oxygen species (i.e. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$). Thus, the overall reaction in the presence of CO becomes $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$, such that minimal CO_2 is net consumed. The forward water gas shift reaction thus plays an important role in conventional methanol synthesis, but the same reaction lowers the selectivity in CO_2/H_2 feeds because the reverse shift sets in and competes for the hydrogen in the feed. Thus, while the industrial methanol synthesis process and its catalyst serve as a mature starting point, further research efforts will be required to realize an efficient CCU process leading to methanol.

In particular, advances in understanding the state-of-the-art $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst are likely to help the field progress [4]. Despite intensive research, there are still many unknowns in terms of the reaction mechanism and roles of the various components in the catalyst. Fundamental research is also needed to develop new materials for example by particle size control [5], better Zn-promotion [6], efficient new promoters [7] or novel bi-metallic catalysts [8, 9].

3.2.2 CO_2 -to- CO

Because synthesis gas (CO/H_2) feeds are compatible with mature conventional synthesis gas processes such as unmodified methanol synthesis, Fischer-Tropsch synthesis (FTS) [10, 11] and possibly higher alcohol synthesis (HAS) [12], developing technologies to efficiently convert CO_2 to CO represents another promising route to fuels and chemical production from CO_2 . As an alternative to co-electrolysis, renewable hydrogen can be reacted with CO_2 to produce synthesis gas feeds (CO/H_2) via the reverse water gas shift reaction (RWGS: $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$). However, for such product streams to be compatible with conventional processes such as methanol production, water would need to be removed first. The direct use of CO_2/H_2 feeds in FTS or HAS, for example, will present

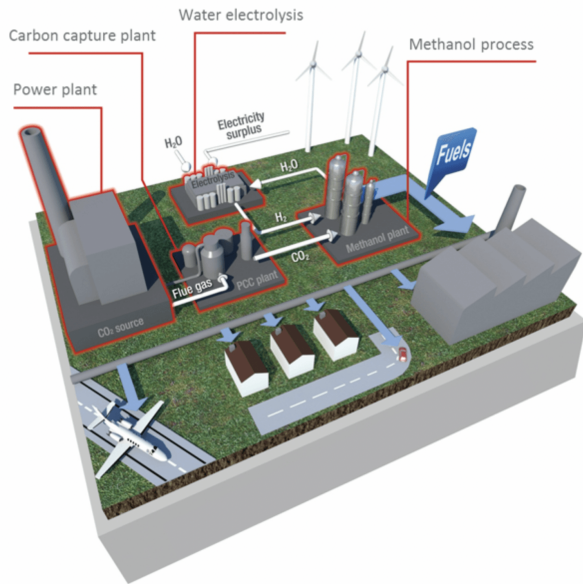


Figure 3.2: The plan of a methanol synthesis plant using solar/wind electricity to produce hydrogen and react it with flue gas from a coal-fired power station [2, 3]. Additionally, downstream processes, such as the methanol-to-olefins process (MTO, Section 4) or direct synthesis of dimethyl ether, can offer further benefit if combined with methanol synthesis in a one-step process (without intermediate condensation and purification) because of the improvement of the CO_2 conversion equilibrium. The light olefins produced by MTO provide a possible route to kerosene through oligomerisation. The potential of such tandem or coupled reactions when paired with new catalyst and reactor concepts, such as operation in the liquid phase, has not yet been fully explored and represents a promising direction for future research.

difficulties for conversion, selectivity, and stability, and will likely require the development of new catalysts. Additionally, while the forward shift is widely applied in industry for cleaning the gas stream from CO, there is no industrial process available for the RWGS. To increase the CO yield, the reaction’s endothermicity suggests higher temperatures should be employed. However, at such temperatures, catalyst stability and suppression of methanation constitute major catalyst development challenges. The so-called CAMERE process in South Korea is an example of a combination of RWGS, water removal and conventional methanol synthesis leading to the net conversion of CO₂ to methanol and demonstrating the general technological feasibility of the process [13], but further research and development is required to reach an economic system. New room for optimization may be found in an alternative two-step route consisting of RWGS followed by water removal and methanol synthesis from pure CO/H₂. This is as opposed to industrial methanol synthesis, in which the feed also contains CO₂. An anhydrous CO to methanol synthesis reaction would be free of the kinetic limitations imposed by site-blocking water species and thermodynamically more favorable ($\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$, $\Delta H^\circ = -91 \text{ kJ/mol}$), which would enable milder conditions. This scenario necessitates further research into the development of catalysts for CO hydrogenation to methanol with optimized activity and stability.

CO₂ can also be reduced by methane to produce syngas via dry reforming ($\text{CO}_2 + \text{CH}_4 \rightarrow 2 \text{CO} + 2\text{H}_2$). This reaction is of special interest when considering production of fuels from biogas. In this context, the impact of biogas composition and purity must also be considered due to possible catalyst poisoning. Another major challenge in dry reforming is the need for abundant catalysts resistant to deactivation by carbon deposits [14]. Operating the dry reforming process under unsteady conditions in a chemical looping mode has shown promise for further breakthroughs in this area [15].

3.2.3 CO₂-to-CH₄

Power-to-Gas is an energy storage technology that consists of the conversion of CO₂ to methane via renewable hydrogen ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$, $\Delta H^\circ = -165 \text{ kJ/mol}$). It constitutes a promising solution for long-term and large-scale energy storage thanks to the readily available natural gas grid, a more than 2 million km transmission and distribution network that includes nearly 800 TWh of underground storage across Europe. CO₂ methanation is operated at about 300-600 °C and moderate pressure. Usually catalyzed by nickel-based supported catalysts, CO₂ methanation has already matured beyond lab-scale. Currently operational demonstration projects based in Europe will provide a basis for the design and economics of full-scale units by yielding information on system flexibility and operation constraints, reactor performance, and long-term catalyst behaviour [16]. Remaining areas for research include addressing robustness against intermittent operation [17] and unsteady state operation [18], and exploring milli- and micro-reactors, sorption enhancement,

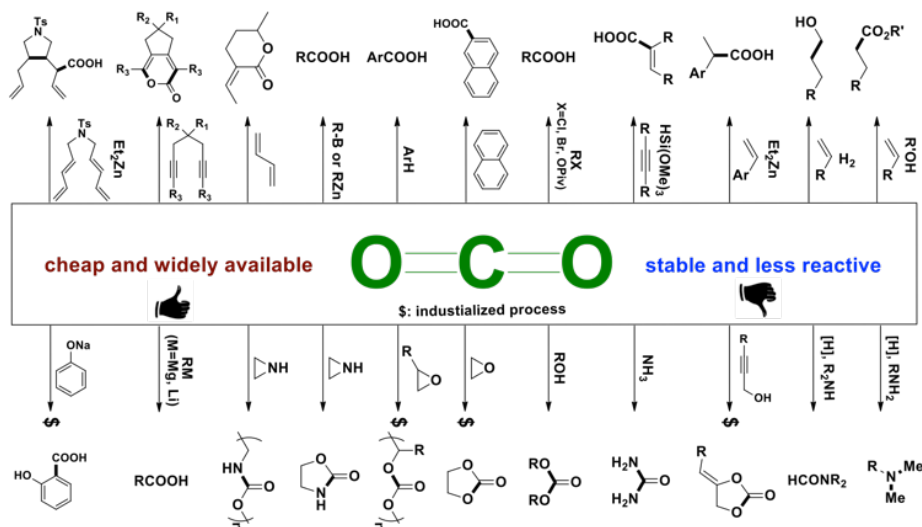


Figure 3.3: Overview of the options to convert CO₂ into chemicals and materials by means other than hydrogenation. Reproduced with permission from [20].

and membrane reactors. Optimization of heat release and management is essential due to the reaction's exothermicity; such work could be appropriately supported by multi-scale modeling [19]. Furthermore, to realize decentralized instances of Power-to-Gas technology, operation at lower temperatures (e.g. < 250 °C) would be valuable. As such work would likely require new catalyst design, i.e. increased activity at low temperature and poison tolerance at these conditions, these are important fields of research that are actively being pursued.

3.2.4 CO₂-to-Materials

At present more than 110 million tons of CO₂ are used to produce chemicals and materials. To significantly increase this number, chemistry in general and catalysis in particular constitute key technologies. To exploit the full potential of CO₂ as a feedstock for fine chemicals and materials, the selective reduction of CO₂ with hydrogen to C1 building blocks, the insertion of CO₂ into chemical structures, and the homologation of CO₂ are important areas to continue directing research efforts. Several such reactions are shown in Figure 3.3.

Co-condensation of CO₂ in polycarbonates and new polyketones are also interesting reactions due not only to the direct CO₂ consumption, but also to the potential for replacement of other high-energy monomers with large carbon footprints. Today, molecularly defined solid catalysts have shown promise in this area [21], but there exist major challenges at the interface of chemistry and engineering that deserve special emphasis (see Section 6). In particular, the implementation of such catalysts, e.g. by transferring their exact molecular environment to heterogeneous single site catalysts, is a current scientific challenge for reaction, catalyst and process design that includes questions of scale-up, product clean-up, catalyst recycling and life cycle analysis.

Small molecule targets of interest include formate and methyl formate [22], as well as light olefins such as ethene, propene, and butenes, which are important building blocks in the manufacture of plastics and rubbers and precursors for a range of industrial chemicals. Presently, light olefins are produced from crude oil, but it is vital to be able to produce them also in a petroleum-deprived future. Furthermore, developing a technology able to utilize CO₂ instead of CO in carbonylation chemistry [23] could pave the way to a C-C coupling method in organic synthesis.

3.3 Future research needs

In several of the aforementioned hydrogenation reactions like methanol synthesis, methanation and FTS (but with the exception of RWGS), the formation of water as a product aids the thermodynamics enough to render the reduction of CO₂ viable. On the other hand, the resulting exothermicity of many CO₂ conversion reactions calls for new catalysts that operate at lower temperatures and/or new reaction engineering solutions that can increase the yields for example by product removal in coupled reactions. Therefore, the crosscutting future research needs with the goal of improved conversion, activity, and selectivity of thermal CO₂ hydrogenations and conversions are several-fold.

3.3.1 Engineering better catalysts

While several of the aforementioned technologies are already in place that are at demonstrator plant level, better catalysts are needed to reach economic viability. By ‘better’ we mean catalysts that (i) operate at lower temperature and/or pressure and (ii) are more hydrothermally stable against water. Research efforts should also then be directed towards examining how developments of type (i) will affect catalyst stability, which might either be higher (lower temperature means lower hydrothermal sintering rates) or lower (water blocking effect). Towards this end, successful catalyst development efforts will rely heavily on continued research in the following areas:

- **Targeted catalyst synthesis.** We need to explore new catalyst materials and new synthesis techniques for known catalysts so that we can more deeply understand the reaction dynamics, such as the role of promoters in catalyst activity, selectivity and stability. With highly accurate catalyst synthesis techniques, correlations can be drawn between catalyst (micro-)structure, composition, and properties. To this end, a framework that bridges from complex high-performance catalysts to highly defined, but functional, model systems is also needed.
- **Modern theory.** Theory can elucidate free energy diagrams and reaction mechanisms for catalysts’ (promoted) active surfaces [24], as shown for example in Figure 3.4, as well as clues to the structure of the active site. Microkinetic modeling can be used to determine key intermediates, e.g. those involved in rate-determining steps, to aid in targeted catalyst development. Machine learning approaches (Section 8) will be important in new materials

screening efforts. As such, theoretical methods should continue to be advanced; to this end, provision of state-of-the-art hardware and software is essential.

- **State-of-the-art characterization.** This area, in particular electron microscopy and spectroscopic methods, has developed and should continue to develop rapidly until we have high resolution at all levels. Atomic resolution of the surface during in-operando conditions is of particular importance. Furthermore, because the catalyst will dynamically change in the presence of the feed, in-situ reactor design should continue to improve such that spatial and chemical resolution is maintained at relevant conditions, [25]. We need to be able to examine the catalyst in detail from the atomic to micro to pellet (e.g. 5 mm cylinders) to reactor tube level. For this purpose, combined facilities and correlative techniques are urgently needed.

The required concerted approach of catalyst synthesis, theoretical modeling and operando experimentation and characterization is schematically represented in Figure 3.5.

3.3.2 Developing new chemistries

While there are ways now of converting CO₂ to simple molecules (such as methanol and CH₄), we also need to advance to more complex molecules and to C-C coupling reactions. Developments are needed in routes to, for instance, formic acid (see Section 6). Considerable developments of the catalysts in these fields will be required to make them feasible on the industrial scale, which will likely require detailed mechanistic understanding.

3.3.3 Engineering new reaction and reactor concepts

New reaction and reactor concepts are needed to face the challenges in thermal CO₂ reduction, such as chemical looping reactors and coupled reaction networks (e.g. coupling methanol synthesis with acid sites to yield dimethyl ether or MTO in a one pot synthesis).

3.3.4 Developing plant design

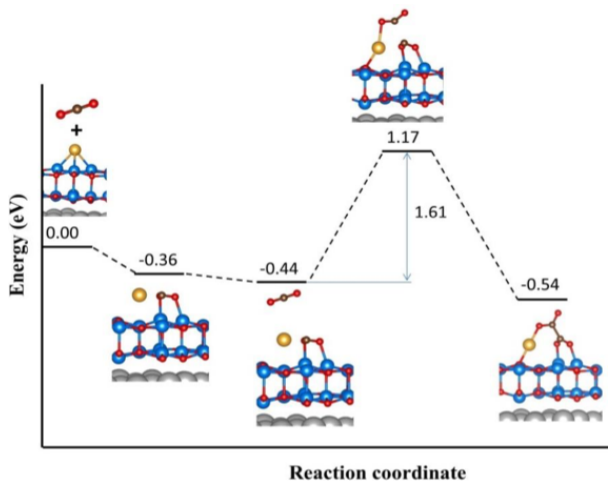


Figure 3.4: Theoretical molecular modeling and calculation of energy pathways for C-C coupling on an advanced model surface. Reproduced with permission from [24].

Plant design developments are required for a number of reasons. First, methods are needed to mitigate the effects of water (membrane reactors, new types of distillation columns, water separation/extractions units/methods). Also, the scale for localized production may need to be reconsidered, especially for semi-tech, pilot and demonstrator plants. Funding should be available for academic use of central pilot plant facilities (similar to the operations of synchrotrons), and more demonstrator projects for the various areas of CO₂ conversion given in this report should be initiated.

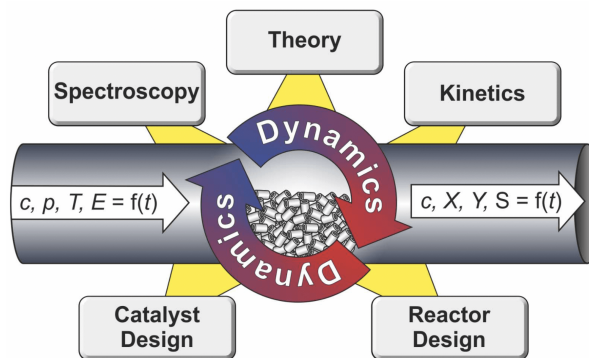


Figure 3.5: Integration of multiple disciplines essential to progress in catalysis. A dynamic change in reaction parameters, e.g. concentration (c), pressure (p), temperature (T), and potential (E), alter the product stream, e.g. conversion (X), yield (Y), and selectivity (S). Adapted from [26].

3.4 Specific research goals

Some specific goals for the thermal CO₂ reduction reactions discussed above are given below depending on the current maturity of the respective technology.

5-year goals:

- Implementation of methanation technology for energy storage via Power-to-Gas based on the current demonstrator projects and identification of the best heat integration system
- Demonstration of modular concepts based on microreactor technologies
- Development of a new methanol and methane synthesis catalyst from CO₂ operating below 200 °C
- Explorative evolution of a catalyst for industrial RWGS and for methanol synthesis from CO
- Demonstration of the potential of chemical looping for RWGS and dry reforming
- Demonstration of the potential of coupled reaction systems via methanol from CO₂
- Lab-scale development of new and better catalyst systems for the transformation of CO₂ into chemicals and materials
- Complete understanding of methanol and methane synthesis from CO₂ over copper- and nickel-based catalysts for further rational optimization by comprehensive modeling and robust operando observations at high pressure

10-year goals:

- New FTS catalysts for selective and stable operation in CO₂/H₂ feeds, e.g. stabilization of iron carbide catalysts at high CO₂/H₂O partial pressures
- Direct synthesis of dimethyl ether from CO₂/H₂ feeds
- Predictive design of CO₂ hydrogenation catalysts and their transient behavior
- Evolution from pilot plants to full scale for methanation and methanol synthesis
- Demonstration of an industrial RWGS process with downstream CO conversion to methanol
- Piloting new CO₂ converting processes for materials and chemicals
- New dedicated catalyst composites for coupled reactions and chemical looping reactors

3.5 Conclusion

The preceding discussion has highlighted a range of excellent opportunities for the production of chemicals, fuels, and materials derived from CO₂ and sustainable hydrogen. Today, several of the presented technologies are within reach, with several having already been developed into demonstrator projects. However, further research on the synthesis of new catalysts, which is coupled to developments in state-of-the-art synthesis, theory, and characterization, and on reaction and reactor engineering concepts, is urgently needed.

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Section 4

Thermal processes for syngas to fuels and chemicals

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4.1 Importance of subject

The catalyzed conversion of CO, CO₂, and H₂ (syngas) has evolved over the last decades to be one of the pillars of the petrochemical and synthetic fuel industries. The reaction's attractiveness lies in its straightforward adaptability, its impressively versatile catalytic chemistry, and the large variety of carbon-based feedstocks that can be used to produce syngas [1]. However, the high investment costs associated with the generation of syngas mean that production at large scale is currently required for economic operation. The availability of economically-competitive, renewable hydrogen will radically change these boundary conditions, allowing the realization of competitive, decentralized processes to power the endothermic carbon conversion and provide the chemically-required balancing H₂. This makes syngas chemistry a key technology, translating sustainable energy harvesting to the existing technologies using hydrocarbons as energy carriers.

4.2 General scientific challenges and future research needs

The high importance of syngas chemistry to access petrochemicals and intermediates via reforming of coal, naphtha, natural gas, and bio-derived oils has led to a broad variety of large-scale processes that, together with oil refining, form the backbone of today's petrochemical industry. Despite this success in industrial realization, severe challenges exist for all processes, the resolution of which crucially depends on atomistic and molecular understanding of dynamic changes of the catalyst under operation and on the development of appropriate reactor systems. Such challenges are

illustrated by the long-standing mechanistic puzzles in Fischer–Tropsch synthesis (FTS), including (i) the higher reactivity of low-index metal surfaces; (ii) the effect of water on turnover rates and selectivity; (iii) the infrequent initiation, but rapid growth of hydrocarbon chains; (iv) the activation of refractory and strongly-bound CO at modest temperatures; (v) the difficulty to control temperature and mass transfer phenomena at the reactor level. Together with the constantly changing nature of the active catalyst surfaces these questions illustrate the complexity that needs to be addressed to advance understanding from the present level and develop the required processes.

The anticipated changes of the currently highly centralized refining and petrochemical industry into decentralized units that link renewable energy harvesting to storage in chemical bonds will lead to drastically different boundary conditions for sustainable production of fuels and chemicals. Sustainability demands the minimization of energy and materials use and waste production, a neutral or negative CO₂ footprint, and the avoidance of generation and emission of (other) green-house gases. The transition to distributed manufacturing of fuels and chemicals requires the development of new processes at flexible (lower) scales, in addition to strategic improvements in existing and anticipated large-scale processes (Figure 4.1).

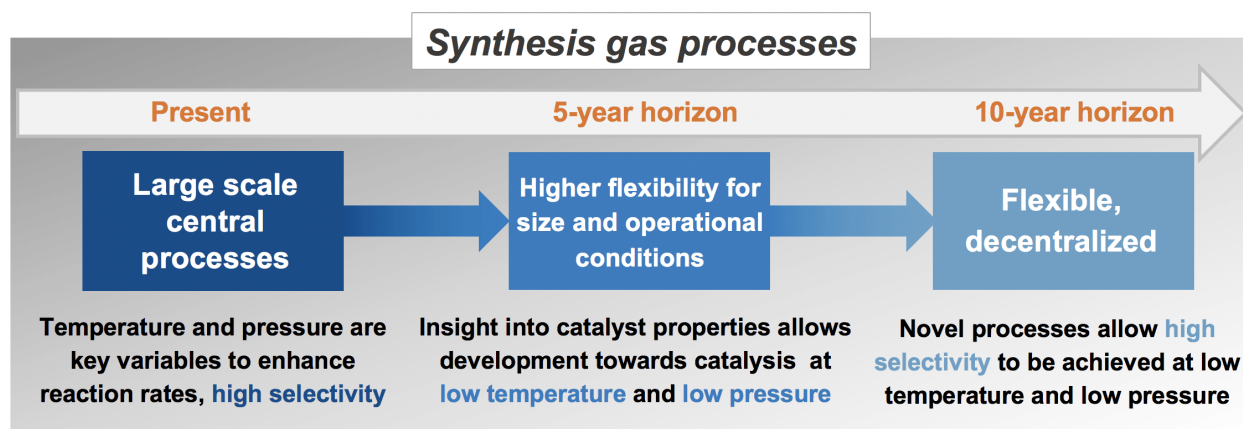


Figure 4.1: Development trajectory for decentralized chemical and fuel manufacturing.

- For all syngas related processes, at least an order of magnitude higher rates of reaction at lower temperatures will be required to substantially increase conversion per pass to near complete conversion of at least one of the reactants.
- The higher rates need to be combined with higher selectivity, which can be controlled by engineering the free energy landscape to minimize the heights of free energy barriers while maintaining specificity to a particular reaction pathway (high selectivity).
- Processes will require single stage design, combining flexibility, robustness, and modularity. They need to be designed for a particular catalyst.

Three research needs stand out as a consequence:

- It is needed to rationally develop catalysts that are active and selective under conditions that are currently not accessible. Fundamental understanding of the free energy landscapes of the desired reaction pathways on a qualitative and quantitative level is to be acquired by combining kinetic measurements with advanced spectroscopy and theory and characterizing the catalyst, its active sites, and the chemical transformation occurring at these active sites under realistic conditions.
- Catalysts are dynamically evolving solids and molecular entities that need to be characterized during the dynamic and frequently reversibly changing operating conditions. Methods to monitor and to synthetically control these changes and their relation to catalytic transformation are needed.
- Flexible sized, robust, and modular reactor concepts are needed to maximize heat and mass transfer. To realize the target, reactors need to be optimally designed for the catalysts used for a particular reaction.

4.3 State of the art, challenges, and goals for specific syngas chemistries

Seven clusters of chemical transformations from syngas are addressed below (Figure 4.2). All of them are currently developed to industrial level and have already seen impressive progress on catalyst, reactor, and process level.

4.3.1 Fischer–Tropsch synthesis

Fischer–Tropsch synthesis is a heterogeneous catalyzed polymerization converting syngas into a wide spectrum of hydrocarbons [2]. Cobalt, Ru, Fe, and Ni are active catalysts, but only Fe and Co are currently used industrially. The high intrinsic selectivity towards long chain hydrocarbons makes Co-based FTS solids the preferred catalyst for gas to liquids processes.

Fe-based catalysts, however, have superior properties over Co-based catalysts, especially for H₂-poor and CO₂-containing syngas. The key advantage of Fe catalysts is that their product slate is more directed to short-chain (unsaturated) hydrocarbons and short-chain oxygenates, leading to

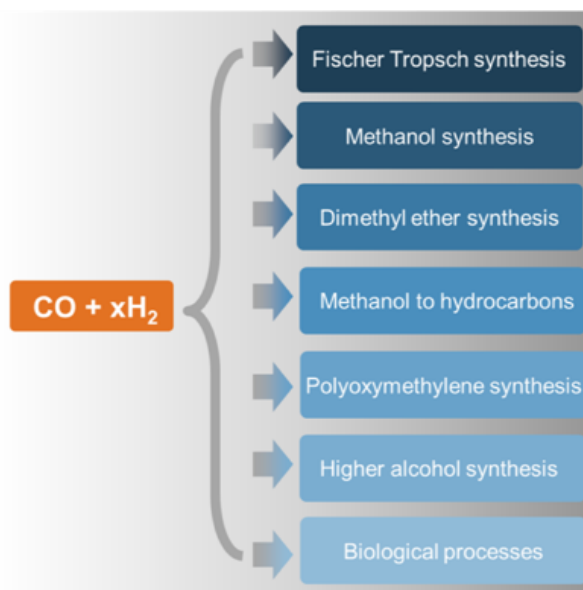


Figure 4.2: Processes from CO/CO₂ and H₂ mixtures in a future, carbon-neutral environment.

important chemical building blocks and precursors for the synthesis of transportation fuels. On a 5-year horizon, the main challenges for the direct production of fuels are as follows.

- Selectivity is problematic, as a wide range of products following the well-known broad Anderson-Schulz-Flory distribution is produced. To narrow this distribution requires a second catalytic function or a confined catalyst showing shape selectivity that modify the hydrocarbon size and operate under identical conditions.
- The required pressures (>20 bar) increase process cost.
- The moderate productivity of state-of-the-art catalysts require large reactors.
- High exothermicity poses challenges in temperature control.

On this timescale, the development of multifunctional catalysts able to selectively produce C7-C12 iso-alkanes, while minimizing the formation of gaseous products, should also be addressed. In parallel, significantly more research at the reactor system level is required to overcome mass and heat transport limitations.

On a 10-year horizon, it is important to develop catalysts for operation at significantly lower pressures, enabling decentralization. This is especially linked to the valorization of CO₂, which requires catalysts able to tolerate the large chemical potential of water.

4.3.2 Methanol synthesis

For methanol synthesis, decentralized syngas conversion will require highly active and selective catalysts, operating under a wide range of reaction conditions near thermodynamic equilibrium and in the presence of large concentrations of CO₂ [3]. Since the first generation of catalysts (Cu-ZnO-Al₂O₃), research has focused on the chemical and structural elements of the catalyst. The ternary Cu-ZnO-Al₂O₃ system, however, has a limited tolerance to water resulting from CO₂ hydrogenation. To improve its stability, the catalyst is applied at temperatures not exceeding 250 °C and pressures not lower than 70 bar. Under these conditions, low conversions per pass are achieved and a large part of the product stream needs to be recycled [4]. This results in high compressor and cooling costs and low productivity per-pass, which are not compatible with anticipated decentralized production.

On a 5- and 10- year horizon, two alternative solutions are envisaged: (i) catalysts able to operate at low temperatures to achieve high conversions per pass at moderate pressures and (ii) catalysts that can maintain high methanol selectivity at higher temperatures and lower pressures with higher cost efficiency and the potential of coupling to higher-temperature processes such as the methanol to hydrocarbons (MTH) reactions, thus avoiding thermodynamic limitations.

Recent research on the synthesis of methanol via hydrogenation of CO₂ has demonstrated that alternative bimetallic catalysts hold great promise in terms of stability and productivity, especially

when redox active supports are used [1]. However, many of these rely on scarce elements, and still very little is known about the reaction mechanism, leading to issues with optimization. Similar catalysts can also be of interest for methanol synthesis from syngas.

4.3.3 Dimethylether

Dimethylether (DME) is an especially interesting product because it can be utilized as a fuel for heating and transportation and as intermediate in the synthesis of olefins, gasoline, and aromatics [5] (Figure 4.3). Compared to methanol, DME synthesis offers the potential for higher single-pass conversions, as judged from the thermodynamic equilibria.

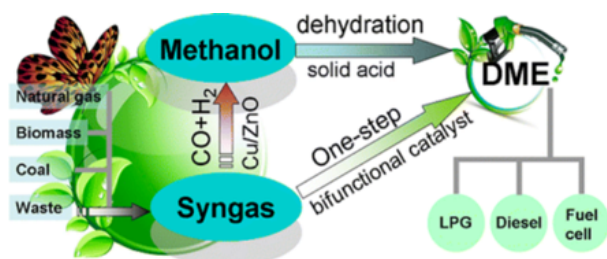


Figure 4.3: Strategies to couple methanol synthesis directly or in sequence with upgrading technologies. Reproduced with permission from [5].

Dimethylether is currently produced at industrial scale from methanol using dehydration catalysts such as γ - Al_2O_3 . Pilot plants for direct conversion of CO-rich syngas either in gas-phase or liquid phase have been explored, using reactors filled with mixtures of methanol and dehydration catalysts. No large-scale implementations for direct DME-synthesis operating at high and/or variable CO_2/CO and H/C ratios are known. New reactor and catalyst concepts should allow synthesis from syngas in a single pass to simplify downstream processing. Such high single-pass conversions, however, may have to be achieved even at high and fluctuating CO_2 -concentrations. New catalyst systems with enhanced stability and reactor design concepts are needed that tolerate water as side-product, for example, multifunctional catalysts with adjustable concentrations of metal and acid sites.

4.3.4 Methanol to hydrocarbons

Direct and indirect pathways for methanol to hydrocarbons (MTH) are of high importance because the current infrastructure is optimized for liquid hydrocarbon fuels. The stepwise route, i.e. syngas to methanol to hydrocarbons, has been commercialized in many variants ranging from a focus on gasoline to one on light alkenes [6]. As currently practiced, syngas is converted to methanol at 50-100 bar and 220-260 °C with >99 % methanol selectivity, and a methanol-to-hydrocarbons step using a zeotype catalyst occurs at 350-500 °C. During the past two decades, substantial progress has been made to decipher the influence of Brønsted (and Lewis) acidity, site distribution, zeolite topology, crystal size and morphology, and process conditions on catalyst activity and selectivity. However, the lack of spatial and temporal resolution of the information makes direct feedback for catalyst and process development complex.

In a 5-year scenario, combination of the two process steps in one process stage would lead to

substantial reduction of investment. If to be realized in one reactor, the focus should be on bridging the temperature gap between methanol synthesis and MTH. For a 10-year horizon, distributed fuels production calls for a radically different approach, ideally one that lowers the reactor temperature to 150-250 °C and operates at moderate pressure. Such a strategy imposes challenges on the MTH side, since the shape-selective hydrocarbon chemistry has high activation energies. The current Cu-based catalysts exhibit lower methanol selectivity at higher temperature, and gradually poison Brønsted acid sites active for the MTH reaction. Hence, novel catalyst sites must be designed for both steps and integrated with new reactor designs able to better dissipate heat. Shape selectivity will remain key to steer the selectivity, but the low temperature operation may open the material basis to include organic-inorganic hybrid materials. The potential for specific stabilization of transition states by such catalysts offers ample space for development using insight from cross-cutting approaches, as described in Section 4.4.

4.3.5 Oxymethylene dimethyl ethers

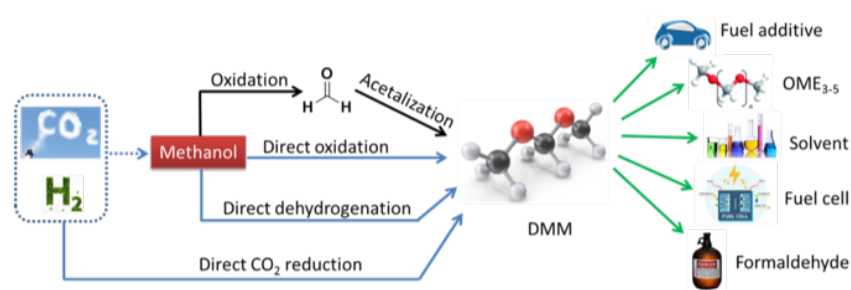


Figure 4.4: Reaction pathways to oxymethylene dimethyl ethers. Reproduced with permission from [7].

produced by water electrolysis and CO₂ captured from atmosphere (Figure 4.4). For OME>1, methanol and formaldehyde are the currently used feedstocks. Two synthetic strategies are dominant, “water-free” and “with water release” [7]. The former gives rise to OME3-5 in high yields, but it is not applied on an industrial level because of the high cost of DMM and trioxane. Notably, the “water-free” oligomerization of formaldehyde has been used for many years in polymer industry. Very recent publications showed a high potential of applying gaseous formaldehyde for OME synthesis as well as direct OME>1 production in gas-phase methanol oxidation.

The currently accessible strategy, “with water release,” utilizes less costly methanol and aqueous formaldehyde or paraformaldehyde as substrates. However, the presence of water in the reaction system causes an equilibrium shift towards the reagents, decreases the yield of target products, and slows the reaction kinetics. Most dramatically for process design, the presence of water results in a challenging separation due to its similar boiling point to OME2. Water also chemically binds to formaldehyde, which significantly complicates recovery of the target products

Oxymethylene dimethyl ethers (OME), especially, OME3-5, are suitable diesel-blends with excellent combustion properties. Longer OME (POM) are used as polymer additives. Most importantly, OME can be conceptually synthesized from H₂

and increases energy demand, capital costs, and operation costs. In this regard, novel “water-free” approaches are needed, e.g. based on dimethyl ether and paraformaldehyde. Within a 5-year horizon, chain-length distribution of OME according to the Schulz–Flory estimate should be addressed, aiming to reduce separation of target products and recycling of co-products. Current results indicate that the equilibrium yield of OME3-5 could be overcome by insight-guided tailoring of pore structure and surface properties. On a 10-year horizon, replacing formaldehyde via direct CO/CO₂ insertion into the growing OME chain should be addressed.

4.3.6 Higher alcohol synthesis

Higher alcohols, including ethanol are used as fuel additives and platform chemicals. Catalysts explored for higher alcohols include Rh-based supported catalysts, metal sulfides or carbides, modified FTS catalysts, and modified Cu-Zn based methanol synthesis catalysts [8]. The Rh-based catalysts (especially for ethanol) have been the state of the art, but significant challenges exist on a 5- and 10-year horizon. On the shorter timescale, selectivity and insufficiently fast rates are the key challenges, with methanol and light hydrocarbons being low-value byproducts. Also, the cost of Rh limits its wide-spread use and catalysts based on (combinations of) more abundant elements have to be discovered. The transition to less severe operating conditions (lower pressure and lower temperature) as mandated by decentralized processes represents the major challenge for the 10-year horizon. Such a radical transition will likely require insight into the molecular details of the process and the atomic details of the catalyst active sites.

4.3.7 Biochemical processes to convert syngas

Biochemical processes to convert syngas into bulk energy carriers are relatively slow processes, albeit operating at much lower temperatures and pressures than the catalysts discussed above [9]. They possess advantages compared to metal catalysis due to their considerably higher tolerance against sulfur and nitrogen impurities and ability to be tailored for high selectivity. The first technical-scale syngas fermenters have been commercially deployed, receiving widespread acceptance, especially when combined with tandem process to produce jet fuel. Challenges on a 5- and 10-year horizon include the limited productivity due to the low solubility of the syngas in aqueous environments and the associated gas transfer limitations. As wild-type strains of the most popular acetogenic bacteria only produce acetate, ethanol, and some 2,3-butanediol (only a few strains also produce minor amounts of butyrate, butanol, caproate, and hexanol), engineering of the bacteria to produce specific chemicals is a key target. Likewise, catalytic tandem processes accessing not only ethanol but also its more oxidized forms, such as acetic acid, and easier separation of the aqueous phase product mixture are important targets.

4.4 Crosscutting and enabling technologies

4.4.1 Developments in reactor technology

Reactor technology for syngas chemistry is currently developed only on very large scale (e.g., > 6000 tpd), with predominantly continuous operation (4-12% load variation) and fixed boundary conditions (homogenous feedstock and energy/water supply). Existing reactors for syngas conversion processes are designed to cope with the high exothermicity, slow reaction rates, and moderate conversions per pass of syngas chemistry. In addition to the abovementioned conventional issues, decentralized syngas conversion imposes the following new challenges: increased tolerance of the reactor to variations in flow rates, residence time, feed composition (including CO/H₂ ratios, CO/CO₂ ratios, and poisons), high single-pass conversion, higher water formation due to the higher CO₂ content in the syngas, and simplified and single-stage configurations (e.g., [10]).

As down-scaling of present technology is economically unfeasible, new reactor designs are required to adapt for operation under changing, transient, and intermittent conditions. Boundary requirements include: the integration of efficient heat transfer into reactor concepts (innovative heat transfer media, structured catalysts, heat pipes for fixed bed, fluidized bed, and membrane reactors), flow distribution (catalyst shape and reactor internals), functional integration of separation and reaction into a single reactor unit, and autonomous operation of reactor and plant.

4.4.2 Knowledge- and insight-based catalyst development using predictive tools

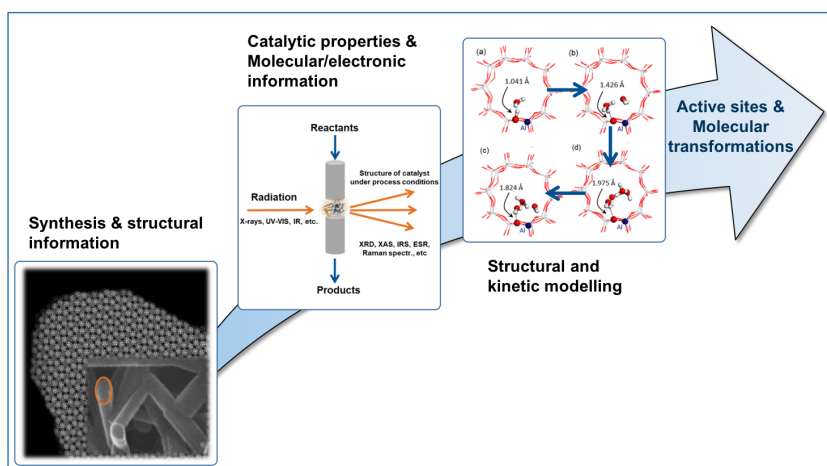


Figure 4.5: Approaches to link structural information with catalytic properties, guided and enhanced by theory.

To determine what controls activity and selectivity at flexible conditions, knowledge- and insight-based catalyst development using predictive tools is key (e.g., [11]). Selectivity may be the result of a complex interplay of various factors, such as stabilization of intermediates by shape selectivity, transport phenomena, and the intrinsic reactivity of complex, inter-

twined cycles. The key challenge is to map these contributing factors, which form the basis of the design of highly active multifunctional catalysts, to the low severity reaction space required

for decentralized operation (Figure 4.5). The development of microkinetic models embedded in multi-scale simulations of these units is of key importance to quantitatively link the impact of key phenomena (observed in model experiments) to the kinetics at large scales (e.g. [12]).

It is, in parallel, mandatory to develop robust operando characterization, imaging, kinetic, and theoretical tools to follow the catalyst along its life cycle, tracing its full dynamic behavior. This requires merging top-down experimental approaches (microscopy, spectroscopy, kinetics) with reductionistic bottom-up approaches (operando modeling, design of model systems). To bridge the spatial and time resolution gap from experiment and theory, operando models accounting for spatial heterogeneities and new tools to acquire and analyze experimental and characterization results using, for example, modulation-excitation and chemometric methods, are required. The expected stronger link between catalyst structure and chemical state and reaction pathways paired with emerging synthesis methods is hypothesized to enable the targeting of metal and oxide nanoparticle with specific shapes and sizes.

4.5 Conclusion

Syngas chemistry will be a key technology to convert carbon oxides and hydrogen to a range of energy carriers and fuels. The variety of products allows, on the one hand, for tailoring the output to a particular usage, but also requires, on the other hand, a wide variability of processes and catalysts. The most significant challenges are linked with the need to decentralize significant parts of future syngas conversion systems to best utilize distributed energy and carbon resources. Decentralization requires that rates be accelerated by at least an order of magnitude at lower temperatures to realize small reactor sizes and low heat losses, and it necessitates higher selectivity and a substantial increase in conversion of at least one of the reactants to reduce separation cost. Processes will require a single-stage design, combining flexibility, robustness, and modularity to minimize capital investment and operation cost. These relatively straightforward boundary conditions will require concerted catalyst-to-reactor development, reducing our two current leverages for enhancing reaction rates, i.e. temperature and reactant pressure/concentration. It requires new generations of catalysts, developed with insight into molecular properties, to achieve the stability and robustness required in this future scenario.

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Section 5

Sustainable N₂ reduction

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5.1 Importance of subject

Currently, ammonia synthesis is based on the Haber-Bosch process $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$. By providing nitrogenous fertilizers for agriculture, its invention resolved what was the most important challenge at the turn of the 20th century: the prevention of mass starvation [1]. Despite the hugely positive impact of the Haber-Bosch process, it also comes with significant disadvantages in its current implementation. Industrially, the reaction is run with pressures above 150 bar and temperatures above 400 °C, thus requiring large, centralized infrastructure. Moreover, the excessive use of nitrogenous compounds saturates soils and leads to substantial run-off into rivers and aquifers, leading to eutrophication and low water quality. Most importantly in the context of sustainable fuel and chemical production, the Haber-Bosch process consumes a colossal >1% of the global fossil fuel production [2], due to its use of methane derived H₂ as a feedstock. *For the 21st century, we need a more sustainable solution* [3].

Ideally, a sustainable N₂ reduction process would take place at low pressures and temperatures, allowing for ammonia to be produced locally at the point-of-consumption. The reaction would rely exclusively on *renewable electricity and feedstocks*, eliminating the need for fossil fuels. Besides its importance as a fertilizer, sustainably produced ammonia is also a highly attractive energy vector thanks to mature technology that allows it to be stored safely and reversibly at high density in benign, low-cost metal halide salts [4]. In this Section, we will explore two distinct routes to sustainable nitrogen reduction:

- Modify the conventional Haber-Bosch process to operate at milder conditions (pressures of 20 to 40 bar) using a sustainably produced hydrogen feedstock from water electrolysis (see Section 1)

- Directly electroreduce N_2 via an efficient electrochemical process at ambient conditions (1 bar, $<100\text{ }^\circ\text{C}$)

The electrochemical route is particularly interesting because the ammonia could be manufactured out in open spaces, capturing sunlight and nitrogen, and using water as part of the irrigation, implying that there would be no need to drive trucks to deliver the fertilizers or use the tractors that apply them. There would be reduced problems with excess fertilizers and runoff, since the ammonia would be slowly produced at the appropriate concentration and then mixed into water during the irrigation process. Moreover, low-temperature operation is particularly amenable to rapid start up and shut down and thus ideal for coupling with intermittent renewable energy sources. The on-site electrochemical production of ammonia would initially be best suited for remote locations in developing countries, which lack the centralised infrastructure and transportation network to distribute ammonia. In Europe, it may be challenging for electrochemically produced ammonia to compete with ammonia derived from the Haber-Bosch process. In the short to medium term, the synthesis of higher value nitrogen-containing molecules such as urea, acetonitrile or even more complex molecules such as pyridines could be more attractive. Whilst the electrosynthesis of these products is at present undeveloped, the scales at which the chemicals are used are much smaller than ammonia and thus a better fit with present electrolysis capability.

Figure 5.1 illustrates the two separate approaches to sustainable N_2 reduction where the similarities and differences of the two prototypical interfaces are highlighted. At a purely chemical interface (top Figure 5.1), heat provides the energy for the adsorbed species to overcome reaction barriers. In contrast, the electrochemical interface (bottom Figure 5.1) drives the reaction through electrostatic potential differences, which drive elementary steps involving charge transfer (ions and/or electrons).

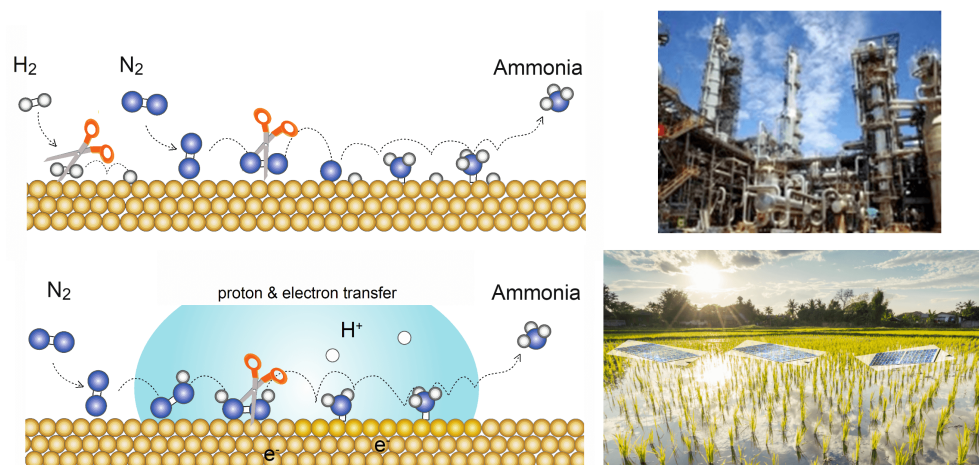


Figure 5.1: Catalytic reduction of N_2 at the gas-solid (top) and gas-solid-liquid electrolyte (bottom). Catalytic scission of the N_2 and H_2 molecules are the first steps in the thermal process followed by step wise hydrogenation of the nitrogen atom. In the electrochemical process, it is considered that protons are transferred across the interface directly to the N_2 molecule and the N-N bond is broken later in the reaction sequence.

In the following, we will separately examine both of these approaches in detail, including the state of the art of current technologies, scientific challenges, and future research needs.

5.2 Thermal nitrogen reduction

5.2.1 State of the art and scientific challenges

The currently implemented Haber-Bosch process is the product of more than a century of optimization and operates at nearly thermodynamic efficiency. The industrial catalyst used is fused iron with promoters Al_2O_3 (structural) and K (electronic). The iron precursor can either be or magnetite or wuberstite. An alternative is to use a supported ruthenium catalyst, which is slightly more active and enables operation at slightly lower temperatures and pressures, but its high cost relative to iron is a major drawback. Nearly all of the energy usage and CO_2 emissions of conventional ammonia synthesis are associated with the production of H_2 and not with the Haber-Bosch process itself. Therefore, replacing the fossil-derived H_2 feedstock with sustainably produced H_2 from water electrolysis is essential to making the Haber-Bosch process sustainable. Assuming that such technology for sustainably producing hydrogen exists, the key obstacles to sustainable ammonia synthesis via the Haber-Bosch process lie at the interface between renewable water electrolysis and the Haber-Bosch process. Specifically, a sustainable Haber-Bosch plant must be compatible with an intermittent influent of hydrogen at relatively low pressure (20 to 40 bar). At present, the N_2 in air is separated from O_2 by the combustion of unreacted methane; should electrolytic H_2 be used instead, alternative means of producing pure N_2 at large scales are required. As current industrial Haber-Bosch plants are run at a steady state for long periods of time, catalysts and other components of the process have not yet been tested under dynamic operating conditions.

The reduced pressure of hydrogen from water electrolysis also represents a significant challenge for conventional Haber-Bosch plants. Current state of the art catalysts operate at temperatures of at least $400\text{ }^\circ\text{C}$ to achieve reasonable reaction rate, which in turn requires high operating pressures of more than 150 bar to maintain a reasonable conversion due to the negative entropy of the overall reaction. Therefore, efficiently operating the Haber-Bosch process at the pressure set by water electrolysis requires the discovery of ammonia synthesis catalysts that are active at lower temperatures than those known today.

5.2.2 Future research needs

Based on the identified challenges associated with coupling renewable hydrogen production to the Haber-Bosch process for ammonia synthesis, we propose two distinct research thrusts that require attention in the near future.

Addressing the implications of intermittent operation on process and plant operation

This first requires investigations into the effect of variable operating conditions (particularly temperature, pressure, and gas composition) on catalyst activity, lifetime, surface morphology, and sensitivity to impurities. As the process is scaled up, plant-level optimization will also be required based on the dynamics of the specific source of renewable electricity as discussed in Section 9. Associated research needs include

- Developing technology to make highly purified, pressurized N_2 (5 year goal)
- Developing technology to store/buffer H_2 or H_2/N_2 mixtures at high pressure (5 year goal)
- Handling of prolonged no-feed situations where e.g. week-long periods of no wind/sun require shutdown or throttle-down of the Haber-Bosch reactor (5 year goal)

Discovering catalysts for ammonia synthesis at lower temperatures

Theoretical studies have demonstrated that catalyst activity is limited by a balance between N_2 dissociation and further hydrogenation of the atomic nitrogen adsorbed on the surface [5]. The N_2 dissociation barrier (E_{N-N}) can be directly linked to the energy of the final state of the elementary step in terms of atomic N binding energy (E_N). A strong binding surface will have a low barrier for N_2 dissociation but will bind the N too strongly such that it will be poisoned by nitrogen species. A weak binding surface will be unable to activate N_2 at a sufficient rate. This is illustrated in Figure 5.2, which shows the rate calculated with this mechanism and a mean-field kinetic model as a function of E_{N-N} and E_N . As shown, there exists a clear linear scaling relation between E_{N-N} and E_N for various transition metals. This means that a single variable is enough to define the catalyst activity, as shown in Figure 5.2b. Note that these results are consistent with the experimental observation that iron and ruthenium are the best ammonia synthesis catalysts [6].

Figure 5.2a indicates that the optimum for catalyst activity (shown in red) is far from the scaling line formed by the transition metal surfaces. It is therefore necessary to find means to break the scaling relation in order to discover significantly more active catalysts that can operate at lower temperatures. Below are two possible research directions that may lead to the discovery of active sites that do not obey this scaling relationship:

- Synthesis of unique active sites where the relationship between transition state and final, dissociated state is different than on transition metals.
- Design of a dynamically generated active site involving the reversible adsorption of co-adsorbed species, such as sulfur, fluorine, or oxygen that breaks the scaling relations between reaction intermediates. This idea is inspired by the nitrogenase enzyme [7].

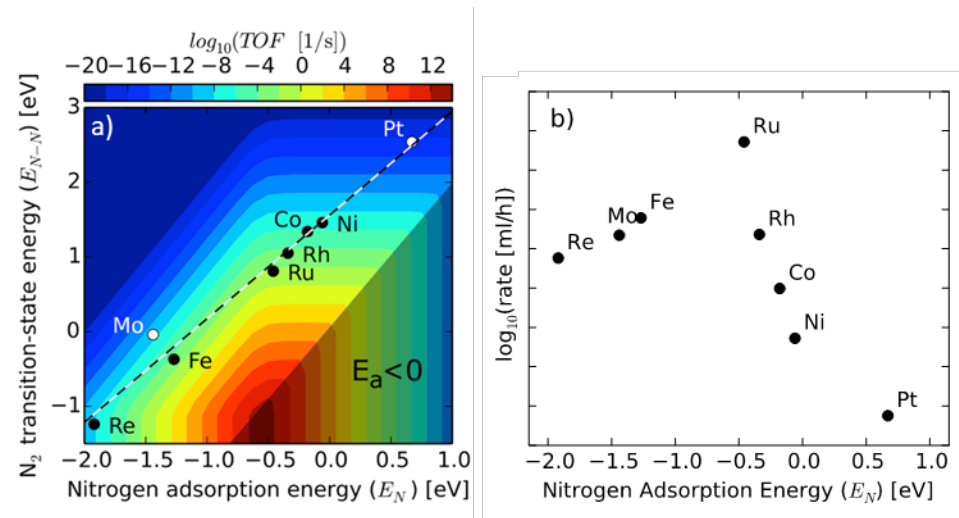


Figure 5.2: a) Ammonia synthesis rate as a function of nitrogen adsorption energy and N_2 dissociation barrier with energetics for FCC/HCP metal step sites and scaling line. Shaded area shows the theoretical limit since the activation barrier (E_a) must always be positive. (b) Rate shown as a function of the nitrogen adsorption energy, utilizing that E_{N-N} is a linear function of E_N for the considered surfaces. Reproduced with permission from [5].

It should also be noted that operating at lower temperatures may lead to new catalyst challenges. Specifically, special attention needs to be given to catalyst passivation and poisoning by oxygen and other contaminants at low temperatures.

5.3 Electrochemical N_2 reduction

5.3.1 State of the art

Electrochemical ammonia synthesis is a very nascent technology compared to its thermal counterpart. The concept is illustrated in Figure 5.3 where water is oxidized at the anode, providing protons and electrons to reduce nitrogen at the cathode. A large number of recent research papers have been dedicated to electrochemical N_2 reduction; however, the reported concentration of NH_3 ranges from the PPB to the PPM level, as described by Andersen et al. and references therein [8]. At such low concentrations, it is challenging to distinguish between ammonia produced from N_2 and ammonia produced from adventitious nitrogen. The only reliable means of verifying N_2 reduction is to employ isotope labelling and confirm a quantitative agreement between the ammonia derived from $^{15}N_2$ and

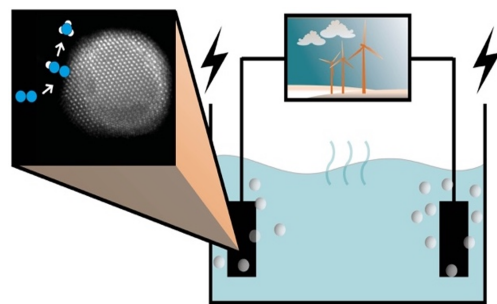


Figure 5.3: Ammonia-producing electrolyzer running on renewable energy. O_2 evolution occurs at the anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. The inset shows an electrocatalyst nanoparticle at the cathode, where N_2 reduction takes place: $N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$. Schematic illustration by Cristofaro Salvato.

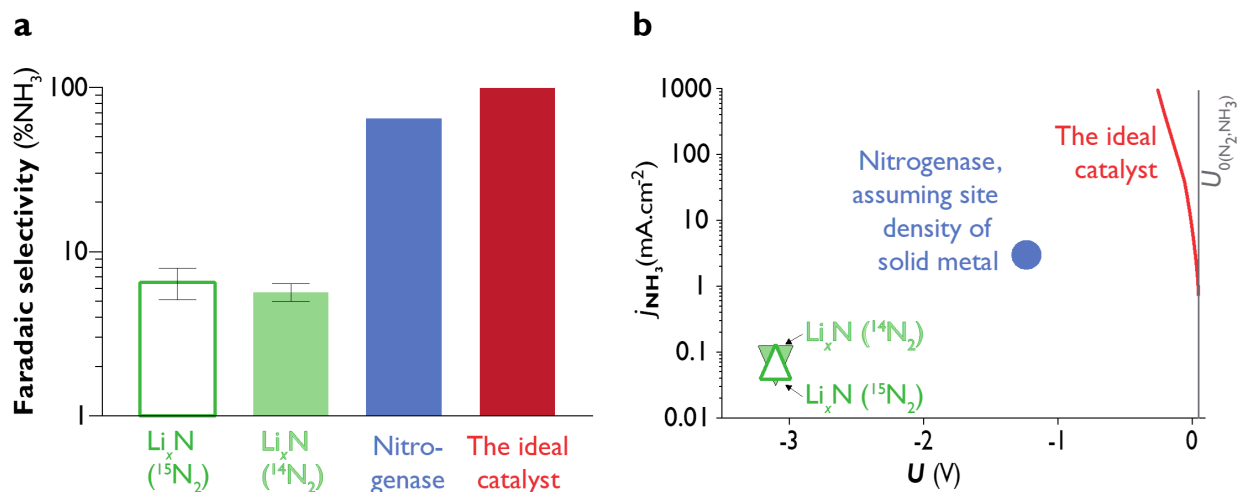


Figure 5.4: Comparison of activity and selectivity for Li_xN , nitrogenase, and the ideal catalyst. Data from references [8, 12–14].

$^{14}\text{N}_2$. Recent reports confirm that Li (or Li_xN) electrodes in 0.2 M LiClO_4 in 1% ethanol in THF can reduce N_2 to NH_3 [8–10], confirming an earlier study from the 1990s [11]. As shown in Figure 5.4, both the rate ($70 \mu\text{A}/\text{cm}^2$) and the Faradaic selectivity (6.5%) are low, while the overpotential is large ($>3 \text{ V}$), demonstrating ample room for improvement. In comparison, nature’s nitrogenase enzyme is far more efficient, with an ammonia production rate equivalent to $3 \text{ mA}/\text{cm}^2$, $\sim 1 \text{ V}$ overpotential and up to 75% Faradaic selectivity. Other studies in the literature lack rigorous control tests, calling into question their reliability.

It is worth perusing upon which of the metrics plotted in Figure 5.4 has the greatest impact on the performance of a real device. There are two different cases: (i) when NH_3 is to be used as a fertiliser, and (ii) as an energy vector (solar fuel). For fertiliser applications, improving the selectivity and current density would have the greatest impact. A recent paper recently emphasised the importance of Faradaic selectivity: it estimated that a 5 m^2 state-of-the-art solar cell would be sufficient to provide NH_3 as fertiliser for a hectare of land, assuming 100% Faradaic selectivity and 1 V overpotential [15]. A 2 V overpotential would require a 45% increase in solar cell area. However, decreasing the selectivity to 1% would require a colossal 100-fold increase in solar cell area, which would be prohibitively expensive. On the other hand, high current densities are also critical to minimise the capital costs. Electrochemical devices run at current densities $\sim 1.5 \text{ A}/\text{cm}^2$; taking into surface roughness, a reasonable surface specific current would be $\sim 10 \text{ mA}/\text{cm}^2$, far higher than the current densities for N_2 reduction shown in Figure 5.4. For energy storage in the form of a solar fuel, overpotential is more important than it is for fertiliser. For instance, even if NH_3 was produced with zero overpotential at the anode and cathode, the cost based on average electricity prices alone would be $\text{€}0.08/\text{kWh}$; with an overpotential of 1 V it would be equivalent to be $\text{€}0.15/\text{kWh}$. For reference, the average cost of methane is $\text{€}0.03/\text{kWh}$ [16].

5.3.2 Scientific challenges

It would be highly convenient to use metal electrodes in aqueous electrolytes to catalyse N_2 reduction, capitalising on the deep understanding from other reactions. However, density functional theory (DFT) calculations suggest a fundamental showstopper: the bond strength of any given metal surface to hydrogen linearly correlates to that of nitrogen, as shown in Figure 5.5a. This leads to the poisoning of metal surfaces by hydrogen, preventing the adsorption and subsequent reduction of N_2 and leading to poor NH_3 selectivity as illustrated in Figure 5.5b [17]. Favouring N_2 reduction over H_2 evolution requires a surface that circumvents this scaling relation. Moreover, additional scaling relations between N-containing adsorbed intermediates of N_2 reduction suggest huge overpotentials for the reaction, as shown in Figure 5.6. The theoretical results in Figures 5.5 and 5.6 provide basis for the incredibly low or negligible concentrations of NH_3 reported, thus far, on metal surfaces in aqueous electrolytes and the significant overpotentials required to achieve them.

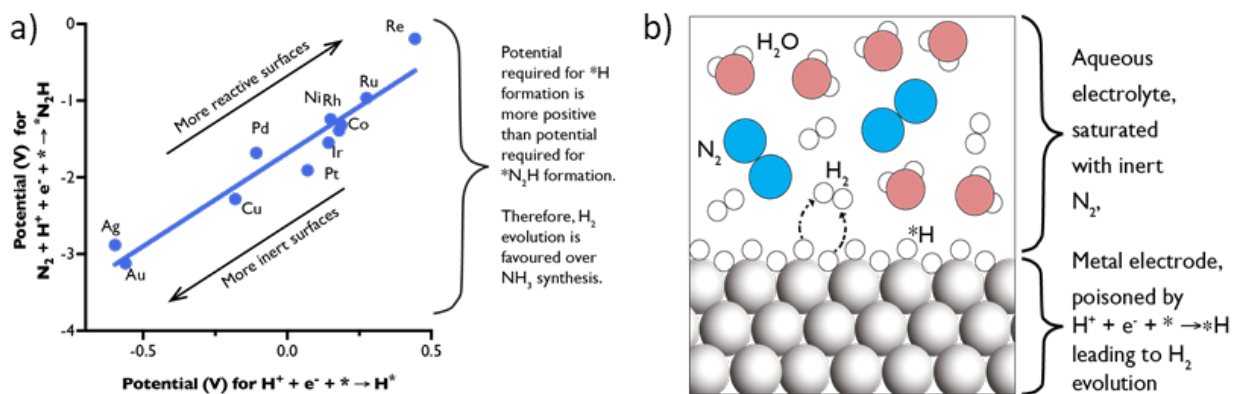


Figure 5.5: a) Linear correlation between potential required to drive first charge transfer step in N_2 reduction versus first step of H_2 evolution on metal surfaces in aqueous electrolyte. Data from reference [17]. b) Illustration of how poisoning by hydrogen prevents N_2 adsorption and subsequent reduction, thereby yielding poor selectivity to ammonia.

5.3.3 Future research needs

Below we propose future research needs that are critical to overcoming the aforementioned scientific challenges associated with electrochemical N_2 reduction.

Adoption of standardised test protocols for N_2 electroreduction and benchmark existing literature

Given that many reports of electrochemical ammonia production in the current literature are tentative at best, the research community needs to immediately work towards adopting standardised test

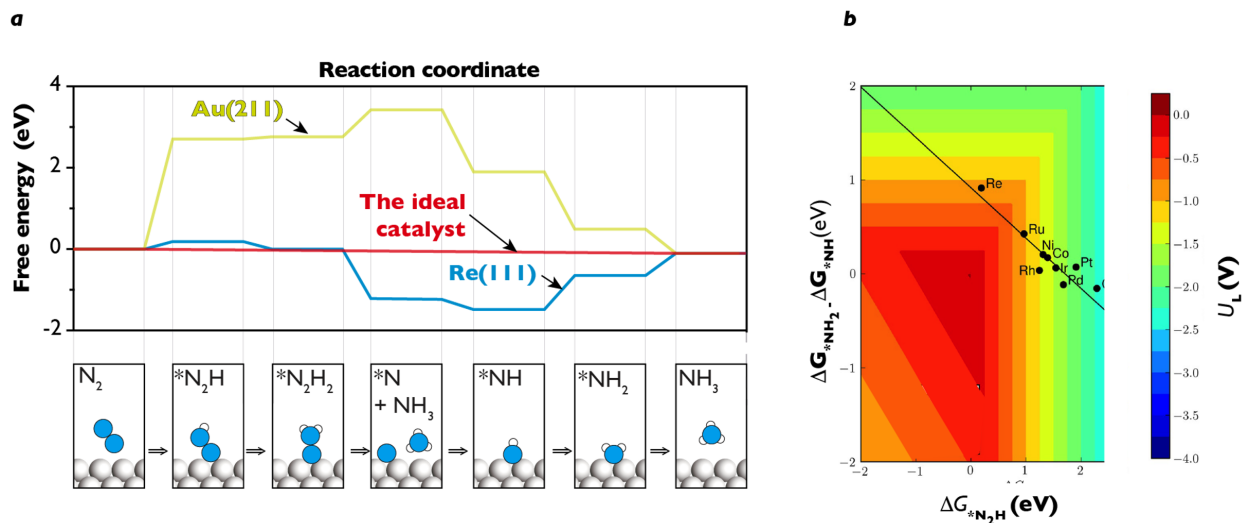


Figure 5.6: a) Thermodynamic free energy diagram for electrochemical N_2 reduction to NH_3 at the equilibrium potential. On the ideal catalyst, the pathway is completely planar. On $\text{Au}(211)$, the most uphill step is $^*\text{N}_2\text{H}$ formation, while on $\text{Re}(111)$, the most uphill step is $^*\text{NH}_2$ formation. b) Linear scaling relationship for closely packed transition metal surfaces between the free energies for $^*\text{NH}_2$ formation and $^*\text{N}_2\text{H}$ formation. Also indicated via contours is the theoretical limiting potential, the maximum of which is shown to lie far from the transition-metal surfaces. Reproduced with permission from [17].

protocols for ammonia testing based on $^{15}\text{N}_2$ isotope labelling [8]. On the basis of the established protocols, previous positive reports of N_2 electroreduction need to be reappraised.

Mechanistic insight into the most promising materials

Those materials identified as promising from the benchmarking activity described should be subjected to detailed investigation, with experiment and theory in synergy. There should be a particular focus on:

- *The structure, dimensionality, and composition of the electrode, electrolytes, reaction intermediates, interfaces, and interphases, bridging information between multiple length scales and domains, especially under reaction conditions.* From an experimental perspective, this includes x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) both in the hard x-ray regime to probe metal sites and soft x-rays for detection of N species. The recent development of high-pressure x-ray photoelectron spectroscopy (HPXPS) (currently up to 2 bar, but potentially 10-30 bar in the future) has enabled probing of the thermal process with high surface sensitivity, and involving electrochemical cells allows detection of electrode oxidation state and species at the solid-liquid interface. Surface-Enhanced Infrared Absorption Spectroscopy (SEIRAS), Surface Enhanced Raman Spectroscopy (SERS) and Sum Frequency Generation (SFG) allow detection of molecular species through N-N and N-H stretches. The utilization of optical and x-ray lasers for ultrafast measurements can provide avenues to probe transient intermediates and transition states. Many of the techniques are

cross-cutting, and hence also relevant for thermal N₂ reduction. Theoretical simulations will need to simulate N₂ reduction and H₂ evolution on the materials of interest at different pH values in aqueous solutions, as well as in non-aqueous solvents, including the calculation of transition states. Data-driven materials and interface models will also need to be developed, guided by physical insights (see Section 8).

- *Elucidating parameters for controlling selectivity: suppressing H₂ evolution and enhancing N₂ reduction.* Aside from elucidating the composition and structure of the electrocatalyst material and the active site, N₂ electroreduction research requires concerted efforts to elucidate the role of proton, electron, and N₂ transport in influencing the dominant reaction mechanism [15].

New materials discovery

Engineering an electrochemical N₂ reduction process that approaches the performance of the nitrogenase enzyme (see Figure 5.4) requires exploring new electrodes (catalysts), electrolytes, and electrolyte additives and combinations thereof. This process may be accelerated using a fully autonomous materials discovery platform (see Section 8). Non-metallic catalysts, such as nitrides, oxides, and sulfides may be able to escape some of the constraints shown in Figures 5.5 and 5.6. We anticipate that optimal catalysts may emulate nitrogenase through the following characteristics [7, 15]:

- Restricted access to protons and electrons, preventing hydrogen adsorption but facilitating N₂ adsorption
- Surrounding of the metal dimer at the catalytically active centre with an inert substrate
- Dynamic adsorption and desorption of sulfur-containing adsorbates to facilitate N₂ adsorption

Development of tailored synthesis and characterization methods may be necessary. For instance, special measures may be needed to prevent air-induced deactivation of the highly reactive surfaces that are capable of activating N₂ under ambient conditions.

The platforms and infrastructure developed above should eventually be applied to more novel approaches, including solid-state proton conductors, electrochemical promotion, plasma catalysis, and photocatalytic and sonochemical systems.

5.4 Conclusion

The Haber-Bosch process for ammonia synthesis is arguably the most important inventions of the 20th century: by enabling the large scale production of fertilisers, it sustained the enormous increase

in the world's population. While it is still hugely important in today's society, the Haber-Bosch process consumes a colossal >1% of the global fossil fuel production, due to its use of methane derived H₂ as a feedstock. We have investigated two potential routes to sustainable ammonia production, namely by using renewable H₂ from water electrolysis or by direct electrochemical reduction of N₂. Both of these approaches have significant technological hurdles that must be overcome to be economically viable at the hundreds of Mt/year scale. Coupling the thermal process to renewable hydrogen production requires addressing the implications of intermittent operation, which is particularly challenging given the high pressures/temperatures required to run the Haber-Bosch process today. Thus, the discovery of a more efficient ammonia synthesis catalyst that enables milder operating conditions would mitigate some of these challenges. The direct electrochemical ammonia synthesis process currently suffers from extremely low selectivity, current densities (i.e. kinetic rates), and energy efficiency, which may be improved via electrocatalyst and electrolyte engineering. Close collaboration between theory and experiment will be crucial in tackling these challenges.

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Section 6

Homogeneous catalysis for the sustainable production of fuels and chemicals

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6.1 Importance of subject

Homogeneous catalysis, i.e. catalytic processes enabled by molecular organometallic or organic compounds as active species, is a vital technology in today's petrochemical value chain [1]. The European chemical industry leads the world in the development of these technologies, defining central pillars of societal welfare in the European Union [2]. High-energy small molecule building blocks, such as H₂, CO, and olefins (all currently derived from fossil resources) are used as starting materials for a large diversity of products with precisely controlled molecular connectivities. Thus, the catalyst performance ultimately defines the application of the chemical compound in the final product. Products include fuel components, high-volume commodity chemicals and polymers, and high-value products (e.g. biologically active compounds such as agrochemicals or pharmaceuticals).

Because they are defined at the molecular level, homogeneous catalysts offer distinctive design features. The availability of spectroscopic tools combined with computational methods from quantum chemistry enable a detailed characterization of molecular structures and facilitate the exploration of catalytic mechanisms, leading over the past decades to the construction of a solid corpus of knowledge on the modes of cleavage and formation of chemical bonds. Combined with the modularity of organic and inorganic synthesis, a fine tuning of the stereoelectronic properties of molecular catalysts is accessible [3]. Additionally, these principles learned in homogeneous catalysis can be implemented in hybrid systems and materials sciences, bridging the fields of enzymatic,

homogeneous, and heterogeneous catalysis [4]. With the pressing need for defossilization of power generation and the chemical value chain, homogeneous catalysis will play a major role in re-defining the energy-chemistry nexus [5].

6.2 State of the art and scientific challenges

Most current technologies using homogeneous catalysts are centralized processes that use fossil-derived feedstocks (oil, natural gas, and coal), generally via CO as an intermediate. In fact, among the many transformations that organometallic catalysts enable in the petrochemical value chain, carbonylation reactions, i.e. the introduction of carbon monoxide (CO), are the most prominent. This reaction class comprises bulk chemical production of acetic acid (5 Mt/y), production of large volume commodities (hydroformylation or oxo-process, 10 Mt/y), as well as pharmaceutical products (e.g. anti-inflammatory agents such as ibuprofen and naproxen).

To achieve defossilization of the chemical industry, these current industrial processes must be adapted or overhauled to consume renewable energy and feedstocks, e.g. CO₂ with green H₂ or CO derived from the co-electrolysis of CO₂ and water. This “harvest” of fossil-free electricity with renewable feedstocks to produce chemical products is referred to as Power-to-X. Recently, molecular catalysts have demonstrated great success in this area, catalyzing the direct transformation of simple raw materials, such as CO₂, N₂, H₂O, and H₂, to chemicals currently produced from energy-intensive, multistep petrochemical processes (Figure 6.1). They include the first examples of reductive functionalization of CO₂ to methylamines (featuring a N-CH₃ linkage) and other organic molecules used as solvents, reagents and agrochemicals [6, 7]. Furthermore, some of these transformations were conducted under ambient pressure and low temperature (<100 °C), thanks to the high reactivity and unprecedented kinetic control of homogeneous catalysts [8]. The potential of homogeneous catalysts to open novel reaction pathways is perhaps best illustrated in considering the direct conversion of CO₂ to formaldehyde. While reduction of CO₂ to formaldehyde using heterogeneous catalysts currently requires CO₂ hydrogenation to methanol and subsequent oxidation at >250 °C, it has been shown that it can be achieved directly from CO₂/H₂ mixtures using organometallic catalysts [9, 10]. Research efforts to fully explore the potential of homogeneous catalysts and to integrate them in realistic settings are thus highly desirable to validate the economic viability of such strategies.

On the atomic scale, the performance of homogeneous catalysts is determined by embedding the metal center in a defined organic molecule, the so-called ligand, allowing for systematic variation of the electronic structure and geometric architecture of the active species and providing a unique methodological basis for rational catalyst design and optimization. This modularity has proven extremely powerful in the petrochemical industry, and it should be exploited in the context of new energy inputs, feedstocks, and building blocks. Already, this emerging strategy has led to significant

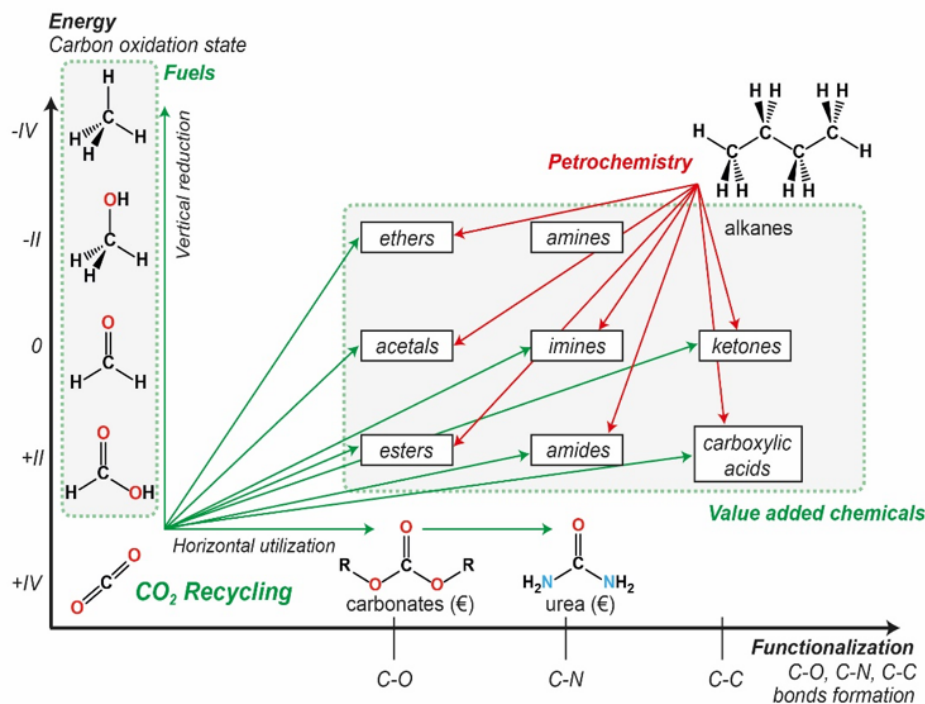


Figure 6.1: Catalytic reductive functionalization of CO₂ to shortcut the production of value-added chemicals from CO₂. Reproduced with permission from [11].

developments in the photocatalytic and electrocatalytic transformation of CO₂, H₂O, and N₂, as illustrated in the photochemical transformation of CO₂ to methane [12] and the electrocatalytic splitting of N₂ to form ammonia [13]. In addition to acting as industrial catalysts themselves, homogeneous catalysts can also be excellent sources of insight and inspiration for heterogeneous catalyst development.

6.3 Future Research Needs

Going forward, challenges include engineering catalytic systems to adapt current industrial processes to the concept of Power-to-X, accelerating the discovery and optimization of catalysts for emerging technologies, and unlocking shortcuts for the production of value-added products from renewable feedstocks and energy sources.

6.3.1 Adapting current processes to renewable feedstocks by systems approaches

Adaptation of key industrial homogeneous catalysis processes (e.g. production of platform chemicals such as organic acids, alcohols, and aldehydes) to use renewable electricity and feedstocks (primarily CO₂ and green H₂) can provide an immediate competitive advantage, thus accelerating the defossilization of the European chemical industry. Current technologies based on homogeneous

catalysts have been optimized to use fossil resources (oil, natural gas, and coal) in centralized processes, often relying on CO or synthesis gas as intermediates. The replacement of these fossil resources with CO₂ and green H₂ or electricity is a desirable opportunity (Figure 6.2) [14]. This transition can occur both at existing industrial sites and also in new, decentralized settings, depending on the availability of the renewable carbon and energy source. Transposing current chemical processes into the framework of Power-to-X will require innovative approaches to **minimize mass intensity** and **maximize step economy**. While these are already important for current, centralized industrial processes, they will become absolutely essential for decentralized production. Approaching the catalytic system holistically will be paramount to ensure catalyst robustness and stability and maintain catalytic performance under the new criteria, including: compatibility with renewable feedstocks, sustainability of the catalyst life cycle (assisted by catalyst retention strategies and/or use of earth abundant metals), and minimization of up-stream and down-stream chemical separations (e.g. by integration of raw material preparation, transformation, and purification).

In the short term, efforts should focus on adapting existing processes, e.g. carbonylation reactions, such as hydroformylation reactions (oxo-processes) and the production of acetic acid, to consume renewable feedstocks (CO₂ with green H₂ or CO derived from the co-electrolysis of CO₂ and water) in place of fossil-derived CO. Figure 6.3 depicts a potential lighthouse project producing formic acid from bio-derived CO₂ and green H₂ with a homogeneous catalyst in a decentralized, agricultural environment. The mature catalyst technology of this process makes it a prime candidate for

addressing the integration problems associated with a decentralized process [15]. Furthermore, while methanizers converting agricultural waste to biogas are readily available in local farms, the resulting CO₂ is currently vented to the atmosphere. Therefore, the catalytic hydrogenation of this renewable CO₂ using green H₂ represents an excellent opportunity to produce formic acid, a useful crop preservative, on site. Such a demonstrator project would offer a key service to the consumer and avoid the current fossil-supported production, transportation, and distribution of this preservative. It is estimated that such a project, which would highlight the potential of a renewable, consumer-oriented service enabled by homogeneous catalysis, could be completed in a 5-10 year timeframe.

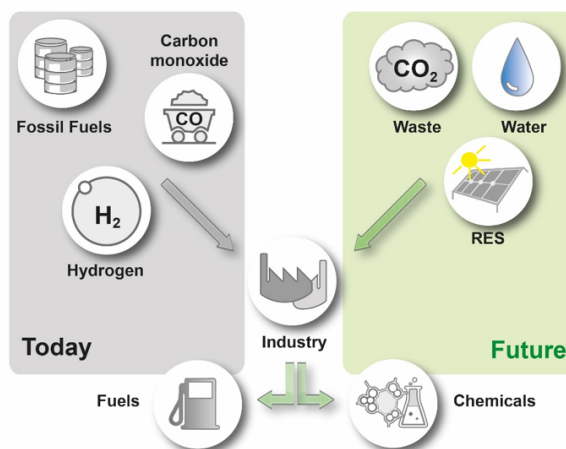


Figure 6.2: Speeding up the defossilization of the current chemical industry with renewable sources of CO or synthesis gas.

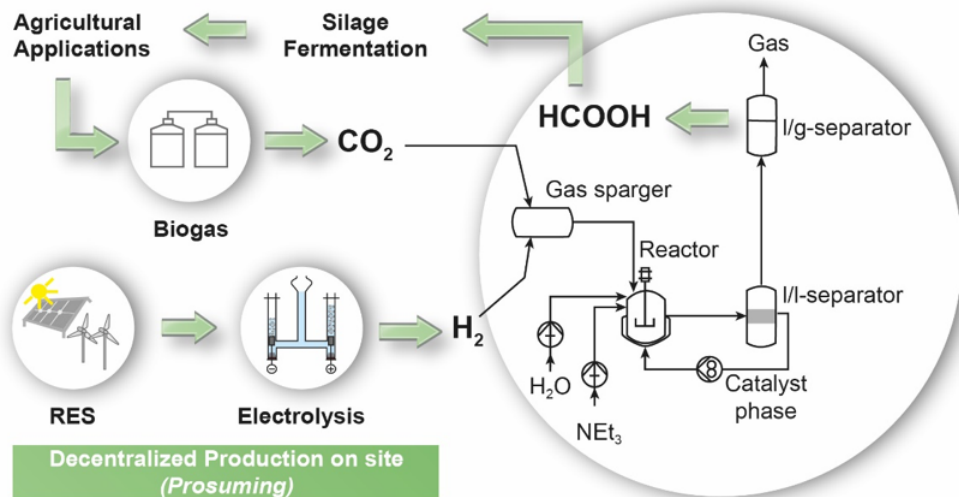


Figure 6.3: Proposed lighthouse project highlighting the potential of homogenous catalysis in Power-to-X scenarios: Decentralized production of formic acid in an agricultural environment. The process scheme is adapted from [16].

6.3.2 Accelerating catalyst discovery via information-guided approaches

Traditionally, homogeneous catalyst development follows a largely linear workflow, in which the starting point is a lead structure derived from chemical intuition, extrapolation of previous knowledge, or even serendipity. Improvements and optimization are achieved primarily by evolutionary modifications of the ligand structure and screening under standard reaction conditions, and theoretical rationalization is deduced *a posteriori* from the obtained data and mechanistic studies. A radically new approach that goes beyond these current linear catalyst development schemes will be crucial in discovering appropriate homogeneous catalysts for Power-to-X transformations in the necessary timeframe. By coupling systematic experimental variation with the rapidly growing potential of digitalization via computational chemistry and artificial intelligence (see Section 8), we expect a robust framework for accelerating catalyst discovery can be established. To support such a goal, there is a need for:

- Novel methods to rapidly generate pertinent, consistent, and accessible data on the molecular and process scale under operating conditions
- *A priori* integration of computational chemistry and experiment to identify desired and undesired reactivity channels
- Dynamic descriptions of catalytic processes and time-resolved analyses of reaction progress, e.g. by monitoring low-concentration side products and short-lived intermediates
- Novel methods for monitoring electrochemical or photochemical catalytic performance, including resolution of elementary steps

- Translation of the systematic modularity associated with synthetic concepts in molecular catalysis to defined architectures, materials, and heterogeneous catalysts
- Deepened understanding of the role solvent and reaction media play on catalyst performance.

Possible Power-to-X transformations whose realization could be facilitated by such a discovery framework include CO₂ (hydro-)carboxylation to organic acids, formaldehyde, formaldehyde derivatives, and higher alcohols (C2+). Using CO₂-derived building blocks such as methanol from upstream Power-to-X conversions may also be considered. Synthetic pathways that combine the CO₂-based routes with other renewable feedstocks, such as bio-derived platform chemicals or recycled monomers, are particularly attractive, as they facilitate the production of value-added and highly functional chemicals (Figure 6.4).

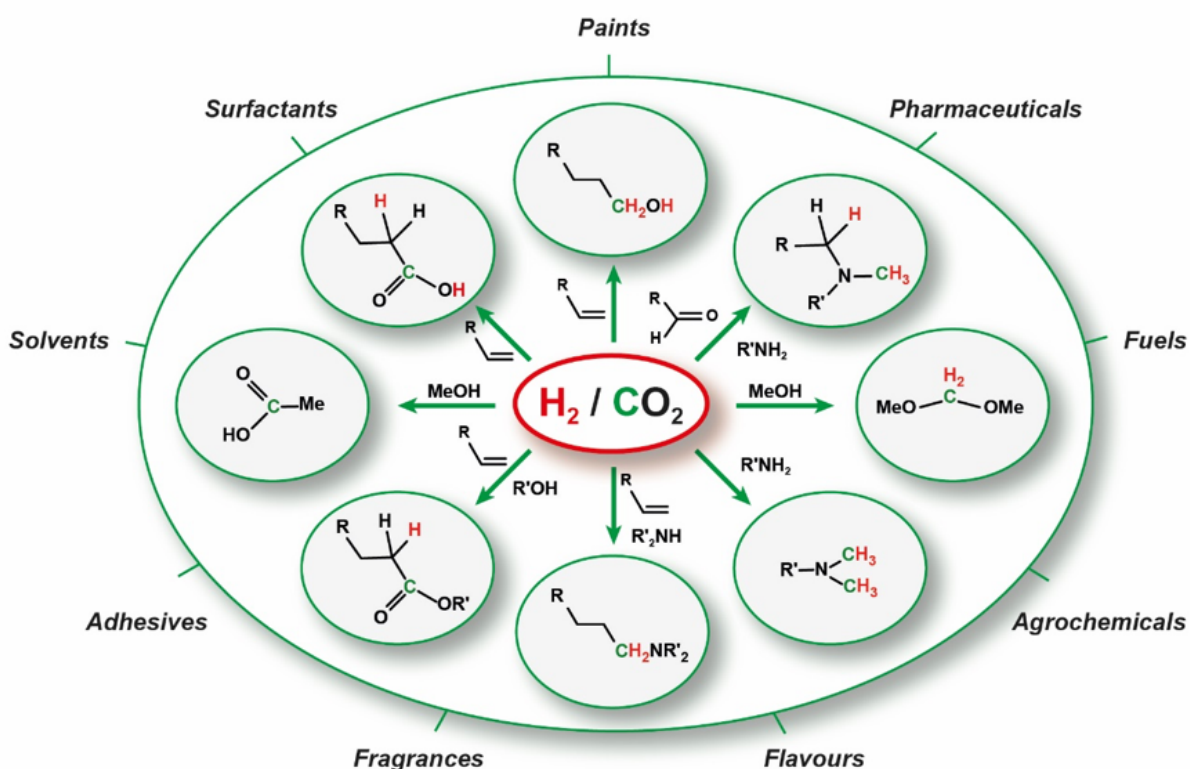


Figure 6.4: Recent examples for chemical transformations using carbon dioxide (CO₂) and hydrogen (H₂) to generate functional groups as found in chemical products and their application. Graphic adapted and modified from [17].

6.3.3 Designing direct Power-to-X pathways: from “dream reactions” to processes

In addition to modifying current industrial processes to be compatible with renewable feedstocks or new synthetic routes that use CO₂ to form C1 products, there is also a need to develop alternative,

direct conversion routes for the production of important chemicals. These co-called “dream reactions” would consume renewable energy sources and materials (ideally those that can be harvested from the air, e.g. CO₂, H₂O, and N₂) and directly convert them to value-added products and essential molecular functional groups, thereby circumventing multistep reaction sequences involving separation and purification of reagents. The high reactivity and excellent atomic-level design control of homogeneous catalysts can be exploited to develop pathways and analyze reaction networks for these complex “dream reactions,” which largely require multi-electron redox processes and sequential bond breaking/forming events. The reductive functionalization of CO₂ has led to recent efforts and successes, which must be pursued and reinforced. For instance, pathways enabling the formation of C-C bonds to give C₂+ products directly from CO₂ have still to be established. Furthermore, these concepts can be transposed to the valorization of N₂ and NO_x for the formation of N-containing chemicals to improve the environmental footprint of agrochemicals.

To realize these processes, more effective strategies for the activation of small molecules, generally, as well as the *reversible* activation of strong bonds (e.g. C-O, C-N, C-C, C-H, and N-N) are needed. Furthermore, while H₂ is a suitable energy carrier (or reductant) in the short term, the direct use of electrons and/or photons is highly desirable in the longer term to minimize infrastructure and facilitate decentralized production routes. To this end, it is crucial to develop efficient photocatalysts and electrocatalysts able to harvest and store the energy of photons and electrons in chemical bonds. It will also be important to ensure closed cycles not only for carbon, but also for nitrogen, in particular, and other critical elements such as phosphorus and sulfur. Coordination of such research efforts across fields, e.g. those mentioned in Sections 1, 2, 5, and 7, will be important for efficient technological development.

A short-term goal (~5 years) related to this future research need concerns the development of novel catalytic reactions for the multicomponent coupling of CO₂ and H₂ or of ammonia to value-added, industrially relevant chemicals. At the horizon 2030, the potential of replacing H₂ with H₂O and ammonia with N₂ or NO_x by using electrolytic or photolytic catalysts could be developed from exploration to validation. Beyond 10 years, the shortcutting concepts learned regarding conversion of carbon and nitrogen feedstocks could be translated to other feedstocks, e.g. those containing phosphorus, sulfur, and halogens.

6.4 Conclusion

Homogeneous catalysis is a key element in our current chemical industry and is essential for the transition to a sustainable future. **Immediate action can be taken** by adapting existing technologies to use renewable feedstocks, e.g. the essential “power molecules” originating from electrolysis or co-electrolysis based on renewable energy (e.g. “green” hydrogen or carbon monoxide) and capitalizing on the proven potential of organometallic catalysts to convert carbon dioxide (CO₂) directly

into value-added chemicals. The lighthouse project exemplified in Figure 6.3 provides an illustrative example of an immediately possible fossil-free development. However, the long-term success of the transition to renewables will rely on new and disruptive approaches for accelerating catalyst development and designing catalytic processes from the molecular to the system level. Ultimately, this will lead to novel technologies that directly utilize electrons and photons to drive chemical transformations of renewable feedstocks via novel pathways, thus providing a new paradigm in the chemical industry. The scientific challenges and goals outlined in this report will require coordinated efforts of interdisciplinary teams involving academic and industrial partnerships at the international level.

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Section 7

Inspiration from biological processes

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7.1 Importance of subject

Over billions of years of evolution, biological systems have optimized cellular energy conversion processes. Hence, as the scientific community searches for sustainable solutions to the world's energy challenge, nature has the potential to provide real answers. For one, nature uses earth-abundant metallocofactors within responsive protein matrices [1] to enable challenging chemical conversions. Both the metal active sites, as well as the hierarchical protein structure, can provide important chemistry and engineering lessons that may be broadly translated in all areas of catalysis. Additionally, nature has evolved photosynthetic pathways that provide inspiration for various forms of artificial photosynthesis technologies: (i) Bioinspired artificial systems can directly use sunlight together with CO₂, H₂O, or N₂ for the synthesis of essential molecules. (ii) Engineered photosynthetic organisms can directly produce target fuels and all chemicals from sunlight. (iii) Non-photosynthetic organisms can serve as catalysts in biohybrid systems, in which sunlight is harvested and provided to the organism by either photoelectrochemical or photovoltaic components.

7.2 State of the art and scientific challenges

Nature possesses a remarkable ability to activate small molecules under ambient conditions by utilizing earth abundant transition metal active sites within responsive protein matrices that optimize electron and proton transfer processes. In fact, many of the reactions of interest to a renewably-powered future that are identified in this report (Sections 1, 2, and 5) possess equivalent reactions in nature. Water is oxidized by the Mn₄O₅Ca oxygen-evolving complex of photosystem II [2], dinitrogen is reduced by Fe/Mo-containing nitrogenases [3], and CO and CO₂ are reversibly converted

by Ni/Fe-containing carbon monoxide dehydrogenase [4]. Furthermore, responsive protein matrices have evolved over billions of years to optimize essential energy conversion processes, such as energy and electron transfers by porphyrin-type cofactors in photosynthetic conversion and respiration.

7.2.1 Bioinspired catalytic systems

The metallocofactor active sites of enzymes provide researchers with key chemistry lessons regarding chemical conversion under ambient conditions. However, such metal active sites generally do not work alone. Biology has carefully engineered responsive protein matrices to control metallocofactor properties, subtly enhancing substrate reactivity by tuning matrix dynamics and energy barriers. Electron and proton delivery pathways are tuned to couple catalytic processes to the energetic constraints imposed by the environment. The clear role of protein matrices in biological systems contrasts sharply with the standard chemists' approach: here, the chemical properties of cofactors are tuned, while modification of the matrix is largely ignored. In recent years, the research community has made great progress in the understanding of metalloenzyme mechanisms, but many important research questions remain unanswered. In particular, the atomic level functioning of many biological systems is not deeply understood, nor is it known how to apply these insights in the context of hierarchical biological and engineered architectures. Rationally designed catalysts could be used in isolation or as modules in artificial photosynthesis of type (i).

7.2.2 Bioengineered and biohybrid systems

Photosynthetic microorganisms can be optimized by metabolic engineering and transformed into *microbial cell factories* to produce highly diverse compounds from abundant chemical starting materials, such as H_2O , CO_2 , N_2 , and O_2 , and sunlight (Figure 7.1A). Technologies employing certain photosynthetic microorganisms, such as algae and cyanobacteria, are already quite developed. Several industrial processes exist, such as [Ecoduna](#), [Algaenergy](#), [Algosource](#) in Europe and [Euglena Co. Ltd.](#) in Japan. These explicit biological systems have been engineered to host novel synthetic production pathways and enzymes. While most of the available prototypes still have low solar-to-chemicals conversion efficiencies and will re-

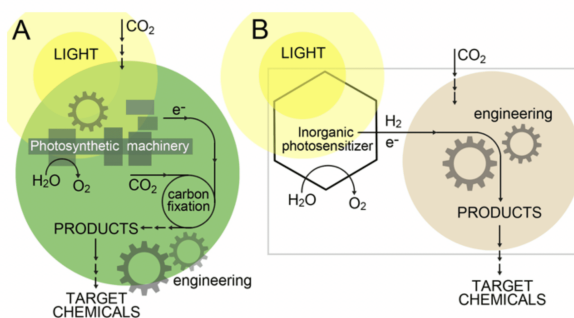


Figure 7.1: Comparison of type (ii) (Genetically engineered photosynthetic microbial cell factories, panel A) and type (iii) (biohybrid systems, panel B) artificial photosynthesis. Both involve microbes and are optimized to produce target chemicals in bioreactors. The inorganic photosensitizer stage in (B) is a complex photoelectrochemical nanostructure matching time, length and energy scales to overcome recombination losses in the four-electron water oxidation process (figure courtesy of P. Kallio, Turku Synthetic Biology team).

quire significant improvements to serve as industrial-scale production platforms, exceptions also exist. For example, lactic acid production by Photanol is expected to be technology readiness level (TRL) 8 by the end of 2020. Thus, exploitation of photosynthetic microorganisms to function as microbial cell factories, which efficiently catalyze the direct production of solar fuels and chemicals, is becoming a reality, supported by advances in synthetic biology technologies.

In contrast to photosynthetic microbial cell factories, which are type (ii) artificial photosynthesis, biohybrid systems (type iii)[5] involve a material–microorganism interaction; they couple non-photosynthetic microbial cell factories to, for instance, a photoelectrochemical stage (Figure 7.1B). The light harvesting stage provides the microorganisms (in a suspension or biofilm) with reducing equivalents in a suitable form, e.g. H_2 , electrons, or small carbon-based intermediates, to drive biosynthetic pathways that produce target chemicals. Thus, the potential of the biohybrid system lies in coupling the better efficiency of a photoelectrochemical stage with the ability of *in vivo* biocatalysis to generate virtually any product.

Several proof-of-concept experiments on biohybrid systems have been recently presented. In one study, microorganisms metabolized H_2 , formed by *in situ* photoelectrochemical water splitting, to drive CO_2 fixation and production of large alcohols with promising H_2 -to-alcohol conversion efficiencies [6]. In other work, bacteria or archaea fed directly on electrons produced by light-harvesting semiconductors to produce ammonia, methane, and other larger carbon compounds [7]. Additionally, in a recent collaboration between Evonik, Siemens, and Covestro, syngas was produced by H_2O and CO_2 electrolysis and supplied to microorganisms to produce alcohols by fermentation [8]. However, integrated devices are largely missing, and the TRLs are typically 2-3. Hence, it is clear that advances in both our fundamental understanding and device development are needed before real technological solutions can be realized.

Two important challenges that remain to be addressed in these systems are the poor understanding of the bacteria-electrode interface and electrogenesis. At present, protein-based photoelectrochemical cells for direct solar fuel production (type i) are not yet cost-competitive with fossil fuels due to issues with efficiency, durability, and scalability. Various cell architectures have been explored, including those using photosynthetic proteins, natural enzymes, or genetically engineered enzymes, combined with metallic or semiconductor electrodes [10].

Having discussed the state of the art for several forms of artificial photosynthesis technologies, we present a summary comparing their attributes in Figure 7.2.

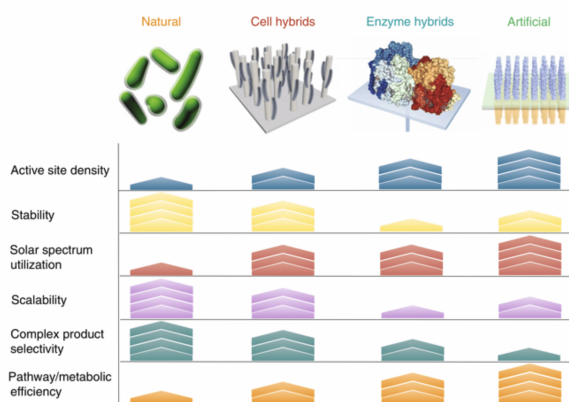


Figure 7.2: Overview of biological to artificial systems highlighting advantages and challenges of each approach. Reproduced with permission from [9].

7.3 Future research needs

Below, we propose several future research needs that will be critical to successfully engineer biological, biohybrid, and bioinspired systems for the renewable production of solar fuels and chemicals.

7.3.1 Rational design of modular biological and bioinspired catalysts for direct energy conversion

One of the “holy grails” in catalysis research is rational catalyst design. In this context, the lessons that can be extracted from natural systems may be great sources of inspiration, but such transfers of knowledge from biological systems to artificial systems (which may be homogeneous, heterogeneous, biohybrids, or engineered biological systems) with optimization of time scales, length scales, and energy scales at interfaces between modules can only be realized through detailed understanding of biological designs in a function-based systems engineering framework [7]. In particular, understanding how biology optimizes catalytic conversion will facilitate the distillation of design principles (DPs) (e.g. cofactor optimization) and functional requirements (FRs) (e.g. electron delivery and proton delivery) to feed into the systems engineering approach described below and illustrated in (Figure 7.3) [7]. To this end, the **development and application of experimental and theoretical tools for studying biological processes in real time** at the levels of the active site, the protein, and interprotein interactions is a critical research aim. Specifically, studies at the level of the metallocofactor active site are needed to reveal how the electronic and geometric structures of the metal active site evolve during the course of a reaction. Furthermore, the role of the primary and secondary coordination sphere, as well as the protein matrix, must be understood, which will require parallel advances in the synthesis of homogeneous molecular complexes and their integration into other higher order structures (e.g. supramolecular structures, polymers, semiconductors, metal organic frameworks, DNA origami, and enzymes). By extracting guiding DPs from understanding the active site and the protein matrix in small molecule activation, electron delivery, and proton delivery, one can exercise a modular approach to realize bio-inspired catalytic devices (Figure 7.3).

Nature’s potential is based on an interplay between diversification at the base level and natural selection at higher levels [12]. To mimic this, a **modular approach to bio-inspired catalyst development relying on systems engineering theory** is required. Such an approach should be function-based to reproduce the selection at higher levels, considering both technological and citizen needs. By defining FRs, mapping those onto DPs, and decomposing to define minimal sets of modules, redundancy can be avoided and robustness obtained [11]. From the diverse set of new scientific findings being constantly produced, molecular entities can be identified, interfaces optimized, and system morphologies determined, facilitating the development of bio-inspired catalysts and photon-to-product reaction cascades that work in synergy across interfaces (Figure 7.3). Since

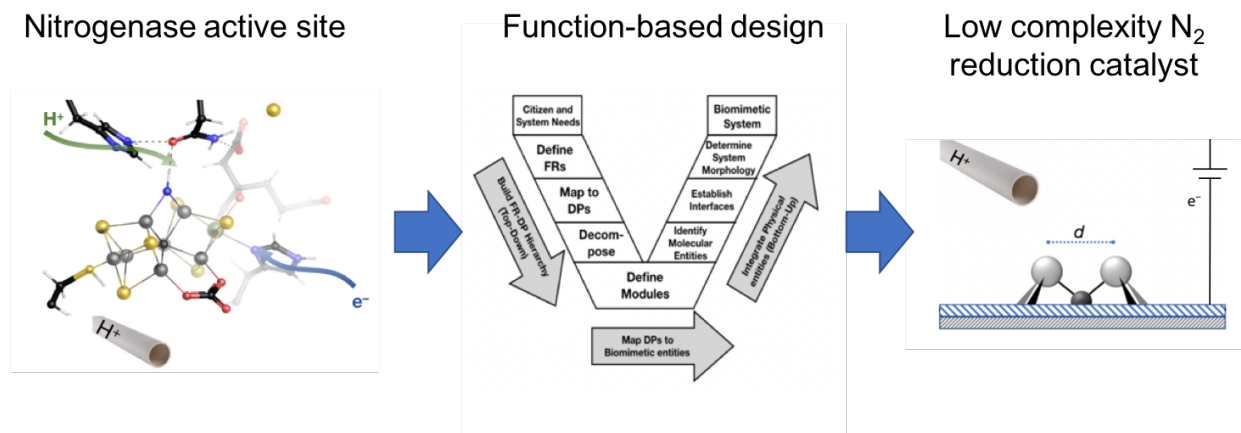


Figure 7.3: Nitrogenase metal active site (left), function-based engineering design (center, reproduced with permission from [11]), and a low complexity engineering model of an N_2 -reducing catalyst (right). The low complexity catalyst illustrates the interplay of three compartments, each representing a DP: a channel for proton transfer, a conductor for electron transfer, and a molecular catalytic site with a distance between active sites, d . Every compartment serves only one DP and FR to (a) maintain independence of the functional requirements and (b) minimize the information content of the design, which are the two engineering axioms for establishing robustness [11]. Optimization of proton and electron transfer rate process variables involves chemical engineering at the interfaces with the molecular catalytic site, and the distance, d , between the two Fe atoms that bind N_2 is thought to be an important parameter for tuning the N_2 reduction rate process variable of the active site.

this systems engineering framework will extend from the scale of molecules and atoms to that of devices and their applications (ideally at high TRL levels, e.g. 6-9), it will address cross-scale systems engineering challenges, identify control points, and predict system-wide effects of individual molecular components. This should extend even to the level of public willingness to act, which is the ultimate FR for success.

Challenging chemical conversions will require systems engineering of chiral responsive matrices that go beyond the adiabatic and nonadiabatic state of the art in catalysis (e.g. Marcus theory and transition state theory) and reproduce the enhanced substrate reactivity in proteins. This may be achieved by tuning matrix dynamics for semiclassical, coherent conversion of reactants into products with high forward reaction rates and low back reaction rates and recombination losses [1]. A comprehensive systems engineering framework will also enable the rational design of semisynthetic systems, i.e. with components obtained from a biological source with subsequent modification, and hybrid systems, which combine biological modules and artificial components (Figure 7.4). These approaches for engineering artificial components and existing natural systems with artificial motifs provide a route to enhanced energy conversion performance and optimized catalysis. To this end, optimization of the attachment of enzymes to surfaces will be necessary for direct electrochemical or photocatalytic conversions. Enzyme-based reaction cascades, or “assembly lines,” can be utilized for increased product selectivity.

7.3.2 Developing microbial cell factories for solar energy conversion to fuels and chemicals

For the application of photosynthetic microorganisms to direct conversion of solar energy into products, **synthetic biology toolboxes will have to be developed**. In particular, several main research objectives are clear. First, CO₂ fixation and uptake should be enhanced upstream. This may be done by optimizing specific existing pathways for CO₂ acquisition and concentration inside the cells, either in the plasma membrane or the thylakoid membrane. This will make maximal CO₂ fixation possible from atmospheric CO₂ concentrations. Once sufficient CO₂ is available upstream, novel metabolic pathways that act as strong electron sinks and target a diverse range of useful products need to be designed, both for direct conversion in photosynthetic organisms and indirect conversion in the non-photosynthetic organisms to be used in biohybrids. A subsequent research aim is to enhance the efficiency of photosynthetic electron transfer by eliminating undesired side pathways, e.g. oxygen reduction to water (the water-water cycle) and natural protection mechanisms that are not necessary when organisms are grown in protected environments. In order to avoid downregulation, inhibition, and negative feedback from overproduction and saturation of sinks, it will be necessary to design systems for the secretion of target chemicals and proteins, e.g. by engineering transporters into the cell membrane for collection of products outside the cell.

In addition to the fundamental and applied research needs related to engineering organisms, there is an urgent need for **industrial research on improving bioreactor designs**. The light exposure of cells needs to be optimized for maximum photosynthetic efficiency towards desired products, a DP associated with the FRs of newly engineered metabolic sinks, either in solution or in biofilms. Methods also need to be developed and implemented for efficient separation and collection of products from the cells in bioreactors.

7.3.3 Valorization of upstream products for feeding into the bio-based production stream

Generally, microbial cell factories will have limited lifetimes, and the biomass left over from these systems can be fed into bio-based production streams, including photocatalytic reforming, for enhanced valorization with cascading (Figure 7.5). This will provide a parallel route to high value,

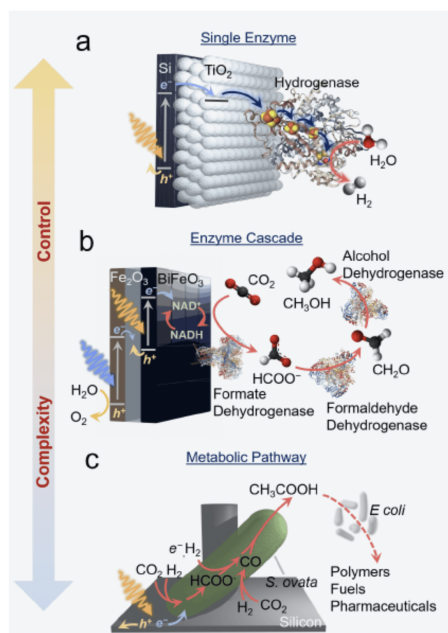


Figure 7.4: (a) isolated enzyme on electrode surface, (b) cascade of enzymes for high product selectivity, (c) biohybrid system. Reproduced with permission from [9].

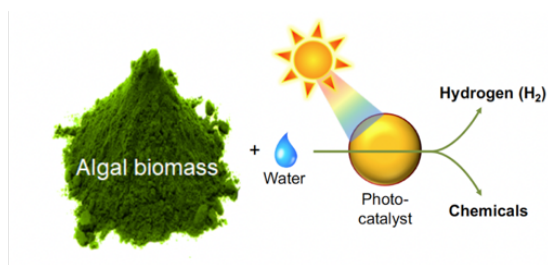


Figure 7.5: Upcycling of waste algal biomass from bioreactors for value creation in the circular economy.

low volume components to support the business case for affordable production of, for instance, jet fuel from the photobiological production stages discussed in previous sections.

7.4 Specific research goals

Some specific goals related to the future research needs discussed above are provided below.

7.4.1 Rational design of modular biological and bioinspired catalysts for direct energy conversion

1-year goals:

- Specification of target materials and device architectures in terms of FRs and DPs following the function-based engineering approach of Figure 7.3. At this early design stage techno-economic requirements to satisfy the FR of public willingness to act might include:
- Use of earth-abundant elements for cost-effectiveness and possible global upscaling
- Low metal content in active sites (only a small fraction of metal atoms in nanoparticle catalysts are surface-exposed and thus catalytically active)
- High selectivity and efficient energy conversion
- Operation under ambient temperatures and pressures in aqueous media, thus reducing the environmental impact of manufacturing (i.e. green, safe processing)

5-year goals:

- Developing mechanistic insight into the function-based biological designs of active sites of metalloenzymes (e.g. developing the DPs associated with the FRs of electron transfer, proton transfer, and catalysis in hydrogenases, dehydrogenases, nitrogenases, laccases, etc.) for the function-based engineering of characteristic proof of concept, modular catalysts for multi-electron/multi-proton reactions (e.g. activation of electron and proton transfer from water, or into CO_2 , O_2 , and N_2)

- Designing catalytic sites in synthetic and biological responsive matrices with enhanced catalytic performance (compared to the current state-of-the art synthetic and biological catalysts) in a laboratory environment (TRL 3) by optimization of process variables (e.g. the rates for proton and electron transfer at the interfaces with the molecular catalytic site and the catalytic conversion rates of the small molecules)

>10-year goals:

- Validation of molecular compartments covering DPs and exploration of their self-assembly into responsive matrices, their optimization at interfaces between compartments, self-repair, and regulation of arrays of responsive matrices to gain a better understanding of how to maximize productive energy gradients while minimizing recombination losses
- Boosting (photo)catalysis with tandem devices that operate on a laboratory scale with a photochemical current of 16 mA/cm² under AM 1.5 irradiation, corresponding to using 70% of incoming photons (TRL 4)
- Validating selected molecular compartments and responsive matrix self-assemblies under relevant field conditions (TRL 5)
- **Major cross cutting initiative:** translation of key biological catalysis concepts to optimized devices to merge the best of homogeneous, heterogeneous and biological processes.

7.4.2 Developing microbial cell factories for solar energy conversion to fuels and chemicals and valorization of upstream products for feeding into the bio-based production stream

1-year goals:

- Genome mining for novel enzymes with either improved catalytic function or novel reactivities.
- Quantum modelling of electron- and proton-transfer processes to establish a selection criterion for the design of metabolic sinks
- Integration of new control systems based on predictable models (e.g. machine learning) for phototrophic cultivation using natural sunlight
- Construction of an outdoor plant at TRL 8 for the production of organic acids (e.g. Photanol)

5-year goals:

- Exploration, selection, and characterization of robust strains and enzymes to be used as starting points in bioengineered systems

- Development and optimization of synthetic biology tools for the strains of interest with a particular focus on phototrophs
- Engineering robust host strains and production processes, with efficient CO₂ capture from the atmosphere and industrial sources to achieve a low (or neutral) carbon footprint.

>10-year goals:

- Developing life cycle assessments (LCA), techno-economic assessments (TEA), and social impact assessments (SIA) for specific processes of fuel and chemicals production.
- Development of large-scale demonstration plants to produce renewable, value-added commodity and bulk chemicals from photosynthetic cells and components.

7.5 Conclusions

The preceding discussion has highlighted a range of excellent opportunities for the production of solar chemicals and fuels from biological and bioinspired devices and catalysts. Automatized synthetic biology toolboxes are currently becoming available at the advanced level for heterotrophic (non-photosynthetic) microorganism systems (bacteria and fungi), and radical progress in the development of synthetic biology tools for photosynthetic microorganisms is underway, opening great prospects for realization of algal/cyanobacterial-based direct production of renewable and sustainable chemicals that are otherwise inaccessible. Today, several of the presented technologies are within reach, with several having already been developed in demonstrator projects. However, further research in real time enzymatic processes, systems engineering of bio-inspired catalysis, and synthetic biology is urgently needed for the sustainable production of solar fuels and chemicals from biological and bioinspired systems to become a reality.

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Section 8

The role of data and artificial intelligence

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8.1 Importance of subject

Scientific data are significant raw materials of the 21st century. To exploit its value, a proper infrastructure that makes it Findable, Accessible, Interoperable, and Re-purposable – FAIR – is a must. The enabling of extensive data sharing and collaboration in data-driven sciences (including the development of appropriate artificial intelligence tools) will advance basic science and engineering and lead to impact in industry and society. An important challenge facing society today is the efficient conversion of renewable solar and wind energy into sustainable fuels and chemicals. This ambitious goal requires the identification and design of new materials with properties tailored to their particular function. For example, many existing catalysts for key processes such as the production of hydrogen from water (Section 1) to be used as a fuel or the electrochemical production of ammonia for fertilizers (Section 5) are not sufficiently efficient or are made from chemical elements too scarce to be used at a large, global scale. Therefore, there is an urgent need for new catalyst materials.

The identification and development of new catalytic materials and their operating conditions have previously been based on experimental trial-and-error. Even though this approach has been successful in providing the large range of materials in use today, it is slow and costly. A more systematic approach is therefore required. Two new developments are useful to this end. One is the establishment of computational quantum methodology to reliably calculate many materials properties efficiently. Another important development is the establishment of experimental techniques for high-throughput screening of e.g. catalyst efficiency, again providing a way for more systematic and

efficient materials design. While these techniques are relatively established for homogeneous catalysis, their implementation remains a challenge for heterogeneous catalysis. Furthermore, these data can be collected in large databases with information about materials and further analyzed using artificial intelligence (AI) techniques.

However, very substantial challenges remain. The working catalyst is a complex, dynamical system, driven by many intricate processes, and to obtain a full characterization of the catalytic behavior under operating conditions including bulk and surface structures, catalyst/support interfaces, defects, molecular modifications is essentially impossible. Even identifying all important descriptive parameters of the catalyst and the overall conversion process is a major challenge.

8.2 State of the art and scientific challenges

Catalysis science is entering an era where the generation of new data from experiment and computation can no longer be handled by established methods. This is reflected in the so-called 4 V challenge, which identifies four characteristics of newly generated data that are rapidly growing: Volume (the amount of data), Variety (the heterogeneity of form and meaning of data), Velocity (the rate at which data may change or new data arrive), and Veracity (the uncertainty of data quality). Fortunately, big data of materials science offers not only challenges but also novel, extraordinary, and expansive opportunities for achieving new scientific knowledge and insight. These opportunities require new research concepts and lines of thought (for a recent review see reference [1] and references therein). Below, we provide a perspective on the state of the art and challenges associated with three areas that are central to the data-driven design of catalysts.

8.2.1 Data sharing

Currently, the common approach to sharing and storing data in catalysis science is to publish results as focused research studies, reporting only those few data that are directly relevant for the particular topic. Even when many different materials and conditions are studied, very few results are shared with the community. Data that are not deemed immediately relevant are often kept private or even thrown away. Over the last few years, however, a change in scientific culture has begun, and the community has started to consider the extensive sharing of data. To some extent, major advancements have already been realized for computationally generated materials science data, and the experimental field has been discussing analogous concepts for about a year. To achieve the goal of sustainable fuels and chemicals, this process needs to be accelerated and more directly involve the catalysis science community. We will now briefly sketch the state of the art of data sharing for computational catalysis science (and materials science in general) and identify significant challenges in translating that progress to experimental catalysis science.

Towards the effective utilization of newly generated computational data, a number of databases with many computed material properties have been recently established as summarized in Table 8.1 [2]. While these databases provide useful information (primarily properties of crystalline, bulk materials at low temperatures), they are too limited for the goal of sustainable fuels and chemicals, which relies on the properties of material surfaces, interfaces, and defects and their interactions with molecules over a wide range of experimental conditions.

Table 8.1: List of current major materials data infrastructures including the services they provide. Open Access: provides partial or full free access to data. Computational data: contains data originating from software simulations. Experimental data: contains data originating from experiments. Data upload: Allows upload of own data, with the possibility of issuing Digital Object Identifiers (DOIs). Workflow management tools: provides or collaborates in the development of open-source software tools for workflow management. Web API: data can be accessed remotely with automated scripts. Data analysis tools: provides online or offline data analysis tools, including machine learning. Reproduced from reference [2]. References for each individual database can be found in reference [3].

*Upload requires access to private/institutional storage space.

**Open Access to a subset of data.

	Open Access	Comp. data	Exp. data	Data upload (DOIs)	Workflow management tools	Web API	Data analysis tools
AFLOW	✓	✓			✓	✓	✓
Computational Materials Repository	✓	✓			✓		✓
Crystallography Open Database	✓	✓	✓	✓			
HTEM	✓		✓	✓		✓	✓
Khazana	✓	✓	✓				✓
MARVEL NCCR	✓	✓		✓	✓		✓
Materials Data Facility (MDF)	✓	✓	✓	✓ (DOI)*		✓	
Materials Project	✓	✓			✓	✓	✓
MatNavi/NIMS	✓	✓	✓				✓
NOMAD CoE	✓	✓		✓ (DOI)		✓	✓
Open Quantum Materials Database	✓	✓					✓
Open Materials Database	✓	✓		✓	✓	✓	✓
SUNCAT	✓	✓				✓	✓
Citrine Informatics	✓**	✓	✓	✓		✓	✓
Exabyte.io						✓	✓
Granta Design		✓	✓				✓
Materials Design		✓	✓				✓
MaterialsZone			✓				✓

In terms of experimental data, there are essentially no open, publicly available databases with extensive amounts of systematic data for heterogeneous catalysis currently. Traditionally, the sharing of data within the field has not been considered a main priority, and building momentum

in this direction is a significant challenge. Additionally, extensive data sharing is only useful when the data are fully characterized by metadata and ontologies, including a detailed description of the catalyst material and the process used to collect the data. While this is relatively straightforward for computational data (i.e. providing calculation input/output files), defining suitable metadata for experiments is a major challenge due to the complexity of catalysis research.

8.2.2 Data reliability

The extreme heterogeneity of experimental data poses a significant challenge to implementing data-driven approaches to heterogeneous catalysis. This heterogeneity arises from a lack of standardization and reproducibility in both synthesis and measurements. Furthermore, only a limited part of the parameter space (e.g. temperature, pressure, feedstock composition) is typically tested, which introduces biases into the data. Finally, long-term tests and those with dynamic operating conditions that are relevant to systems powered by renewable energy are rarely performed.

Although computational data are inherently more standardized than experimental data thanks to established metadata frameworks, there still exist significant challenges associated with the validation of computational data. Most first-principles calculations performed for heterogeneous catalysis rely on Kohn-Sham density functional theory (DFT), the accuracy of which, unlike some rigorous mathematical models, cannot be systematically improved. There is a need to validate computational data against more accurate and systematically improvable models, but despite decades of research in condensed-matter physics, such methods do not yet exist. The problems are aggravated in the field of heterogeneous catalysis, where we know from the outset that reaction barriers are difficult to reliably compute because the electronic wave function cannot be represented by a single Slater determinant (strong correlation). Essentially all first-principles methods become inaccurate in such situations.

An additional challenge facing computational simulation is the need for reliable data on the performance of catalysts under realistic conditions. This is not possible at present, as the continuously changing surface structure and composition of the catalyst are dynamically generated under operating conditions. It is unlikely that the working surface structure corresponds to known thermodynamically stable bulk structures. Beyond the active phase itself, catalyst performance is further influenced by microstructure, heat and mass transport, process conditions (e.g. reactor technology, electrochemical interface) (see Figure 8.1). Addressing these complexities and dynamics in a traditional multiscale framework is not feasible with present methodology. For instance, the microkinetic model for a simple, selective oxidation process on a well-defined single crystal model catalyst depends on a few dozen reaction barriers. A more complex process like ethanol synthesis on the same catalyst already requires hundreds of barriers. This complexity is exacerbated when higher structural complexity of the catalyst is taken into account.

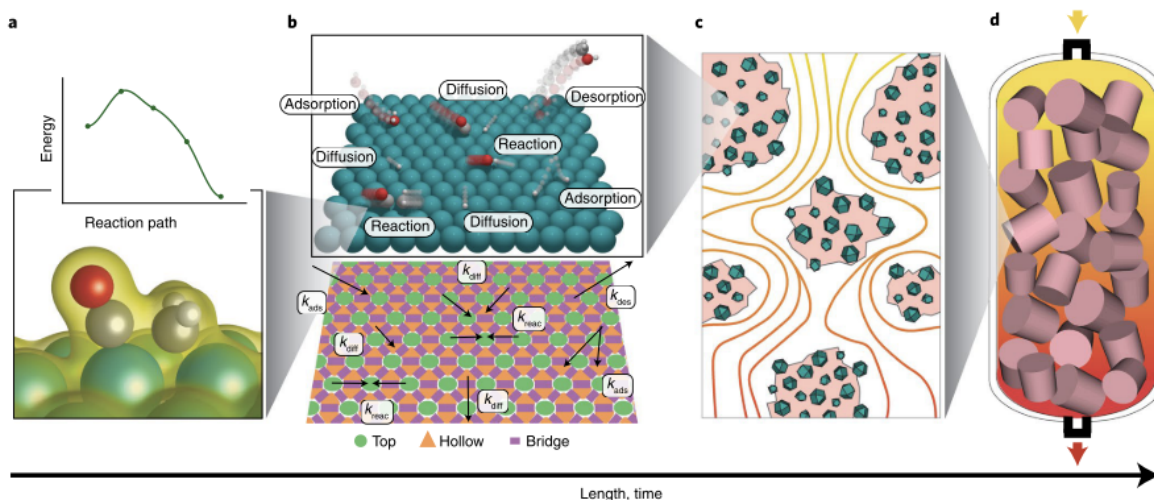


Figure 8.1: The multi-scale nature of heterogeneous catalysis. a) Electronic structure calculations provide information on individual elementary processes in the catalytic cycle. b) First-principles microkinetic models use this information to evaluate the interplay between all elementary processes and establish the intrinsic catalytic activity. d) The integration into transport models determines how this activity interfaces with the overall macroscopic flow of heat and mass. c) For real catalysts, this integration requires an intermediate step appropriately coarse-graining over the catalyst microstructure. Note that the direction is not just from left to right but e.g. step b) may indicate that more studies of step a) need to be performed. Reproduced with permission from [4].

8.2.3 Artificial intelligence

Artificial intelligence tools promise to decipher and take advantage of the data deluge introduced by the 4 V challenge. Note that we use AI as an umbrella term that includes all of the machine learning methodology as illustrated in Figure 8.2. While many powerful AI techniques have already been devised and are readily available e.g. as open source, many challenges remain for their effective use in catalyst design. The efficiency of AI methods depends strongly on the problem representation (i.e. the employed descriptors), and a large effort is necessary to translate the domain knowledge of catalysis science into efficient representations/descriptors for AI applications.

8.3 Future research needs

Based on the current state of the art and scientific challenges outlined above, we have identified the following five research areas that deserve and urgently need attention in the near future.

8.3.1 Establishing the wide use of FAIR data infrastructure, metadata, ontologies, and databases

Open and effective data sharing implies the consideration of what are now called the FAIR data principles [5], which state that data are Findable for anyone interested, that they are stored in a

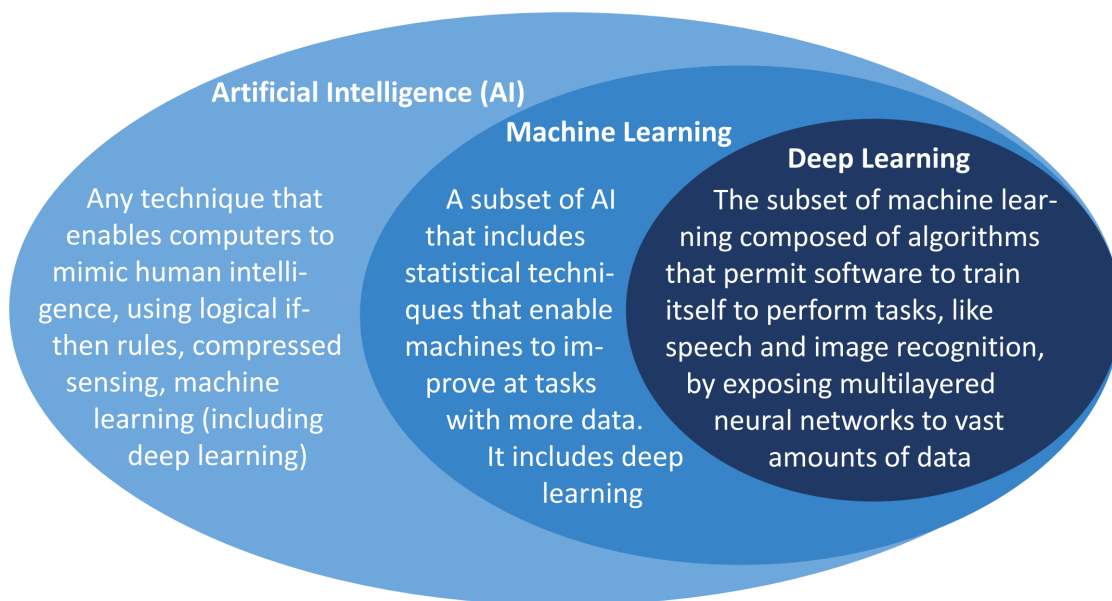


Figure 8.2: The concept of artificial intelligence includes and expands on machine learning and deep learning techniques.

way that make them easily Accessible, and that their representation follows accepted standards [6] and all specifications are open – hence data are Interoperable. These criteria enable the data to be used for research questions that could be different from their original purpose; hence data are Re-purposable or Reusable. If data were openly available and well described, many more people would work with the data, not only researchers within catalysis, but also for example computer scientists and applied mathematicians. We can expect surprises about what people will do with data when they are well characterized and made available, probably using tools that the current catalysis science community is unaware of. This was, for example, the case with a Kaggle challenge for an optoelectronic materials search [7], where nearly 900 groups of different backgrounds and approaches participated.

The basis of useful data sharing is a suitable research-data infrastructure that facilitates efficient data collection and description in terms of metadata and ontologies. In order to achieve the widespread adoption of these data-sharing principles by the catalysis community, we foresee the need to establish a new data infrastructure for materials data relevant to sustainable fuel and chemical production, both experimental and computational. This includes the definition of suitably descriptive metadata, which will then be provided by users for each uploaded entry. For computational data, this implies that the full input and output files of the computations are provided, preventing the need to repeat calculations. Such a complete characterization of experimental data is more challenging, as it must encompass the sample (including its synthesis and history), the apparatus, and the measurement conditions and quantities.

In general, the infrastructure should be as flexible as possible by not enforcing particular

standards, and participation should be by choice. It should be possible to store data both at research institutions and on central servers, but the overall management of the infrastructure, e.g. linkage of distributed servers, user management, metadata infrastructure management, should be the responsibility of central data infrastructure services. Such a scheme is illustrated in Figure 8.3.

Once the infrastructure is established, useful data-access tools (e.g. search engines, user-friendly graphical user interfaces, a “Catalysis Encyclopedia”) should be developed to engage the greater catalysis community and provide a means for designing new catalyst materials. The completed data infrastructure should support several levels of exposition to raw and derived data. An expert user with specialized knowledge should be able to navigate complex, low-level data, while newcomers should be able to easily access useful high-level data. Experimentalists should be able to efficiently query computed data and test their hypotheses based on built-in models. For instance, an experimentalist should be able to propose a new defective catalyst surface and receive on-the-fly information such as adsorption energies or projected catalytic activities from different higher-level models. This could be based on results of newly submitted first principles computations (using automatic workflows) or using interpolated data from machine learning models. Likewise, experimental data should be easily browsable, and users should be able to tag missing experimental data of interest, thereby motivating new experiments.

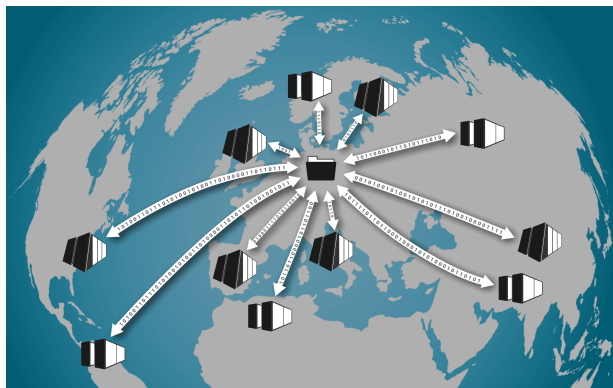


Figure 8.3: Open and effective data sharing will require the establishment of an infrastructure that facilitates data collection and description in terms of metadata and ontologies.

8.3.2 Improving reliability of experimental data through standards and benchmarks

To enable the evaluation of experimental data reliability, future catalysis experiments need to meet certain requirements. The synthesis of a catalyst material must be carefully documented such that reproduction is possible without consulting the original author. Complete characterization of materials and reference compounds (benchmarks) including detailed structural (bulk, local structure, defects, surfaces) and thermodynamic characterization should be the goal. It is highly desirable to augment classical structural data (from diffraction studies) with information on local structure and short-range order (from spectroscopic studies). Catalysts should ideally be tested across a broad range of process parameters including temperature, pressure, and various feed compositions following standardized procedures since the optimal operation conditions may depend strongly on the chosen catalyst. Because catalysis is a kinetic process, a detailed characterization of the dynamics

is crucial as well. The catalytic experiment should also be compared with respect to a standardized benchmark that is included in each measurement. Obviously, the metadata belonging to catalyst performance data need to be documented together with the performance data. Physical and chemical properties of catalysts, which will correlate with performance data, should be measured during operation. Catalysis studies should report on both successful and unsuccessful results, the latter of which is largely missing from current literature.

8.3.3 Improving reliability of computational data through higher level methods

The currently available tools that can be used to help validate Kohn-Sham DFT calculations can be roughly divided into three categories: diagrammatic methods, Monte-Carlo methods, and embedding methods.

Diagrammatic methods including RPA, Møller–Plesset perturbation theory, coupled-cluster theory form a hierarchy with the scaling of the methods increasing from cubic in system size to the 7th order in system size. The accuracy of the methods roughly increases along the hierarchy. However, because of the detrimental scaling, applications to heterogeneous catalysis are difficult. To reduce the scaling applying the locality principle, e.g. using some sort of embedding, seems to be a highly promising research route. First examples demonstrate an enormous potential, but work needs to be done to make these methods more automatic and routine and reproducible. Monte-Carlo methods of various flavors have improved scaling. The advantages are offset by the statistical noise and some additional approximations, making the reliability of calculated energy barriers uncertain. More research is required, in particular, on how to handle all-electrons calculations and core states.

8.3.4 Generating reliable computational data that correspond to realistic operating conditions

In order to assess the accuracy of present-day theoretical methods and understanding it is necessary to decide, together with experimental groups, on model systems of relevant but feasible complexity and study them jointly by theory and *in situ*/operando experiment, providing high quality benchmark data.

8.3.5 Leveraging artificial intelligence for challenges in catalysis

As more data is generated and made available, AI tools will play an integral role in accelerating catalysis research (Figure 8.4). For example, AI can analyze results of experimental or computational studies and suggest the next experiment or computation through active learning. Here we outline some major application areas for AI in future catalysis research.

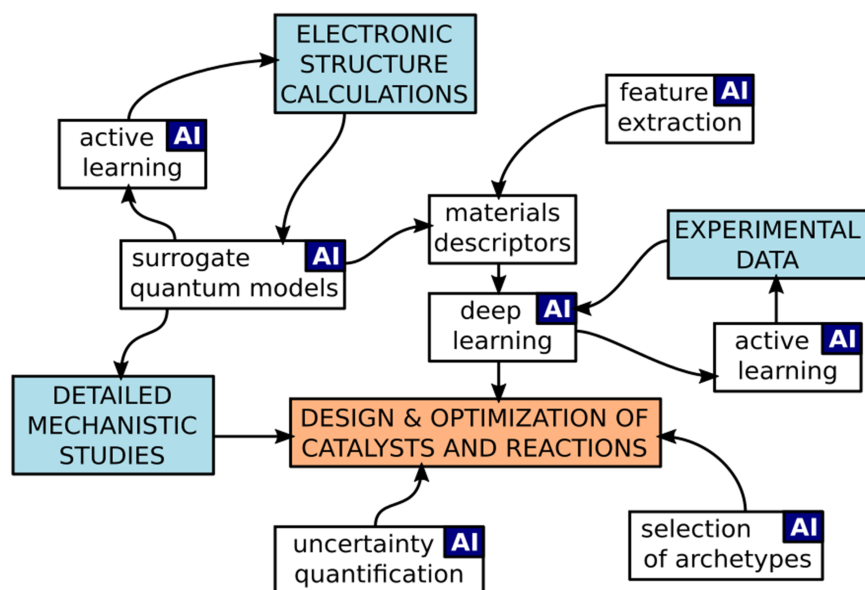


Figure 8.4: Artificial intelligence is expected to play an important role in a multitude of ways in catalysis research.

- Identifying correlations that are not obvious from current physical/chemical understanding:* AI is often used for automatic pattern recognition because it can analyze high-dimensional representations much more efficiently than a human. The goal is to identify whether a set of features (possibly a subset of initially proposed features) correlates with a given target property. The latter could be a performance figure of merit of a catalytic process (activity, selectivity, stability) or an “intermediate descriptor” (e.g. an adsorption energy of an intermediate on a given surface site). Feature selection/extraction methods should be able to provide new fundamental understanding in catalysis and make useful predictions of materials properties.
- Identifying statistically exceptional data points:* The space of different chemical and structural materials is practically infinite. However, there may be only a few suitable materials to catalyze a particular chemical reaction efficiently. Hence, the relevant data are a statistically exceptional minority (see reference [1] and references therein), and if this fact is ignored, a statistical analysis that assigns the same importance to all data will encounter problems. Importantly, these statistically exceptional data points may also be the result of errors in the database or data collection. Compressed sensing, subgroup discovery, machine learning, and other AI methods can identify the validity of data points and identify descriptors that characterize a “subgroup” of the statistically exceptional data points, i.e. of the possibly interesting catalyst. While progress in recent months has been noticeable, it is clear that significant advances of the AI methodology are still needed.
- Making faster and/or more accurate predictions than are possible with first-principles meth-*

ods: A promising application of AI to chemistry is to learn surrogate potentials/force-fields that enable the statistical sampling of thermodynamic and/or kinetic quantities that are orders of magnitude faster than DFT. Furthermore, if experimental data or higher level theoretical data are used to train the AI model, its predictions may also be more accurate. Much fundamental work has been done in this direction [8], but more work is needed to streamline the AI learning, especially for multicomponent systems, and to improve the accuracy for defects and chemical reactions. This field is rapidly developing and should provide interesting results on a 5-year timescale.

- *Combining first-principles, statistical mechanics, and experimental data*: Purely theoretical simulations and purely experimental measurements cannot easily provide some quantities relevant to catalysis under operating conditions. AI can potentially be utilized to find surrogate models that bridge the gap between theoretical and experimental data, overcoming the need to construct a fully detailed atomistic model of the various intricate processes that rule the catalysis. This area is largely unexplored and may well take 10 years or more to mature.
- *Using active learning to guide experiment and simulations*: Rather than (only) predicting properties for a given test data point, AI models can be designed to suggest new points for improving the model itself (i.e. where the model’s predictive uncertainty is large) or for optimizing a given property. In either case, the new data point must then be evaluated using experiment or computation. Several active learning schemes have been proposed in the literature, especially in the context of Bayesian learning, and some are already used in materials science [9]. However, this aspect of AI needs more exploration on a 5-10 year timescale.

8.4 Conclusion

The 4V challenges will become severe for catalysis research in the rather near future, especially for experimental studies where the amount of data collected by e.g. TEM or XPS will become enormous. Simulations will face similar challenges, in particular when exascale computers become available and more and longer molecular dynamics runs are being performed. The field needs to define what data are relevant and should be stored on a fast, easily accessible, and most likely (largely) decentralized storage system. Building a FAIR data infrastructure for catalysis data is the first and urgent step. With all the metadata, ontology, and technical issues, this may well take 3-5 years and will have to be continuously expanded upon and improved. Here, encouraging the wide acceptance of data sharing and open science by the community still needs special attention. Several databases exist already, and all this information should be made accessible by simple tools, such that the researcher does not even realize where the data are stored. However, we also note that

the amount of data relevant to heterogeneous catalysis is still very small and the documentation of many data is very incomplete. Thus, there is an urgent need to create more data that is reliable and well-described. It is crucial that both computational and experimental researchers increase their efforts in establishing benchmarks and assessing the accuracy and precision of their studies. Eventually, AI tools can be applied for analyzing the data on a large scale to help the design new experiments and predict statistically exceptional materials that fulfill the conditions of a promising catalyst (e.g. stability, synthesizability, selectivity, activity). In this process, we also foresee an exciting opportunity for even closer collaboration (if not a complete merging) of computational and experimental studies. While important contributions from the discussed AI applications will come in the following years, significant breakthroughs can be expected during the next decade and beyond.

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Section 9

Scale-up of electrochemical processes

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9.1 Importance of subject

Scaling up electrochemical processes is an essential premise for the production of sustainable fuels and chemicals in a defossilized society. Electrochemical processes enable the conversion and storage of intermittent renewable electricity (from e.g. solar, wind) into the same variety of chemicals and fuels needed and used by our society today. Historically, thermochemical processes have been economically favorable compared to their electrochemical counterparts for most products. Hence, the latter have only been developed to scale for products not easily obtained by the former (e.g. chlor-alkali process for Cl_2 production). Therefore, electrochemical processes for most products are not yet developed and implemented at a scale that can sustain the global need for chemicals and fuels. The time horizon of conventional process scale-up from the laboratory, i.e. technology readiness level (TRL) 1, to industrial deployment, i.e. TRL 9, in the chemical and fuel industry (typically 20+ years) is too long to meet EU goals for the transition away from fossil resources. Therefore, there is an urgent need to accelerate the scale-up process of important electrochemical processes (e.g. those investigated in Sections 1, 2, and 5) and their integration with established chemical processes up- and downstream (e.g. those investigated in Sections 3, 4, and 5). This Section outlines the requirements and related recommendations to achieve this.

9.2 State of the art and scientific challenges

An integral part of innovation is the evaluation of technical, economic, and social feasibility, which must be performed at every stage of the scale-up from TRL 1 (observation of basic working principles) to TRL 9 (competitive manufacturing in operational environment). The state of the art for

scale-up is to consider and integrate technical challenges at low TRLs. Above TRL 5, it is critical to think in terms of industry value chains including both technology providers and potential end users and to consider present and future stakeholders. Testbeds, which are sites that provide infrastructure for demonstration of processes ranging from TRL 5-8, are useful to facilitate scale-up of chemical processes in general. Successful testbeds focus on a well-defined class of technologies and bring together upstream and downstream stakeholders from industry with academia and applied research institutions. Below, the state of the art of various electrochemical processes of interest is examined in more detail.

9.2.1 Water electrolysis to produce hydrogen

Hydrogen production via the electrolysis of water (Section 1) is a key bridge between renewable electricity and synthesis of commodity chemicals and fuels such as ammonia, methane, and methanol (see Sections 3, 4, and 5). Water electrolysis is currently performed at the industrial scale, but improvements are needed to realize plants that are compatible with utility scale photovoltaic and wind farms (100+ MW) while remaining economically viable.

Alkaline water electrolysis (AWE) is a mature technology and the basis of industrial plants with capacities of the order 100 MW. The state of the art AWE stack size is approximately 2.5 MW with lifetimes greater than 40,000 hours. Because of the technology's maturity, efforts to improve AWE are primarily focused on total plant optimization to minimize the balance of plant cost. While the improvement of electrocatalysis for AWE is a highly active field of research, new academic findings have had limited impact on the electrodes used in commercial plants. Other early stage ideas relevant for scale-up focus on completely new engineering concepts such as operation at high temperature/pressure and usage of anion exchange membranes.

Proton exchange membrane water electrolysis (PEMWE) provides advantages over AWE by reducing ohmic resistance and allowing for pressurized operation. System sizes are at the 10 MW size, with stack sizes of 2.5 MW and lifetimes of more than 40,000 hours. A significant obstacle to further scale-up is the scarcity of iridium, which is used in the electrocatalyst at the anode. Alternative materials that are both catalytically active and stable in an acidic environment remain elusive despite significant research efforts; hence the remaining options are to significantly reduce iridium loadings (by a factor of 50; see Section 1) or develop and introduce anion-conducting membranes to obviate the need for stability under acidic conditions. Additional challenges for scale-up of PEMWE result from the lack of multiscale modelling tools at the cell and stack level and automated production technologies.

High temperature solid oxide electrolysis cell (SOEC) based systems have smaller system sizes on the scale of 100 Nm³/h with stack sizes on the order of 1-3 Nm³/h and lifetimes of more than 10,000 hours. The efficiency of SOEC technology benefits from operating at higher temperatures

where both the thermodynamics and kinetics of water splitting are improved, and these systems are especially attractive when waste heat sources are used to bring the system to the operating temperature. Because of the small stack size and modularity of SOEC systems, there are particular needs for automated production technologies and better multiscale modeling tools at the cell and stack level to determine the optimal design for industrial-scale plants.

9.2.2 Electrochemical synthesis of organic products

Conceptually suitable feedstocks for the sustainable production of all organic compounds used by society today include CO₂, biomass, and plastic waste. Plastic waste is currently not considered as frequently as CO₂ and biomass because of competing effective thermochemical recycling approaches based on existing technology. Organic products can be generally classified into fine chemicals, commodity chemicals or fuels, according to their market volume. Electrochemical processes that produce compounds with smaller market volumes are naturally at higher TRLs, because they can be industrially deployed at a smaller scale, require less complex integration with upstream and downstream processes, and typically have higher margins resulting in easier economics even in a difficult market environment. Industry sees the development of technologies for the production of fine chemicals, commodity chemicals, and fuels as consecutive steps in scaling up electrochemical production of organic compounds, as comparable process technology is used that can be the basis for the next step in scale-up (Figure 9.1). In the case of using a given process technology as a basis for scale-up to target a larger market size (e.g. CO₂ to CO switching target from fine chemical to commodity market), the corresponding TRL is logically reduced in the new context (e.g. from TRL 8-9 to 5-6), as the plant size has to be scaled-up again for commercial application.

Fine chemicals are already produced electrochemically on the kilogram scale economically in the pharmaceutical industry where production volume is low, requiring minimal scale-up, and product margins are high. Other processes for fine chemical production that are currently being scaled up industrially include low-temperature conversion of CO₂ to CO for use in laboratories (TRL 5-6), glucose to sorbitol (TRL 4), and acetonitrile synthesis.

Chlorine and aluminum are inorganic commodity chemicals historically and still today produced via electrochemical processes, because of their difficult accessibility via thermochemical processes. This showcases the feasibility of large scale electrochemical production of commodity chemicals.

Promising electrochemical processes for the production of organic commodity chemicals are currently being developed industrially for the conversion of CO₂ to CO at both low temperature via aqueous electrolyte electrolyzers (5 kW, TRL 5-6) and high temperature via SOECs (TRL 8-9) for low volume industrial applications (e.g. for phosgene, polycarbonates, polyurethane, isocyanates production). Production of light organic molecules from CO₂ (e.g. formic acid, methanol,

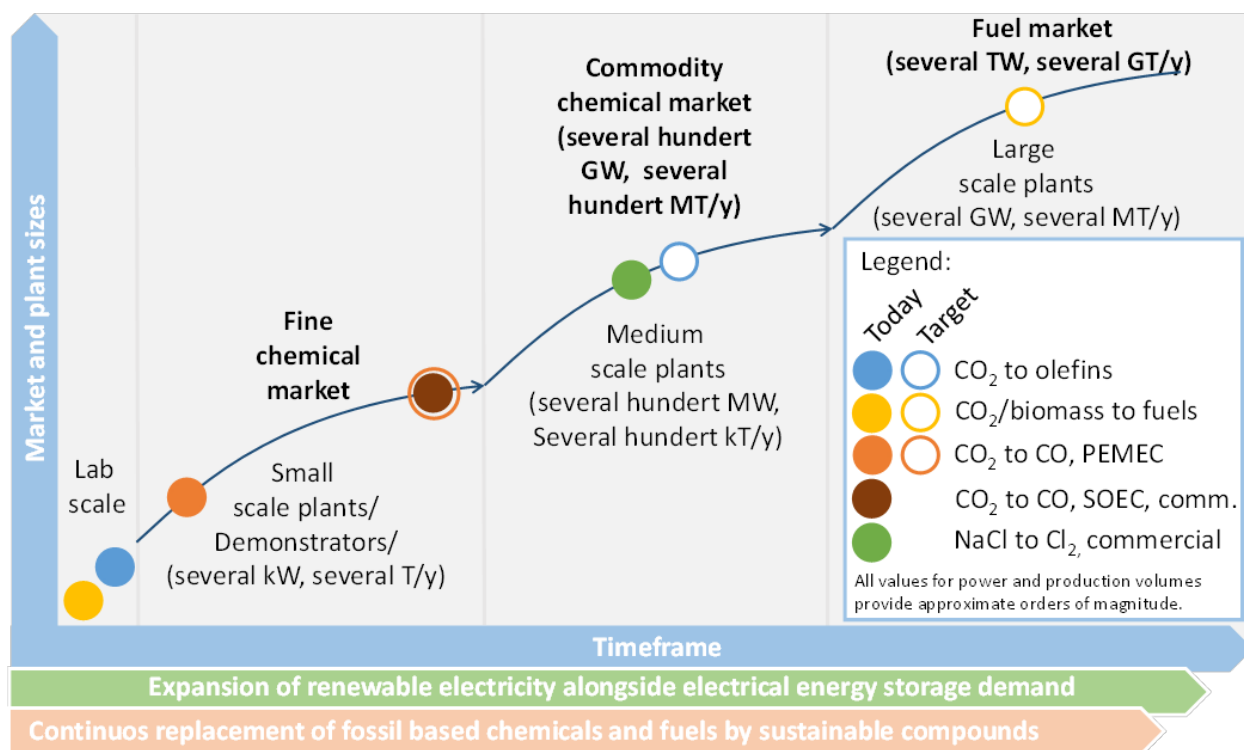


Figure 9.1: Consecutive steps in scaling up electrochemical production of organic molecules.

ethanol, oxalic acid, ethylene) has received considerable academic interest (currently at TRL 3). Particularly outstanding performance has been demonstrated for ethylene production, attracting industrial attention. Electrocatalytic conversion of biomass to commodities is also of interest from an industrial perspective (e.g. HMF to FCDA).

Electrochemical production of fuels is still nascent, with only methanol (TRL 2) gaining significant interest in academic literature. Other promising pathways to sustainable fuels involve coupling to established thermochemical technologies such as those discussed in Section 4, e.g. CO₂ to kerosene via CO and Fischer Tropsch, methanol to gasoline, and CO₂ to oxymethylene dimethyl ethers. It is essential to carry out preliminary system cost and sustainability studies to compare such renewable electricity based fuels to alternative energy carriers for mobility (e.g. batteries, biofuels).

Common challenges for the scale-up of all organic product categories involve complex reactor and process engineering. Due to the scale of envisaged technology for commodity chemical and fuel production, there are additional challenges related to integration with other infrastructure (e.g. electricity input, reactant input, reactant and product transport). Another important challenge in these cases is identifying a complementary anode reaction that produces a valuable product with market volume comparable to the cathode reaction product. As discussed in Section 2, improving the selectivity and stability of CO₂ reduction electrocatalysts is also a core challenge for

the technology that is actively being pursued in academia and must be considered in the context of scale-up.

Across all product categories, academic research has tended to focus primarily on catalyst research and development, with less attention given to other essential elements of electrochemical technology such as membranes (e.g. anion exchange membranes for direct CO₂ electro-reduction), gas diffusion electrodes, and reactor design. Furthermore, academic research is often carried out under conditions not relevant to industrial applications (e.g. room temperature, low current density, absence of impurities). This misalignment is a hurdle for later technology scale-up and must be overcome by increased collaboration and communication between academia and industry. The reliability of commodity and fuel production electrochemical units must eventually be tested under industrial conditions with realistic electrode sizes and with statistically relevant stack sizes (100-200 cells). Setting the scale-up challenge for electrochemical production for organic compounds into perspective, current scale plants and demonstrators (kW or T/y) have to be scaled-up to the scale of several hundred MW or kT/y for the production of commodity chemicals and to the scale of several GW or MT/y for the production of fuels.

9.3 Future research needs

Scale-up is a complex optimization problem. Compromises typically have to be made between performance, durability, and cost (see Figure 9.2). The optimal compromises will differ from one use case to another. In the following, we have identified three future research needs that are critical to the scale-up of electrochemical processes and cut across the renewable production of hydrogen, fine chemicals, commodity chemicals, and fuels.

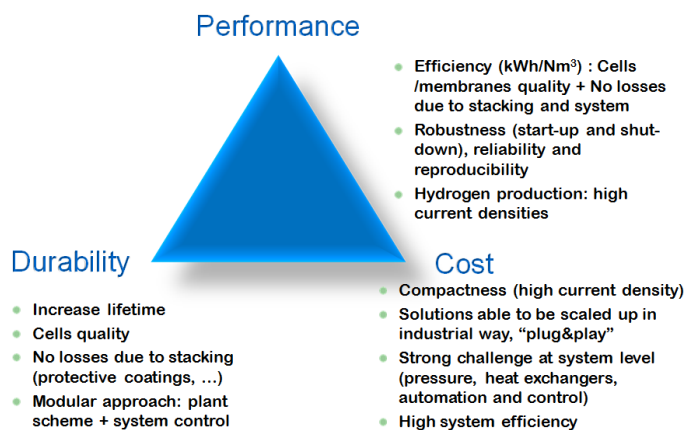


Figure 9.2: General challenges to consider when scaling up electrochemical processes. Figure courtesy of Julie Mougín, CEA.

9.3.1 Scaling up early-stage ideas (TRL 1 to 5)

The process of scaling up from initial idea to prototype must be accelerated. The fundamental challenge is that early-stage ideas require constant iteration before and during the process of scale-up to assure their feasibility in subsequent scale-up steps and large scale deployment. Cross-cutting objectives for scaling up early-stage ideas across hydrogen, fine chemicals, commodity chemicals, and fuels include

- Creating a governance structure that includes constant exchange between research institutions and industry while still allowing room for breakthrough innovation
- Establishing efficient feedback channels between early-stage ideas and pilot-scale demonstrations
- Defining test standards relevant for scale-up jointly by research institutions and industry
- Identifying feasible pathways and potential pitfalls in perspective of scale-up and large-scale deployment of technologies together with all relevant industrial stakeholders

The state of the art section above outlines early-stage ideas such as CO₂ electroreduction to light organic compounds and hydrogen production. Specific objectives for these technologies include

- Develop one electrochemical process for production of a light organic compound (e.g. methanol, ethanol, ethylene) to TRL 6 (5-15 kW stack level) within 5 years.
- Develop industrially relevant multiscale modelling tools for cell and stack modeling within 5 years.
- Develop one electrochemical process for production of a light organic compound (e.g. CO) to TRL 8-9 (1 MW capacity) for low volume commodity chemical applications within 10 years.
- One of the presented new electrochemical processes achieves 10% global market share within 15 years.

9.3.2 Scaling up pilot-scale stacks and small-scale plants to industrial processes (TRL 5 to 9)

The primary objective here is to identify the key performance criteria for industrial-scale deployment even in absence of a clear, economically viable perspective at that stage. This requires instruments in place to facilitate scale-up, integration with upstream and downstream processes, and life-cycle/technoeconomic analyses. Cross-cutting goals include

- Setting up feedback loop with lower TRL ideas
- Creating innovation instruments such as testbeds that facilitate high-risk prototype testing and demonstrations by sharing the risk among public and private stakeholders

Presently, the two most promising technologies at this stage of maturity are electrolysis of CO₂ or CO₂/water to either pure CO or syngas (CO/H₂) at low temperatures using silver catalysts (10-15 kW, 1.5-3 Nm³/h demonstration plants) or at high temperatures (100 Nm³/h plants). The

most promising short-term (5-10 year) application of these technologies are for the production of fine chemical precursors (c.a. 2000 Nm³/h or 22 kT/y of CO required). Due to the modularity of electrochemical processes, initial application to fine chemical production is a stepping stone for deployment alongside large-scale thermo-catalytic processes (order of 10,000-100,000 Nm³/h to or 100-1,000 kT CO/y). Specific goals for these technologies include

- Demonstrating that the smallest repeat unit is scalable to 2,000 Nm³/h (~22 kT CO/y) at TRL 8 and can be successfully integrated with downstream chemical conversion technologies within 5 years
- Developing an industrial plant capable of electrochemically producing 2,000 Nm³/h of CO or syngas within 10 years

9.3.3 Integrating electrochemical hydrogen production with large-scale thermocatalytic processes

The integration of sustainably produced hydrogen with large-scale thermocatalytic processes is already possible with known technology today. The key obstacle in making this a reality at the industrial scale is the cost of the electrochemically produced hydrogen. This is mainly driven by the high electricity price and the CAPEX of the electrochemical process, which is still orders of magnitude higher than for the competing thermochemical process (steam methane reforming). Figure 9.3 illustrates the key performance indicators (KPI) of AWE, PEMWE, and SOEC technologies. The specific KPIs that need improvement should be determined by performing a total plant optimization, but cross-cutting short-term research goals that have already been discussed include the development of multiscale cell and stack modelling, scalable manufacturing technologies, and online monitoring technologies for industrial plants.

Specific research goals for AWE include

- Transferring low TRL catalyst technologies to commercial electrodes (TRL 8) within 5 years
- Alternative innovative processes with optimal performance, durability, and cost structure for integration with downstream thermocatalytic upgrading processes (TRL 6) within 5 years

Specific research goals for PEMWE include

- Operation of a 100 MW PEMWE-based hydrogen plant integrated with a downstream thermocatalytic process within 5 years
- Development of competitive non-Nafion membranes within 5 years
- Introduction of alternative commercial anode catalyst material to iridium on the market within 10 years

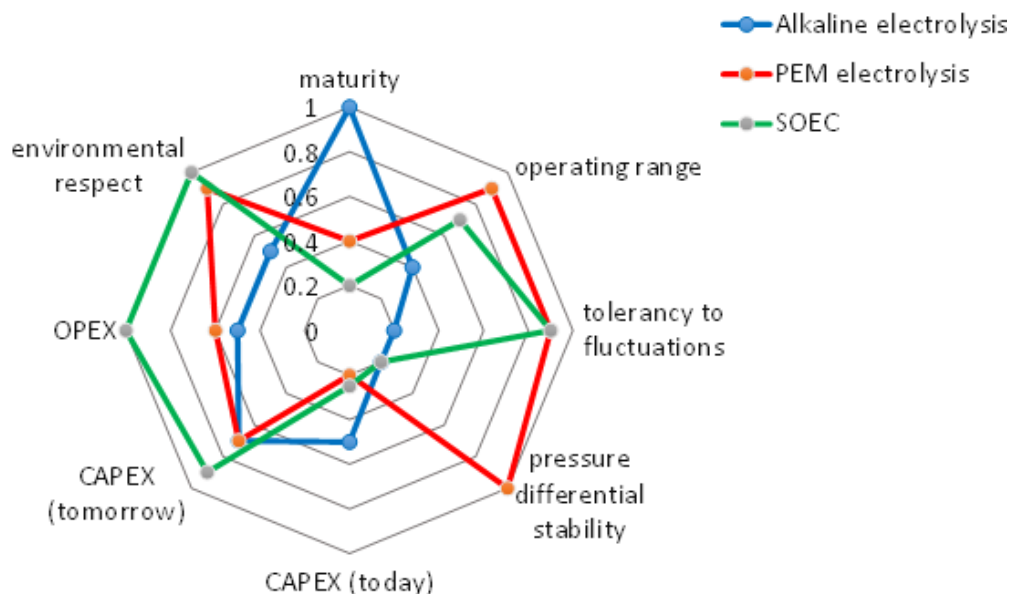


Figure 9.3: Key performance indicators of AWE, PEMWE, and SOEC technologies. Figure courtesy of Julie Mougin, CEA.

Specific research goals for SOEC systems include

- Demonstration of stack and system with durability, performance, and cost parameters sufficient for scaling to 10 MW (c.a. 3,000 Nm³/h or 2.4 kT H₂/y) within 10 years
- Integration of 10 MW SOEC-based plant with downstream thermocatalytic processes within 10 years

9.4 Conclusion

To meet EU goals for the transition away from fossil resources, conventional scale-up processes from the laboratory (TRL 1) to industrial deployment (TRL 9) in the chemical and fuel industry (20+ years) have to be significantly accelerated. Today's electrochemical commodity chemical production of chlorine and aluminum showcases the feasibility of scaling up electrochemical production to a large scale. In the perspective of using renewably generated electricity for the production of organic chemicals and fuels, R&D efforts on scale-up need to be strongly increased, as current plants and demonstrators (kW or T/y) have to be scaled up to the scale of several hundred MW or kT/y for the production of organic commodity chemicals and to the scale of several GW or MT/y for the production of organic fuels. A cross-cutting requirement to accelerate the scale-up of electrochemical processes from early-stage ideas to pilot-scale stacks and small-scale plants is the intimate cooperation of academia and industry in a continuous structured and iterative process, identifying feasible pathways and potential dead ends in perspective of scale-up and large-scale deployment of technologies. Innovation instruments such as testbeds that facilitate high-risk

prototype testing and demonstrations by sharing the risk among public and private stakeholders are required to overcome reluctance to scale-up in an uncertain economic environment.

A particularly important process that requires accelerated scale-up and integration with current infrastructure is the electrolysis of water to produce hydrogen. The key obstacle for integration of sustainably produced hydrogen from this process with large-scale thermocatalytic processes is the cost of the hydrogen, which is mainly driven by high electricity prices and the CAPEX of electrochemical processes. The scale-up challenges are a combination of new electrochemical process design, new materials, and integration with thermocatalytic processes, requiring collaboration across industries and research institutions.

Section 10

CO₂ extraction

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10.1 Importance of subject

The strategic goal to be addressed here is the *sustainable production of fuels and chemicals*. In the spirit of a recent high-level report [1], *production of fuels and chemicals* is interpreted as a means to deliver societal services, namely the provision of heat and power; propulsion through *fuels*; and products, from bulk petrochemicals to consumers products, through *chemicals*. Because of its scope, this Section deals only with carbon-containing (C-rich) fuels and chemicals, without implying that the former services above cannot be provided by C-free fuels [2] (see also Sections 1 and 5).

Defining *sustainable production* is also necessary. This Section considers a process *sustainable* if it complies with the net-zero-CO₂-emissions scenarios prescribed as a target for the period 2040-50 by the IPCC special report on “Global warming of 1.5 °C” [3]. Such a constraint requires all technology chains to recover any CO₂ generated due to the production or consumption of fuels or chemicals and to further store that CO₂ either permanently underground, which is compulsory if the carbon has fossil or mineral origin, or in a new fuel or chemical. It is therefore obvious that CO₂ extraction technology is essential to achieve the overall strategic goal of the *sustainable production of fuels and chemicals*.

Four simplified technology chains that involve CO₂ production are illustrated in Figure 10.1 (also see Figure 10.3 for a more detailed scheme). The first technology chain shown uses fossil carbon (red arrow) to produce a fuel or a chemical for service delivery (red box, this needs some power or heat – yellow bolt), which is dumped in the atmosphere as CO₂ at the end-of-life (dark grey arrow pointing upwards). This is today’s chain, which yields net-positive CO₂ emissions. The last chain shown captures CO₂ from air (green arrow) through direct air capture or managed

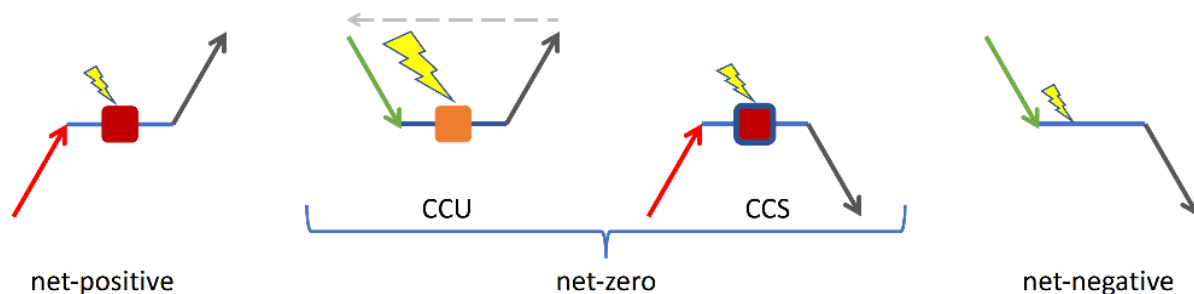


Figure 10.1: Simplified illustration of technology chains considered in this Section and their impact on carbon pools in the atmosphere and in the geosphere.

biomass growth and stores it in the subsurface (dark grey arrow pointing downwards). In this case, if biomass is used as the input, heat and power can be generated before CO₂ capture and storage (BECCS, Bio-Energy with Carbon Capture and Storage), whereas if ambient air is used as the input, only the environmental service of removing CO₂ from the atmosphere is fulfilled (DACCS, Direct Air Capture with Carbon Storage), which requires a C-free energy input. BECCS and DACCS yield net-negative CO₂ emissions (NET, Negative Emissions Technologies), of which IPCC experts project a cumulative need of 100 to 1000 Gt between now and 2100 based on today's CO₂ emissions, which are 35-40 Gt/y.

The two chains in the middle of Figure 10.1 are compatible with a net-zero-CO₂-emissions scenario. In the third chain, labeled CCS (Carbon Capture and Storage), fuels and chemicals are produced using fossil carbon and the resultant CO₂ is captured either directly from point sources (blue line around the red box) or after emission to the atmosphere and finally stored underground. Such systems exist today in the form of commercial technologies. In the second chain, labeled CCU (Carbon Capture and Utilization), CO₂ is extracted from the atmosphere via DAC or biomass and converted into fuels and chemicals by emerging technologies such as those covered in Sections 2, 3, and 4. This type of cycle is also illustrated in Figure 2 of the introduction. Upgrading CO₂ requires significant energy input, which may come in the form of electricity, heat, or hydrogen, and must ultimately be derived from renewable (C-free) sources. Note that among the four schemes only the CCU system realizes a closed cycle of carbon atoms. While this system technically satisfies the definition of *sustainable* given above, care must be taken in evaluating the sustainability of those technologies that are necessary to provide large amounts of C-free energy, specifically their reliance on scarce materials and minerals.[4]

10.2 State of the art and scientific challenges

At the core of CO₂ extraction is the CO₂ capture process, where a separation technology produces a high purity CO₂ stream from a CO₂-containing gas stream. Depending on the overarching application, e.g. power plant, steel or cement manufacturing, there exists a plurality of possible

inlet gas streams, which are characterized by different CO_2 content, temperature, pressure, and flowrate. Notably, these features may change in time and space depending on the operation of the associated plant and boundary conditions defined by the geographical location. Additionally, the process that ultimately receives the purified CO_2 stream sets constraints on the output of the capture process, e.g. purity level, amount, operating time. Accordingly, in order to describe the current state of the art of CO_2 extraction, it is key to consider the CO_2 capture process in the context of the applications that i) deliver the CO_2 -containing stream and ii) receive the high purity CO_2 product. We therefore identify two control volumes, as shown in Figure 10.2, namely:

1. Control volume Capture: includes the CO_2 capture as a standalone process, considering only the thermodynamic states of the influent and effluent streams but not the nature of the source and sink processes.
2. Control volume SCS: includes the source process (S), the CO_2 capture process (C), and the sink process (S). It therefore accounts for the effects of coupling source, capture, and sink.

CO_2 Planetary boundaries

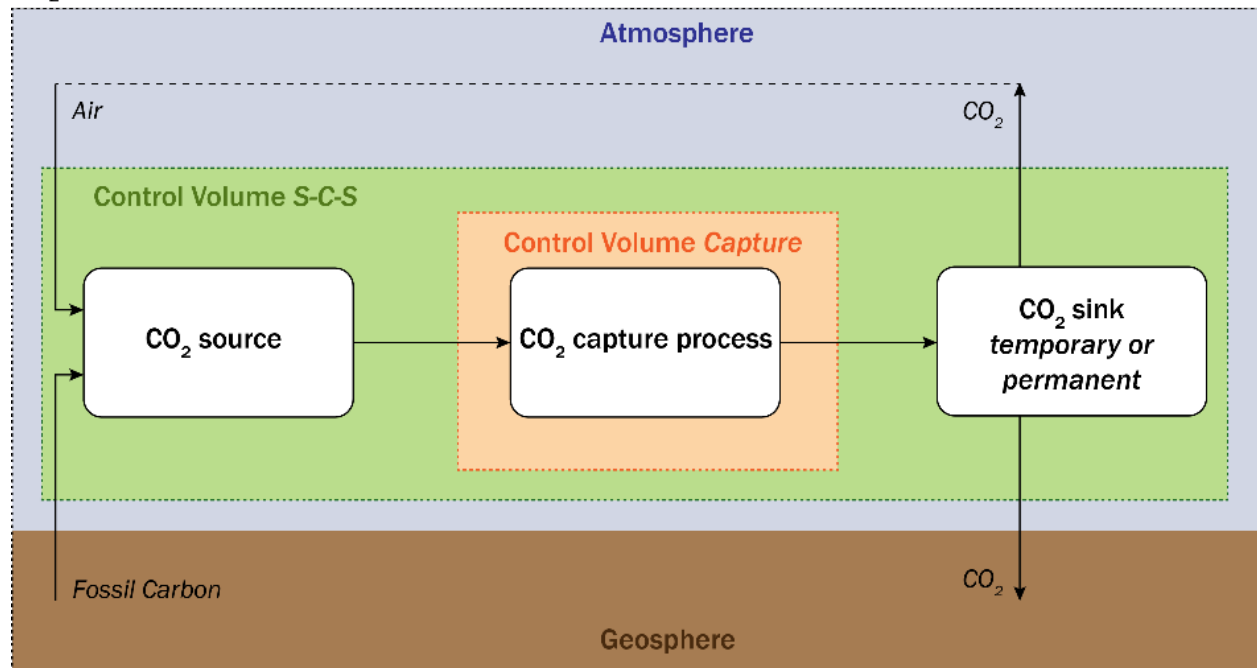


Figure 10.2: Control volumes considered for CO_2 extraction: Control volume Capture includes the stand alone capture process; Control volume S-C-S (source-capture-sink) includes the CO_2 source, which can be from fossil carbon, biomass or simply air, the capture process, and the CO_2 sink, which can be temporary as for fuels production, or permanent as for underground storage. Control volume S-C-S is directly linked to the CO_2 planetary boundaries.

10.2.1 Control volume Capture (CV-C)

While extensive literature reviews on CO₂ capture processes exist [5–7], Table 10.1 provides an overview of CO₂ capture processes for different separation routes (pre-, post-, oxy-combustion, air) and applications. We note that demonstrated technologies exist for all the relevant streams, with these being either well established (e.g. syngas plants and natural gas cleaning), commercial (e.g. post-combustion capture from power plants and steel mills), or pre-commercial (e.g. post-combustion capture from cements). Direct air capture has been demonstrated and is commercially offered by a few companies, e.g. Climeworks and GlobalThermostat. In terms of the technology used for separation, CO₂ scrubbing via liquid solvents (chemical or physical) is a mature process that builds upon several commercial solutions employed in hundreds of plants. However, as is the case for many other energy processes (e.g. gas turbines and pollutant abatement), CO₂ capture technology calls for continuous development to make the process more efficient and less expensive. Challenges remain regarding how to make 2nd and 3rd generation technologies competitive with existing solutions and on the likelihood of disruptive solutions.

Table 10.1: Overview of (i) capture processes for different applications, (ii) commercial status, and (iii) relevant existing projects from [7].

CO ₂ capture process	Application	Status	Relevant projects
<i>Post-combustion</i>			
Absorption-based	- Power plants (natural gas and coal)	Commercial	Boundary Dam (CAN), Petra Nova (US)
	- Steel mills	Commercial	Abu Dhabi Uthmaniyah
	- Waste-to-energy	Commercial	AVR-Duiven (NL)
	- Cement	Pre-commercial	Norcem-Brevik (NO)
	- Steam reformers	Commercial	
	- Refineries (cracking flue gas)	Pre-commercial	
<i>Pre-combustion</i>			
Absorption-based	- Syngas	Well established	Urea plants, Quest (CAN)
	- Natural gas treating	Well established	Gorgon (AU)
Adsorption-based	- Syngas	Commercial	Port Arthur (US)
<i>Oxy-combustion</i>	- Power plants	Pre-commercial	Schwarze Pumpe (DE)
<i>Direct Air CO₂ Capture</i>			
Absorption-based		Pre-commercial	Carbon Engineering (CAN)
Adsorption-based		commercial	Climeworks Hinwil (CH)

10.2.2 Control volume S-C-S (CV-SCS)

Here we identify the state of the art and challenges associated with connecting CO₂ sources, CO₂ capture, and CO₂ sinks in a chain. We note three critical aspects that arise when considering this control volume: (i) the scale of the three processes, which can be expressed via the CO₂ amount that is generated, separated, and used/stored, (ii) the intermittency (i.e. extent and type of dynamic operation) of the three processes, and (iii) the interconnection of the three processes with the external networks. Table 10.2 shows an overview of the status of CO₂ extraction in terms of these features. Important challenges to consider moving forward include

- Coupling processes that feature different scales while meeting the required specifications
- Reconciling the dynamic characteristics of the capture technology with the intermittent operation of the source and sink processes (e.g. decreasing the minimum load available, enabling fast switch between different operating conditions, enabling fast startup/shutdown)
- Developing an optimal CO₂ infrastructure that connects all relevant actors and tackles both the geographical diversity (e.g. in terms of CO₂ purity) and temporal evolution (both on operational and long-term timescales) of the system
- Integrating a sustainable and large supply of biomass and/or a large supply of undispachable renewables

Table 10.2: State of the art of the CO₂ extraction in terms of important features for CV-CSC.

<i>Scale</i>	State-of-the-art
Concentrated point sources	Commercial for 1- 2000 kton _{CO2} /year
Direct air capture	Commercial for 0.05-1 kton _{CO2} /year
<i>Intermittent behavior</i>	
Minimum load	Achievable performance is limited
Rate of load change	Achievable performance is limited
On/off	Not available
<i>Network</i>	
CO ₂ infrastructure	Not existing, with the exception of the CO ₂ pipeline in the US gulf area
Biomass supply	Well established, but maturity and sustainability are location dependent
Energy provision	Limited to cases where source-capture-sink are located in the same plant

10.3 Future research needs

Based on the definitions provided at the outset of this Section and on the assessment of the state of the art and scientific challenges above, we propose the following five key challenges and corresponding strategic goals for scientific research and technical development. It is worth underlining that improved versions of established technologies and systems need to be demonstrated at scale within the next 5-10 years in order to be applied at the gigaton scale by 2050, whereas brand new technologies require possibly 15 years or more to be introduced. Disrupting technologies that lead to major structural changes of the sustainable fuels and chemicals system (e.g. the emergence of DAC in the last few years or the introduction of CO₂ geological storage in the 1990s) may emerge, but with a timeline that is unpredictable.

10.3.1 Providing a system perspective to assess sustainability

Figure 10.3 shows in detail the block elements that constitute each of the four technology chains in Figure 10.1. The complexity of the actual chains is reflected by the complexity of the figure. It is worth emphasizing that sustainability implies that all CO₂ emissions to the atmosphere must be counteracted by equivalent amounts of extracted CO₂ from the atmosphere (green arrows) and that all fossil carbon extracted from the subsurface (as fossil fuel or limestone) must be reinjected into the geosphere after capture (red arrows). A life cycle analysis (LCA) around the system boundaries in Figure 10.3 is needed, quantifying carbon balances (to assess net-CO₂-emissions), energy balances (to quantify the overall energy chain efficiency in the use of renewable electricity), material flows (related to the development of the needed infrastructure), and possibly costs. LCA may provide a fair assessment of the performance of any value chain proposed in this framework, as well as a thorough accounting of the carbon credits and carbon debits to be assigned to each stakeholder in the chain (see Sections 9, 11, and 12 that also advocate the need for LCA).

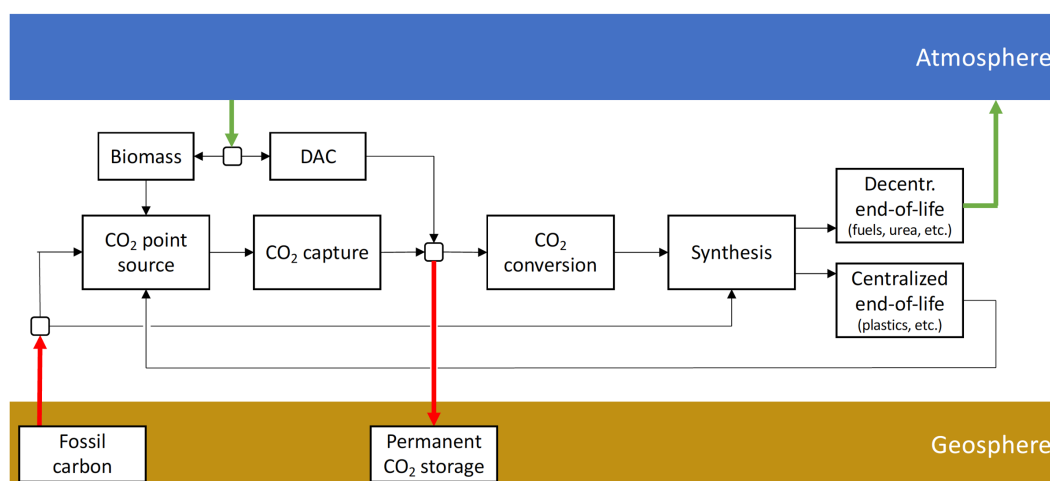


Figure 10.3: Technology blocks and material fluxes associated to all possible schemes of Figure 10.1.

10.3.2 Designing the CO₂ network infrastructure

When net-zero (CCS and CCU) and net-negative technology chains are deployed at the gigaton scale, CO₂ will have to be collected and distributed across different components of the chain. This will require a CO₂ network across geographies and nations (as illustrated in Figure 10.4) that does not exist today. Major challenges to be addressed are the design and optimization of such a network including regulatory, economic, and social considerations as well as the transition from today's infrastructure to the fully developed one.

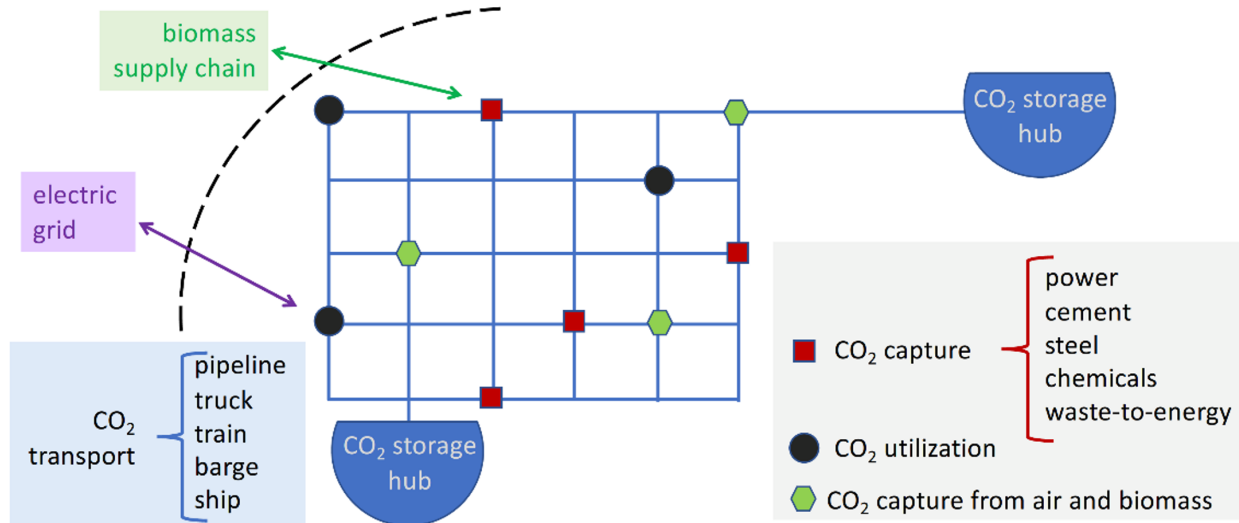


Figure 10.4: Carbon dioxide gigaton scale network infrastructure, comprising many different operators, and transportation connections both onshore and offshore.

10.3.3 Optimizing the source-capture-sink chain

Connecting the CO₂ capture process with the CO₂ source upstream and the CO₂ sink downstream (temporary in the case of CCU, permanent in the case of CCS) has the potential to yield synergistic breakthroughs but also introduces many new challenges to tackle including:

- Scales of operation that vary significantly (0.01 to 1 million tons CO₂ per year) among elements connected in same chain
- Plant location-specific issues related to capture/sink connection and integration with the electricity grid
- Ensuring operation is reliable, efficient, and economical when dynamics vary across individual elements of a chain (e.g. steady-state DAC vs. intermittent CO₂ reduction based on renewable energy sources)
- Differences in process specifications along the chain, e.g. CO₂ purity, means of CO₂ transport

- Model-based optimization of the chain

10.3.4 Advancing science and technology: CO₂ capture from point sources

The commercial benchmark technology for CO₂ capture from point sources is scrubbing, which uses liquid scrubbing, e.g. amine mixtures, to absorb CO₂ and is offered by companies such as Mitsubishi or Shell. It can currently be applied at scale with no major challenges. Nevertheless, further improvements can be made to reduce costs and increase efficiency by developing 2nd and 3rd generation technologies (e.g. NH₃ solutions, adsorption, membranes, looping cycles). Development of new technologies should integrate the three elements of the technology triangle depicted in Figure 10.5 to be competitive with amine scrubbing.

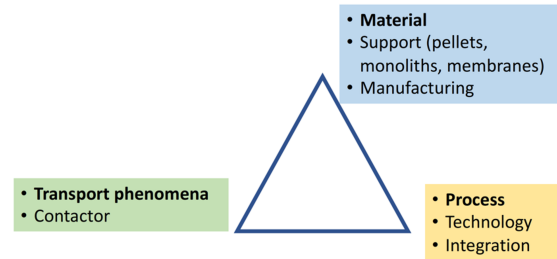


Figure 10.5: Technology triangle illustrating key elements that require consideration when developing a new CO₂ capture technology for point sources.

10.3.5 Advancing science and technology: CO₂ extraction from air

Managed biomass growth and direct air capture enable the extraction of CO₂ from the atmosphere but face obstacles that prevent their deployment at the gigaton scale. As to the former, its potential integration into the energy system at scale has to be assessed and demonstrated, particularly when considering the great variability of biomass in terms of sources and their geographical distribution and availability and in terms of the processes used to extract heat, power, or chemicals from them. As to the latter, technological challenges include integrating current and future DAC technologies with renewable sources of electricity and heat and reducing costs significantly. More generally, viable business models need be identified to move DAC from demonstration to deployment, advancing along the technology development curve and demonstrating scalability.

10.4 Conclusions

Production of carbon-containing fuels and chemicals is a means to deliver societal services, namely provision of heat and power; propulsion by fuels; and consumer products (i.e. chemicals). Their production is sustainable if it complies with the net-zero-CO₂-emissions constraint (by 2040-50) established by the IPCC. We have analyzed four technology chains and their components, identifying three of which that can deliver the societal services above. These chains are either carbon-positive (today's systems) or carbon-neutral (CCU if using captured CO₂ as carbon-provider or CCS if

based on fossil carbon and CO₂ storage). Carbon-negative systems are possible and have the additional environmental benefit of removing CO₂ from the atmosphere, but they cannot deliver all of the aforementioned societal services.

After establishing state of the art and scientific challenges related to CO₂ extraction, we have identified five key challenges and corresponding strategic goals for scientific research and technical development. They are summarized below in terms of highlights and take-home messages.

- Technology chains for the *sustainable production of fuels and chemicals* must be designed to be carbon neutral and analyzed using the methods of systems analysis to assess their sustainability (in terms of carbon), energy efficiency, resource utilization, and costs.
- To realize the vision of a sustainable production of fuels and chemicals, a CO₂ network infrastructure will be needed; this must be designed and optimized accounting for different indicators, and a pathway for its development from the current status must be devised.
- Connecting the CO₂ capture process with the CO₂ source upstream and to the CO₂ sink downstream yields new challenges related to differing dynamics and scales of operation that must be tackled with scientific research and technology developments.
- While liquid scrubbing, e.g. amines, is the commercial benchmark technology for CO₂ capture from point sources, new and improved technologies must be developed by integrating the technology triangle (material, transport phenomena, process).
- Major challenges need to be tackled to efficiently capture CO₂ from air using either managed biomass growth (variability, geographical distribution and availability, scalability) or direct air capture (integration with renewables, costs, scalability, long-term business model).

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Section 11

The Role of Industry

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11.1 Importance of subject

In 2017, industry was responsible for 22 percent of global greenhouse-gas (GHG) emissions [1]. Lowering these emissions will be crucial to reach the goal set under the Paris Agreement of a net 80 to 95 percent reduction by 2050. Technologies developed to meet this goal should also contribute to the Sustainable Development Goals put forward by the United Nations [2], such as ending poverty, ending hunger, providing clean and affordable energy to everyone, promoting sustainable industrialization, fostering innovation, and building resilient infrastructure. In response to these needs, there is increasing evidence of an irreversible, rapid transition to energy production via renewable energy sources (RES) (the so-called “energy transition”) and great interest in the progressive substitution of fossil carbon with renewable carbon feedstocks, such as biomass, CO₂, and recycled carbon (the so-called “feedstock transition”).

There is a common consensus in industry that electrons will be the dominant energy carriers in such an RES-driven system, and that they will also play an important role as clean oxidation/reduction reagents in the production of chemicals, fuels and fertilizers. It may be said that “electrons are the new oil.” The development and implementation of new technologies based on RES will enable Europe’s industry to take steps toward defossilization and comply with climate change policies. Furthermore, these new technologies have to be scaled up and commercialized, which will create “green” jobs in Europe. However, it is also important to note in this context that the production of chemicals, fuels, and fertilizers is a global commoditized market, rendering Europe prone to carbon leakage. It is of the utmost importance that carbon leakage be avoided and that RES technology development and commercialization stay in Europe.

11.2 State of the art

Generally, E.U. companies in many sectors, including chemicals, fuels, and fertilizers, are committed to more sustainable production of chemicals and fuels. Company performance is no longer measured only in terms of business targets and profitability; sustainability targets are increasingly included as key performance metrics. Similarly, investors and shareholders are demanding that companies develop and execute their strategies to be consistent with the Sustainable Development Goals [3].

Correspondingly, many companies are converging on the production of hydrogen from water electrolysis, an alternative to Steam Methane Reforming (SMR), as a primary development goal. Every ton of hydrogen produced by SMR releases 9-10 tons of CO₂. Thus, using renewable energy to produce hydrogen represents an enormous opportunity for CO₂ emissions reductions. Today, water electrolysis is already technologically feasible at the scale of 5-10 MW plants. However, the production cost of this green (e.g. fossil-free) hydrogen is 2-3 times higher than the hydrogen produced via SMR. In principle, the E.U. Emissions Trading System (ETS) that fixes the market CO₂ price should be the link between the fossil and the renewable world; however, its current pricing scheme does not facilitate massive investment in Power-to-X. In this context, some regions in the world, such as Canada, Australia, and California, are considering or have initiated an imposed CO₂ price to make RES viable [4].

With the availability of green hydrogen, other important technologies such as the reduction of CO₂ to hydrocarbons and oxygenates (e.g. methanol) (Sections 2 and 3) and the reduction of N₂ to fertilizers (Section 5) become possible. A small methanol plant in Iceland is already using geo-thermal electricity to electrolyze water and subsequently reduce CO₂ to methanol [5]. In fact, power to methanol technologies that employ waste CO₂ may already be cost-competitive compared to SMR if the price of electricity is <6 cents per kWh [6]. Furthermore, Sunfire and Audi have demonstrated the conversion of CO₂ and water into liquid hydrocarbons via electrolysis and Fisher-Tropsch technology [7].

The CO₂ used for such processes can be captured either from point sources or via direct air capture. The costs associated with technologies for direct air capture are decreasing; currently, CO₂ can be captured from air for €600 per ton [8]. Fermentation of carbohydrates produces free CO₂ as a byproduct, and combustion of biomass or municipal waste may also provide a reliable and cheap source of CO₂. However, it should be noted that gasification of biomass can already produce syngas (a mixture of CO and H₂) directly [9].

11.3 Challenges

While many important technologies are already available via green hydrogen or carbon capture, integration and scale-up as part of the whole production chain remain to be demonstrated. There-

fore, economic outlooks regarding the transition to sustainable production of fuels and chemicals are complex and uncertain. For the industrial sector, it is necessary to understand the bottlenecks in terms of technological aspects, associated risks, production costs, and current and future capacity of RES.

11.3.1 Capacity and a levelized cost of RES

The capacity and levelized cost of RES are two crucial factors that will determine the success of industrial transitions to sustainability [10]. In the last decade, the capacity of RES has grown vastly. However, the capacity rate in the last two years stalled, both overall and with regard to individual technologies, including wind and solar (Figure 11.1). More investments in RES are crucial to reach our sustainability goals; recent reports indicate that defossilization of the industrial sector will require access to 4-9 fold more RES-derived power than is currently used [10]. In this context, it is important to note that different sectors (e.g. transport, fuels, chemicals, and fertilizers) will likely compete for access if renewable power is limited. A lack of access to renewable energy in any of these sectors would have dramatic implications for related industries in Europe attempting to meet proposed targets for greenhouse gas emissions reductions.

In addition to capacity, the levelized costs of RES will also be important. Although the production costs of RES have trended downwards—even reaching a value lower than 3 USD cents per kWh (lower than conventional power production) in certain specific applications (Figure 11.2)—whether this trend will continue is unclear. In particular, increased grid stabilization costs (as result of increased RES capacity) and increased electricity trans-

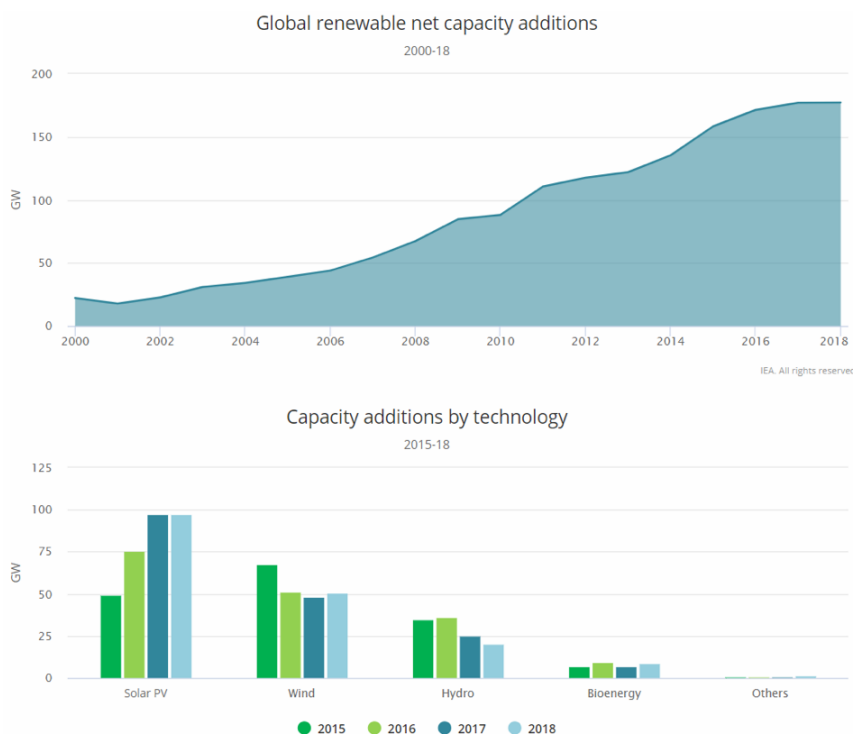
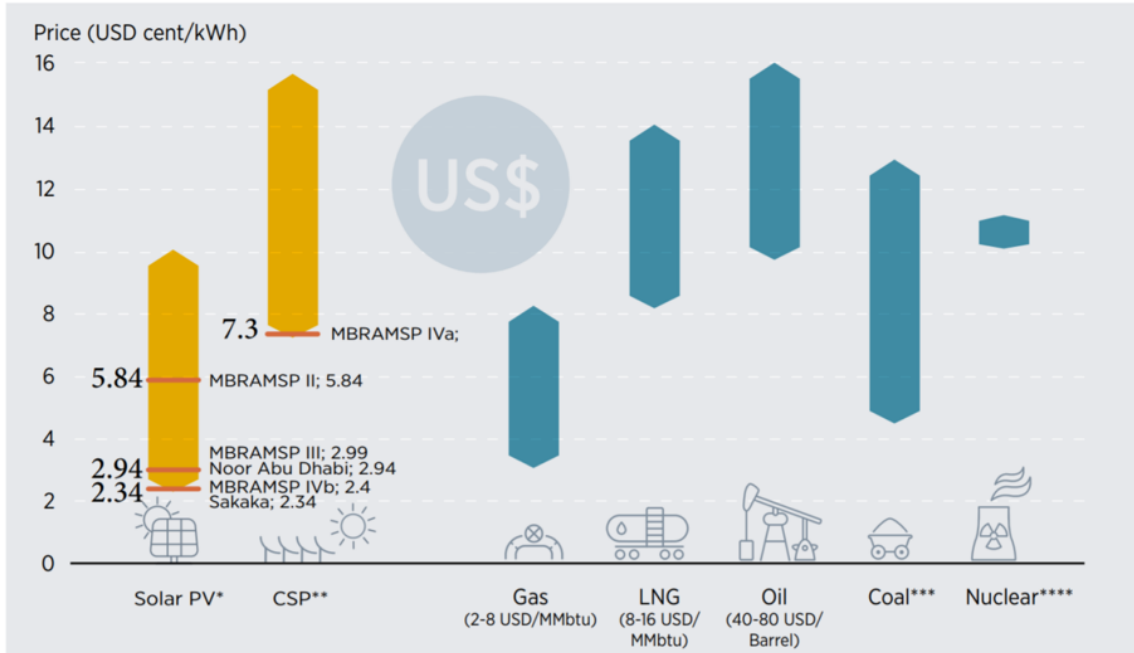


Figure 11.1: RES capacity additions by year and by sector. Reproduced with permission from [11].

port costs associated with decentralized RES may be significant. In other words, the production cost of RES is not aligned with the market price of RES-derived electricity. In fact, the market

price of electricity is significantly higher than the production cost and is forecast to increase in coming years [12]. As electricity is a commodity, its access is governed by price, not by cost, with the exception of systems that are not connected to the grid. While one potential strategy might be to couple RES to the chemical industry, which could provide grid-balancing services, the chemical industry cannot generally operate with daily intermittency; starting up and shutting down most current chemical processes takes hours or even days. Therefore, investments in RES conversion and storage technologies are of particular importance.



Sources: Derived from Mills, 2018; Channell et al., 2015; Manaar, 2014; Scribblers, 2015.

* Low = price for 300 MW Sakaka solar PV; and High = a conservative assumption based on project data and expert opinion

** Low = price for 700 MW MBRAMSP IVb in Dubai; and High = price for Morocco's Noor II

*** Low = price for the Haysan Clean Coal Power Plant; and High = estimate for coal with CCS

**** Estimated range for nuclear power based on (Mills, 2012) and (Scribblers, 2015)

Figure 11.2: Production cost of electricity by source. CSP: concentrated solar power, LNG: liquefied natural gas, PV: photovoltaic. Reproduced from [13].

11.3.2 Economic feasibility

In general, industry will only invest in showcases beyond proof of principle when there is a perspective on economic feasibility. A crucial parameter in this context is the price of fossil carbon vs. the price of renewable carbon. While the ETS system that fixes the market CO₂ price should link these prices, it has had mixed success in practice. Additionally, hydrocarbons and fertilizers are currently produced by very large (low CAPEX per ton) and very efficient (low OPEX) plants, at a size for which hydrogen electrolysis has not yet been demonstrated. Downscaling these plants to the size of the currently available water electrolysis systems becomes an economic bottleneck, as both the

CAPEX per ton and the OPEX increase. In fact, around 70% of green hydrogen production costs in the case of continuous operation are OPEX. Furthermore, as the OPEX is largely composed of electricity prices, it follows that defossilization of the chemical industry is highly dependent on the price of electricity. The CAPEX/kWh will also become significant if these plants are only operated when access to intermittent renewable electricity is available, jeopardizing the investment opportunity and posing challenges to using the chemical industry for grid-balancing.

11.4 Future research needs

Below, several objectives that will be crucial in the move towards a sustainable future are discussed. From a time-horizon point of view, such needs may be considered in the short, medium, or long term.

11.4.1 Optimization and integration of RES into current processes and development of hybrid systems

In the short term, significant savings can be achieved by optimizing current processes to be compatible with RES. In some cases, integration of RES may consist of implementing hybrid systems, in which the heat of reaction is provided by electricity. For example, if SMR technology were hybridized, the amount of CO₂ emitted per ton of hydrogen produced could be reduced from ~9-10 to 5 [14]. Another short-term strategy is the adaptation of current SMR plants to produce blue hydrogen by mineralizing or storing any CO₂ produced by the plant (See Section 10 for details). The production costs of this hybrid process and the related carbon capture and sequestration may be lower than water electrolysis costs today. This technology is ideal for the period of transition from fossil fuels to RES, as it continues to provide the required volume of hydrogen while the capacity for green hydrogen production by electrolysis can be expanded.

11.4.2 Development of fully-integrated demonstration projects at industrially relevant scales

Scaling up a technology, such as water electrolysis, is only one of the challenges associated with its successful and complete integration into the energy ecosystem (also see Section 9). To reach the final product, the entire chain must be integrated and demonstrated. Therefore, an important goal in the mid-term future is the development of demonstration projects that are fully integrated and operate at industrially relevant scales. Primary targets for such demonstration projects could be the reduction of CO₂ to hydrocarbons/methanol and N₂ to fertilizers using green hydrogen, as these products constitute key components in the chemical industry. Several important purposes of these demonstration projects are as follows:

- To develop a learning curve for integrated operation and economy of scale (e.g. reducing the CAPEX of the water electrolysis systems to below €500/kWh) by determining reliability issues and improving energy efficiency
- To connect the energy sector to the production of chemicals, fuels, or fertilizers (i.e. sector coupling)
- To demonstrate financial bankability
- To create awareness and cultivate public acceptance

The timelines and associated support milestones for these large demonstration projects need to be sufficiently long, as building larger installations will take significant time. To complete site selections, secure permits, and engineer and build the plant will require roughly a 10-year horizon.

11.4.3 Developing technologies beyond water electrolysis

To meet the long-term goals described above, we need to develop technologies beyond water electrolysis. These long-term technology developments should aim for novel and effective solutions with the capacity to minimize capital investments and operating costs by, for example, reducing the number of unit operations or making each step more energy efficient. These breakthroughs would allow such technologies to compete at small-scale capacity, well suited for coupling with the decentralized RES. Examples of promising breakthrough technologies include:

- Producing chemicals directly from renewable carbon sources (CO₂, recycled carbon, biomass). For the electrochemical reduction of CO₂ (Section 2), there is a need to develop innovative value chains by considering products further downstream with added market value, e.g. C-C bond formation products such as acetic acid/acetate, ethanol, or ethylene. Toward this end, the development of more selective electrocatalysts and novel scalable electro-reactors, while avoiding the use of critical raw materials, is needed.
- Producing fertilizers directly from N₂ (Section 5). The production of ammonia is an excellent example of the potential use of RES to obtain a basic commodity that is used as raw material for several industries, including fertilizers, explosives, and plastics.
- Identifying suitable oxidation reactions that produce value-added chemicals with market volume comparable to H₂. This technology has potential to reduce OPEX by effectively using electricity at both the cathode and the anode. When green hydrogen is deployed at large scale, there will be hundreds of MW of electrical power available for selective oxidation.

- Technologies disconnected from the power grid, e.g. photocatalytic H₂ production and CO₂ and N₂ reduction. This would address issues of discrepancy between the production cost of RES and market price of electricity.

11.4.4 Fostering strong research collaborations with academia

To facilitate the development of the aforementioned breakthrough technologies, a strong link between industry and academia through all stages of development is paramount. In particular, it is crucial to ensure that researchers have a good understanding of the economic targets from the outset. However, working with universities and research institutes should not only be limited to breakthrough technologies. In the short term, new front-end technologies like water electrolysis can be further developed to sustainably produce H₂, which can then be coupled to conventional downstream processes. In the long term, entirely new Power-to-X processes can be designed and developed as well.

11.4.5 Ensuring good LCA practices as prerequisites to any developments or demonstrations

Realizing a circular economy will require closing the utilization loop not only for carbon utilization, but for all raw materials (see Section 12). In this context, Life Cycle Assessments (LCA) are of special importance to ensure the permanent removal of CO₂ from the atmosphere, prevent additional fossil CO₂ from entering the atmosphere, and protect the use of water and other critical raw materials. It is especially important to focus on adequate systems boundaries that cover the whole life cycle of the applied technology, consumed goods, or services. Ideally, these would be “cradle to cradle” (i.e. infinite recycling or circular economy) for Power-to-X and “cradle to grave” for CO₂ removal. CO₂ removal must be independently verified through the development of measuring, monitoring, and verification measures.

11.4.6 Encouraging regulatory action

It is important to note that the fuel, chemical, and fertilizer industries feature high volumes and high capital investments, and the total project life cycle for typical plants is on the order of decades. Early adopters need to be rewarded so that bigger volumes can be reached and economies of scale developed. This implies that legislation should be introduced to support defossilization and carbon recycling, not only for fuels, such as in the Renewable Energy Directive (RED II) [15], but also for chemicals and fertilizers. While imposing a CO₂ tax may help facilitate the economic viability of RES, other promising strategies include (i) enforcing Power-to-X blending quotas (i.e. setting a minimum percentage of Power-to-X products that must be used as fuels or chemical feedstocks in

a given industry) and (ii) gradually lowering the CO₂ emissions quotas of individual sectors over time.

11.5 Conclusion

A sustainable energy system, including the sustainable production of chemicals, fuels, and fertilizers, is crucial for our society. Industry is committed to more sustainable production of chemicals and fuels. For the initial transition, many technologies are already available. Many developments are converging to produce hydrogen by water electrolysis, enabling the foundations of the transition to sustainable production of chemicals. The capacity and levelized cost of renewable energy are two crucial factors determining the successful implementation of such a transition, but the current trends of RES capacity and electricity price are a barrier to investments in larger scale deployment. **Legislation should be introduced** that supports defossilization and carbon recycling to produce chemicals and fertilizers, and such measures should **consider the risk of carbon leakage**. In the short to mid term (<10 years), **demonstration projects at industrially relevant scale are needed** to integrate all processes and technologies. Scaling up one technology, such as water electrolysis, is only one part of the puzzle; for successful deployment, the entire chain must be integrated and demonstrated. In the longer term (>10 years), new breakthrough technologies are needed that go beyond water electrolysis, including **direct carbon reduction technologies** (i.e. that do not rely on H₂ as an intermediate) and processes that are **disconnected from the commodity power grid**.

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Section 12

Managing the transition to a circular economy

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12.1 Importance of subject

Transforming industrial sectors that are strongly based on fossil resources and frequently do not address the complete life cycle of their products, such as the chemical industry, might prove a Herculean challenge. However, managing the transition to an economy that is based on sustainable raw materials, production processes, and consumption patterns is indispensable for a successful climate policy that also creates and sustains economic prosperity.¹

This holds especially true for the chemical industry, which currently emits substantial amounts of CO₂ due to its large energy demand and production processes. Furthermore, its products litter the oceans (plastic waste) and harm ecosystems (eutrophication). Therefore, current production processes and business practices are increasingly subject to both tightening regulation and intense public discussion, ultimately threatening the industry's license to operate.

A transition to new production and business models is therefore of major importance to both the environment and the industry itself. Effective solutions will use renewable sources as primary input, both for energy and raw materials, and 'close the carbon circle' i.e. develop products which can be recycled at end of life (Figure 2). Such a system is referred to as a 'circular economy'. However, for the transition to such a circular economy to be successful, substantial changes are needed. Specifically, volumes must be reduced, primary and recycled materials integrated, and

¹The OECD [1] provides an overview of the consequences of climate change on economic growth and on different drivers of growth, in different sectors across the world, while Tol [2] documents a remarkably wide range of estimates of the welfare impacts of climate change.

downcycling minimized. Effectively managing a circular economy will also entail new business models, intensified customer integration, and appropriate regulations.

12.2 Preliminary Remarks

While the other Sections focus on technological innovation and development, this Section addresses all-encompassing aspects of the transition, including economics, enterprises and business models, political processes, governance and regulation, the formation and conduct of social groups, the role of consumers (with increasingly multifaceted preferences and behaviors), and rapidly changing social norms.² In line with this ambition, this Section considers the involvement and participation of all stakeholders in all phases of the transition, including initiation. This treatment transcends the outdated perspective that it is sufficient to ask for social acceptance after the major decision have already been made by businesses, policy makers, and scientists.

The overarching principle of our considerations has been to stay prepared for incorporating new innovations and challenges towards a widely de-fossilized economy as they arise over time, i.e. to pursue a technologically neutral approach where possible. Important dimensions to respect as cross-cutting issues throughout are:

- “Integration”: simultaneously considering possible developments both on the side of industry, especially comprising issues of production and materials supply, and on the side of consumers, especially pertaining to consumption patterns and preferences
- “Involvement”: understanding the all-encompassing nature of the transition, relying on various scientific disciplines and a wide spectrum of stakeholders and generating the need for discussion of governance issues
- “Intelligence”: devising methodological tools and protocols to identify, assess, and monitor developments and their unintended side-effects, to determine policy success, evaluate the urgency of decisions and identify corresponding actions

To provide a comprehensible structure for the emerging research questions, this overview uses as key elements the respective actors involved and, specifically, the levels of political decision making addressed by the results of this research, leading to a three-dimensional hierarchy, from the global to the national/local level. Therefore, an integrated policy framework needs to support the joint transition to a net-zero-GHG and circular society, on an international (global, EU), national and regional level – as energy and industrial transitions take place on all these levels.

²Cherp et al. [3] and Roberts et al. [4] provide comprehensive conceptualizations of energy transitions from the special perspective of political science, while Hsiang and Kopp [5] provide a brief introduction to the physical science of climate change for economists and other social scientists, and discuss areas in which they consider economic science to potentially provide a particularly useful contribution to climate science and policy.

12.3 Challenges and future research needs

12.3.1 Solving the overarching global coordination problem

Globalization has led to efficient resource flows and increased consumer welfare over the last century, providing a leading historical example of successful division of labor. Global markets for resources and goods have served as an efficient coordination mechanism, bringing together supply and demand and signaling scarcity by (global) prices. However, global markets have not yet been able to address the increasingly urgent challenge of climate change, as management of global commons and associated externalities will require additional global institutions which are not yet installed.

As climate change is a problem of global dimension, its institutional solution should include developing and emerging economies. It requires global carbon neutrality by middle of the century. However, both the burden posed by climate change and the benefits associated with its alleviation are distributed unevenly across countries, leading to heterogeneous incentives to participate. To inform policy makers, it will be crucial to research how the international distribution of the costs and benefits of climate change and climate policy could be affected by various compensation mechanisms and institutional solutions.

Furthermore, technologies and business models to close material cycles must be developed. These should follow the waste hierarchy: reducing material use and wastes, reusing products, and recycling materials. Combustion, in combination with Carbon Capture and Storage (CCS) or Carbon Capture and Utilization (CCU), is an option for materials which cannot be recycled. Technologies and business models that should be developed include recycling design, logistics for the collection of discarded products, sorting and recycling technologies, as well as the digitalization of material flows. Economic incentives will strengthen the implementation of these technologies.

To identify optimal institutions which could successfully address climate change, it is conceptually useful to recognize climate change as a problem of global policy coordination, in which the strategic interaction of actors determines the individual and social desirability of outcomes.³ Solutions to such problems have to be resilient against the ubiquitous issue of potential free-rider behavior. In the case of climate change, the problem is particularly intricate as international actors are involved. Research from both game-theory and political-economy perspectives will be important to address this global policy coordination problem.⁴

The complexity of the problem is increased further by taking a global fairness perspective, in which the large development needs of poorer countries and the incentives of the owners of fossil

³Auerswald et al. [6] and Buob and Stephan [7] discuss the intricate relationship between mitigation and adaptation efforts, showing that unilateral mitigation efforts might even increase global emissions.

⁴Nordhaus [8] suggests an approach for overcoming free-riding in international agreements on climate policy based on the idea of climate clubs: stable coalitions might be encouraged by implementing a regime with small trade penalties on non-participants.

fuels to protect their privileges are also considered. Additional research is necessary to explore the possibility of forming an international alliance for joint mitigation efforts. The potential and limitations of installing a global carbon market as the principal coordination device should be confronted with research on alternative instruments. Specifically, further research should compare the bargaining approach (insistence on reciprocity) with an approach of leading by example.⁵

Functional global institutions require ongoing effectiveness evaluations and processes for their corresponding adaptation. Therefore, the establishment of global monitoring efforts and observatory processes is needed to assess progress and quickly identify unintended side effects and their origins. Future research should provide the conceptual basis for this endeavor. Monitoring efforts should adhere to harmonized measurement procedures and accounting rules, ideally via a global system that accounts for entire life cycles of goods (in Life Cycle Assessments, LCA).

Similarly, it will be crucial to identify and estimate the total system cost of traditional and future patterns of production and consumption in a comprehensive approach that considers externalities. Further research will be required to clarify whether important prerequisites for sustainable production are met, e.g. the sufficient provision of sustainable resources or energy sources at the right location. Research might focus on questions of whether, how, and from where sufficient sustainable input factors could be produced or, if necessary, imported.

This discussion holds especially true for the chemical industry. For example, is it optimal to use renewable raw materials or to recycle waste? Are differences between continents and regions significant? And can the utilization of waste as raw materials contribute to economic growth and job creation? Generally, research is needed to deepen our understanding of the impact of a circular economy on future material flows, including inputs, products, and residuals/waste. Research should aim to understand not only the requirements, solutions, economics, and logistics of technological innovations, but also their societal consequences and resultant regulations.

Global regulation will have to reflect the global markets for energy-intensive goods, e.g. many metals and basic chemicals. As competition in these markets is global, companies will only be able to pursue sustainable production technologies if the negative externalities arising from other approaches are fully internalized (also see Section 11). If such a level playing field cannot be established, regulated, energy-intensive industries might suffer from carbon leakage. Further research is needed to establish which industries and companies would be particularly prone to this problem. Building upon that, economically sound as well as practically feasible instruments to counteract carbon leakage must be developed.

⁵Cramton et al. [9] and MacKay et al. [10] suggest an approach to international climate negotiations which instead of a “pledge and review” approach pursues a “common commitment” scheme involving reciprocity.

While global regulation must certainly be ramped up, its acceleration should not be hasty.⁶ Disruptive developments could seriously harm financial market stability, and research is needed to establish optimal time frames for regulatory measures.

More research is also needed to discuss if and how negative emissions could contribute.⁷ Considerations should include how carbon could be stored and used and at what cost (e.g. Section 10), as well as what might impede public acceptance of such practices.

Finally, digitization could be a game-changer for climate change mitigation and sustainable production efforts. A whole array of research questions arises in this realm, such as understanding the technical aspects of using artificial intelligence (see Section 8) and the societal implications of the resultant human-machine interactions.

12.3.2 Designing effective and efficient solutions for Europe

In addition to analyzing issues on a global level, research needs to address institutional development on a national or, in case of the EU, European level. It is of major importance to understand governance and political contexts so that narratives may be developed to ensure the transition is widely regarded as just and broadly supported. Otherwise, both the public and ‘the markets’ might not trust governmental efforts and plans. It is important to understand that the transformation of energy- and/or carbon- intensive industries and systems is a large investment, which needs to be quantified and financially endowed. As substantial economic resources will have to be spent outside these industries, it remains uncertain whether the often-told narrative that export chances of domestic industries will be enhanced by industrial policy can be true.

A fundamental dilemma of industrial policy must also be addressed. As the public sector intervenes in market affairs, its decisions will unavoidably focus on specific technologies. Further research should thus explore to what extent these decisions might preclude (the desired) openness towards yet-to-be-developed technologies (neutrality) or lead to path dependence and lock-in effects. Closely related to this research question is whether the pursuit of geopolitical and “strategic” energy independence is feasible or will simply create a new import dependence now involving large-scale importing of renewable energy. These imports, however, might allow developing countries to industrialize as energy exporters.

Another research question involves devising an encompassing regulatory framework, i.e. whether and how to extend the European emissions trading system (ETS). Should it be augmented with harmonized carbon taxation in other sectors not falling under the current realm of the ETS? How can we tap the potential of the division of labor in European emission avoidance?

⁶The ESRB [11] discusses that the transition away from relying on fossil fuels should, from the perspective of retaining the stability of financial markets, occur gradually. By contrast, if this transition to a low-carbon economy were to occur too late, the then necessarily abrupt repricing of carbon assets would entail serious systemic risks.

⁷ IPCC [12] discusses the need for negative emissions to implement a highly ambitious climate policy.

And what additional complications arise from the undeniable fact that new and old EU member states differ in their stages of economic development?

CCU and CCS may have the potential to decarbonize existing industrial infrastructure, reducing the risk of stranded assets. CCU, in particular, could generate options for industrial symbioses between industries, i.e. between iron and steel or cement and the chemicals industry.

Developing technologies, reducing costs, and setting up economic incentives, Europe can generate large positive externalities for global climate policy.

According to the key dimension of “involvement”, research on the development of European regulation can only be one, albeit indispensable, aspect of further research efforts. In particular, it is critical that different stakeholder groups be placed under the scrutiny of further research efforts:

From the perspective of investors and the (chemical) industry, political reliability is important. What are the (regulatory) drivers and impediments to developing new business models (e.g. re-use and recycling)? What is the outlook on the challenge to supply sufficient energy in the future and how is this related to potential relocation (carbon leakage)? What instruments have the potential to effectively prevent carbon leakage (for instance, carbon border adjustments)?

From the consumer perspective, consumption and investment decisions (for example, to purchase appliances or vehicles) and their effects on household budgets should be analyzed, keeping in mind the lump-sum nature of such purchases. For the consumer, there is an intrinsic cost to emissions avoidance, and it will be important to explore which regulatory arrangements could supplement carbon pricing to help consumers avoid emissions. The consumer perspective is also important with regard to recycling systems. To close the plastic (carbon) cycle in particular, functional recycling and waste collection systems are crucial. They must be technically advanced while also being accepted by consumers, so methods to increase consumer involvement, such as incentives, are important.

It is also important to consider the perspective of policy makers. Governments have a legitimate interest in safeguarding the stability of tax revenues and public finances in general so they may continue to provide public goods. Various instruments involved in European climate policy and regulation could influence these financial systems. Further research is needed to estimate the magnitude of these effects and devise alternative approaches to achieve stable public finances.

Technological innovation and industrial transformation will be subject to potential public objection. Therefore, public acceptance and a broader stakeholder perspective is important. Research should identify how to involve stakeholders at the European level, how increased participation could be achieved, and what (if any) kind of monitoring tools could help.

Furthermore, a dynamic perspective must be considered. The role of technological advances and progress as driving forces need to be addressed, for example, development of energy-efficient, flexible storage technologies, demand-side management techniques, and advanced efficiency achieved via transcending sectoral boundaries.

Finally, according to the key dimension of “intelligence” the issue of advancing technological progress is of utmost importance to the EU and its member states. How can Europe foster technical and social innovations (i.e. technological progress as an object of policy), especially by instruments other than carbon pricing incentives (e.g. regulation, market design, taxes)? What political-economy issues are involved in pursuing targeted support for potential innovators (e.g. creating soon-to-be entrenched privileges)? There is additional research needed from an innovation systems perspective on how to organize cooperation between industry and academia, provide sufficient R&D incentives to facilitate development of the necessary technologies (from low to high TRL levels), and involve societal groups throughout the process.⁸

12.3.3 Accelerating national energy transformations within Europe

A third and final set of research questions confronts the national level; some research questions resume from the global or European levels, while others arise only at national or even local levels. One research issue at national and local levels is the development of practical avenues to work toward overarching European solutions more quickly. Specifically, understanding the extent to which (harmonized) national carbon taxes in non-ETS sectors could pave the way to a medium-term or long-term solution involving a fully-fledged encompassing ETS would be valuable. Expanding local infrastructure for collecting, sorting, and processing wastes seem to be a necessary prerequisite for a net-zero greenhouse gas (GHG) and circular society. Identifying best practices would benefit developing nations faced with the challenge of closing material cycles.

There exist country-specific obstacles to transformation which simply arise from established regulatory frameworks and industry structures. Such idiosyncrasies exist in Europe’s national housing markets, for example, where regulation has been tailored to address the needs of renters in Germany and house-owners in Italy. A question related to this issue of nationally idiosyncratic regulations is the following: Do members states need to address competition concerns from their domestic companies via only partial auctioning of ETS emission certificates and other devices? If so, how would they avoid conflicts within the European competition framework?

On both the European and national levels, there exist sincere needs to form political coalitions and compose convincing political narratives to make climate policies viable. Research is needed to establish the importance of governance and stakeholder participation in nurturing democratic climate-policy participation and to explore the consequences of failing to provide these participation opportunities. What would be (efficient) ways to effectively involve civil society in decisions that cannot function without acceptance, such as extending the energy grid or erecting wind turbines?

⁸Carayannis et al. [13] suggest embedding the traditional “Triple Helix” innovation model which focuses on university-industry-government relations into a more comprehensive “Quadruple Helix” framework by adding the ‘civil society’, and an even more comprehensive “Quintuple Helix” innovation model by also adding the perspective of the ‘natural environments of society’.

How can social equity concerns related to climate policy be addressed successfully? Would an elaborate system of taxes and transfers be sufficient, or is targeted redistribution of the revenues derived from carbon pricing also necessary? How would such mechanisms affect public acceptance of carbon pricing?⁹ As a last set of research questions, it is important to learn how the cognitive basis, e.g. underlying attitudes, to climate change and climate policy could be strengthened and a supportive societal mindset for sustainability could be formed. What could be the role, for instance, of increased education efforts, especially in the STEM fields? How important is transparency in political actions and communications? And, finally, how can we encourage sustainable consumption behavior while maintaining consumer sovereignty?

12.4 Conclusions

Energy- and material-intensive sectors that are strongly based on fossil fuels face enormous challenges in transforming their products, processes, and business models. A prominent example is the chemical industry, which currently uses fossil fuels both for its energy and its raw material needs. The sector needs effective technological, regulatory, and business solutions to transform into a sustainable circular economy, while taking into account the interests of the various stakeholders to the industry. Technological neutrality is key for an efficient transition, as this paradigm ascertains flexibility regarding both innovations and future challenges. Therefore, we suggest an integrative, involving, and intelligent approach which considers developments (i) from the industry and consumer perspectives, (ii) in an interdisciplinary approach, and (iii) with smart regulation and governance. The research questions emerging from this conceptualization of the task of managing the transition to a circular economy are structured along the lines of relevant actors and levels of political decision making, leading to a three-dimensional research hierarchy, from the global to the national and local levels.

On the global level, the research question of how to find an effective, efficient, and fair governance structure is of major importance from societal, political, technological, and economic perspectives. For Europe, the challenge of finding the best governance structure is also of utmost importance. However, the corresponding research questions are more concrete: for example, how to trigger and secure investments, regulate emissions, and involve consumers and other stakeholders effectively. On the local level, the research questions become naturally even more applied. Again, dealing with governance issues, aspects of national regulation, economic incentives, distributive

⁹Cronin et al. [14], Goulder et al. [15], and Williams et al. [16] provide empirical assessments of the distributional effects of carbon taxation on US households and, in particular, of the redistribution of the corresponding revenues which might be implemented to fend off the potentially regressive nature of carbon taxes. Feng et al. [17] provide similar estimates for households in the UK. Ganapati et al. [18] and Weyl and Fabinger [19] document for the US the intensity of the pass-through of energy price-driven changes in input costs to consumers and discuss the key aspects of tax incidence under imperfect competition.

effects, and social acceptance should all be elements of future research to manage the transition to a global circular economy.

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Appendices

Appendix A

Panels

The format of the workshop was such that the scientific steering committee (see page [i](#)) invited the chairs of the different sessions. The chairs then put together a representative group of scientists, to provide a broad perspective of their topic. The chairs are responsible for the report from their session. The members of each session are shown below and a complete list of all workshop attendees can be found in [Appendix C](#).

Name	Affiliation
1. Water Splitting and sustainable H₂ production	
Grimaud, Alexis (chair)	CNRS - College de France
Rossmeis, Jan (chair)	University of Copenhagen
Strasser, Peter (chair)	Technical University Berlin
Bernt, Maximilian	Technical University of Munich
Carmo, Marcelo	FZ Jülich
Crema, Luigi	Fondazione Bruno Kessler
Escudero, Maria	University of Copenhagen
Friedrich, Andreas	German Aerospace Center
Herranz, Juan	Paul Scherrer Institute
Hu, Xile	Ecole Polytechnique Federale de Lausanne
Krtil, Petr	Heyrovsky Institute Prague
Kulesza, Pawel	University of Warsaw
Martens, Johan	KU Leuven
Risch, Marcel	Helmholtz-Zentrum Berlin
Rutkowska, Iwona	University of Warsaw
2. Electrochemical CO₂ reduction	
Koper, Marc (chair)	Leiden University
Roldan, Beatriz (chair)	Fritz Haber Institute of the Max Planck Society
Artero, Vincent	CEA
Atwater, Harry	California Institute of Technology
Broekmann, Peter	University of Bern
Buonsanti, Raffaella	Ecole Polytechnique Federale de Lausanne
Burdyny, Tom	Technical University of Delft
Chan, Karen	Technical University of Denmark
Janaky, Csaba	University of Szeged
Lopez, Nuria	Catalan Institute of Chemical Research
Kulesza, Pawel	University of Warsaw
Rabaey, Korneel	Ghent University
Robert, Marc	University of Paris Diderot
Rodriguez, Enrique H.	University of Alicante
3. Thermal CO₂ reduction	
Behrens, Malte (chair)	University of Duisburg-Essen
Bowker, Michael (chair)	Cardiff University
Hutchings, Graham (chair)	Cardiff University
Artz, Jens	Aachen University
Beller Matthias	Leibniz Institute for Catalysis
Bengaouer, Alain	CEA
Christensen, Jakob M.	Technical University of Denmark
De Jongh, Petra	University of Utrecht
De Leeuw, Nora	Cardiff University
Galvita, Vladimir	Ghent University
Grunwaldt, Jan-Dierk	Karlsruhe Institute of Catalysis
Jensen, Anker D.	Technical University of Denmark
Muhler, Martin	Ruhr-University Bochum
Pacchioni, Gianfranco	University of Milano
Palkovitz, Regina	Aachen University
Prieto, Gonzalo	ITQ Institute of Chemical Technology (CSIC-UPV)
Roger, Anne-Cecile	University of Strasbourg
Urakawa, Atushi	Catalan Institute of Chemical Research

4. Thermal process syngas to fuel

Bordiga, Silvia (chair)	University of Torino
Lercher, Johannes (chair)	Technical University of Munich
Artz, Jens	Aachen University
Bialkowski, Michal	Casale SA
Gläser, Roger	University of Leipzig
Groppi, Gianpiero	Polytechnic University of Milano
Hansen, Emiel	Technical University of Eindhoven
Khodakov, Andrei	University of Lille
Lauritsen, Jeppe V.	Aarhus University
Olsbye, Unni	University of Oslo
Palkovitz, Regina	Aachen University
Gascon, Jorge	Kaust Catalysis Center
Sauer, Jörg	Karlsruhe Institute of Catalysis
Thybaut, Joris	Ghent University
Tromp, Moniek	University of Groningen
Van Spreybroeck, Veronique	Ghent University

5. Sustainable N₂ reduction

Nilsson, Anders (chair)	University of Stockholm
Stephens, Ifan (chair)	Imperial College
Centi, Gabriele	University of Messina
Einsle, Oliver	University of Freiburg
Ellis, Peter	Johnson Matthey
Geisbauer, Andreas	Clariant
Hansen, John B.	Haldor Topsoe
Koroidov, Sergey	University of Stockholm
Kulesza, Pawel	University of Warsaw
Lopez, Nuria	Catalan Institute of Chemical Research
Makepeace, Josh	University of Oxford
Muhler, Martin	Ruhr-University Bochum
Perathoner, Siglinda	University of Messina
Rutkowska, Iwona A.	University of Warsaw
Skulason, Egil	University of Iceland
Symes, Mark	University of Glasgow
Vegge, Tejs	Technical University of Denmark
Vesborg, Peter	Technical University of Denmark

6. Homogenous catalysis for sustainable fuels and chemicals

Cantat, Thibault (chair)	CEA
Leitner, Walter (chair)	Max Planck Institute for Chemical Energy Conversion
Clot, Eric	University of Montpellier
De Vos, Dirk	Katolieke Universiteit Leuven
Gonsalvi, Luca	Italian National Research Council
Lloret-Fillol, Julio	Catalan Institute of Chemical Research
Nolan, Steven P.	Ghent University
Quadrelli, Elsje A.	University of Lyon
Repo, Timo	University of Helsinki
Saeys, Mark	Ghent University
Waser, Jerome	Ecole Polytechnique Federale de Lausanne
Wass, Duncan	Cardiff University

7. Inspiration from biological processes

DeBeer, Serena (chair)	Max Planck Institute for Chemical Energy Conversion
De Groot, Huub (chair)	Leiden University
Aro, Eva-Maria	University of Turku
Einsle, Oliver	University of Freiburg
Leitner, Walter	Max Planck Institute for Chemical Energy Conversion
Magnuson, Ann	University of Uppsala
Parkin, Alison	University of York
Reisner, Erwin	University of Cambridge
Vincent, Kylie	University of Oxford

8. Role of data and artificial intelligence

Jacobsen, Karsten W. (chair)	Technical University of Denmark
Matthias, Scheffler (chair)	Fritz Haber Institute of the Max Planck Society
Bligaard, Thomas	SLAC National Accelerator Laboratory
Cerioti, Michele	Ecole Polytechnique Federale de Lausanne
Draxl, Claudia	Humbolt University of Berlin
Ghiringhelli, Luca	Fritz Haber Institute of the Max Planck Society
Glaum, Robert	University of Bonn
Hautier, Geoffroy	University of Louvain
Kresse, Georg	University of Vienna
Lopez, Nuria	Catalan Institute of Chemical Research
Margraf, Johannes	Technical University of Munich
Reuter, Karsten	Technical University of Munich
Rinke, Patrick	Aalto University
Schlögl, Robert	Fritz Haber Institute of the Max Planck Society
Trunschke, Annette	Fritz Haber Institute of the Max Planck Society

9. Scale-up of electrochemical processes

Moses, Poul G. (chair)	Haldor Topsoe
Schreiber, Moritz (chair)	Total
Geerlings, Hans	Shell
Geisbauer, Andreas	Clariant
Goetheer, Earl	TNO
Grimbergen, Reinier	TNO
Fleischer, Maximilian	Siemens
Jongsma, Tjeerd	ISPT
Kintrup, Juergen	Covestro
Moser, Peter	RWE Power AG
Mougin, Julie	CEA
Tsampas, Michail	DIFFER
Van Geem, Kevin	Ghent University

10. CO₂ extraction

Gazzani, Matteo (chair)	Utrecht University
Mazzotti, Marco (chair)	ETH Zurich
Anantharaman, Rahul	SINTEF Energy
Arias, Borja	CSIC-INCAR
Bitter, Harry	Wageningen University
Joss, Lisa	University of Manchester
Kofoed, Niels Peter	NPK ERHVERV
Ostuni, Raffaele	Casale SA
Rajendran, Arvind	University of Alberta
Romano, Matteo	Politecnico di Milano
Sutter, Daniel	Climeworks
Zabukovec, Natasa	National Institute of Chemistry

11. Role of industry

Iaquaniello, Gaetano (chair)	Nextchem – Marie Tecnimont
Schouten, Klaas Jan (chair)	Avantium
Beuttler, Christoph	Climeworks
Buonerba, Luca	DeNora
De Coninck, Eric	ArcelorMittal
Dekeukeleire, Stijn	Ghent University
Dobree, Joey	Stamicarbon
Haustermans, Luc	Yara International
Kintrup, Juergen	Covestro
Marin, Guy	Ghent University
Moser, Peter	RWE Power AG
Seeberg, Inger	Copenhagen Airports
Vermeiren, Walter	Total

12. Managing the transition to a circular economy

Growitsch, Christian (chair)	Fraunhofer Institute
Schmidt, Christoph (chair)	RWI - Leibniz-Institut für Wirtschaftsforschung
De Roeck, Frederik	Ghent University
Frondel, Manuel	RWI - Leibniz-Institut für Wirtschaftsforschung
Grunwald, Armin	Karlsruhe Institute of Catalysis
Kuchta, Kerstin	Technical University of Hamburg
Paredis, Erik	Ghent University
Requate, Till	University of Kiel
Rettig, Rainer	Covestro
Rezabek, Pavel	Czech Power Company
Worrel, Ernst	Utrecht University

Appendix B

Workshop program

1-3 July 2019, Hotel Radisson Blu Royal, Brussels:

Day 1

9.00 – 10.00	Registration and coffee
10.00 – 10.20	Welcome, Jens K. Nørskov
10.30 – 11.15	The Joint Center for Artificial Photosynthesis, results and lessons – Harry Atwater (Caltech)
11.15 – 12.00	Storage needs of the energy system of the future – Maximilian Fleischer (Siemens)
12.00 – 13.15	Lunch
13.15 – 14.00	Towards a large-scale application of electrochemical conversions on synthesis of solar fuels – Hans Geerlings (Shell)
14.00 – 14.45	Q&A session (plenary speakers)
15.00 – 15.30	Coffee break
15.30 – 18.00	Breakout sessions, start
18.00 – 20.00	Session mixer

Day 2

8.30 – 10.00	Breakout sessions continued
10.00 – 10.30	Coffee
10.30 – 12.00	Breakout sessions continued
12.00 – 13.00	Lunch
13.00 – 15.00	Breakout sessions continued
15.00 – 16.00	Coffee
16.00 – 18.00	Reports from panels
18.00 – 19.00	Dinner, no host
19.00	Writing starts

Day 3

8.30 – 10.30	Writing by session chairs
10.30 – 11.00	Coffee
11.00 – 14.00	Writing by session chairs
14.00	Hand in of written report

Scientific steering committee

Jens K. Nørskov – Technical University of Denmark
Gabriele Centi – University of Messina
Robert Schlögl – FHI, Max Planck Society
Bert Weckhuysen – Utrecht University
Ib Chorkendorff – Technical University of Denmark
Christoph Schmidt – RWI Essen

Organizational committee:

Kathrine Nielsen – Technical University of Denmark
Sabrina A. Müller – DECHEMA
Andreas Förster - DECHEMA
Elena Guarneri – Technical University of Denmark
Lars Brückner – Technical University of Denmark
Maximilian Kotzur – DECHEMA
Ivan Matejak – EERA
Petra Frömel – DECHEMA
Yoan Stanev – EERA
Aizhan Mamyrkhanova - EERA

Appendix C

Complete workshop attendee list

Surname	First name	Affiliation
Anantharaman	Rahul	SINTEF Energy
Arias	Borja	Spanish National Research Council
Aro	Eva-Maria	University of Turku, Finland
Artero	Vincent	CEA, Univ Grenoble Alpes
Artz	Jens	RWTH Aachen University
Atwater	Harry	California Institute of Technology
Behrens	Malte	University Duisburg-Essen
Beller	Matthias	Leibniz Institute for Catalysis e.V.
Bengaouer	Alain	CEA
Bernt	Maximilian	Technical University of Munich
Beuttler	Christoph	Climeworks AG
Bialkowski	Michal	Casale SA
Bitter	Harry	Wageningen University & Research
Bligaard	Thomas	SLAC National Accelerator Laboratory
Bordiga	Silvia	University of Torino
Bourrel	Patrick	European Commission
Bøwadt	Søren	European Commission
Bowker	Michael	Cardiff University
Broekmann	Peter	University of Bern
Brückner	Lars	Technical University of Denmark
Buonerba	Luca	Industrie De Nora S.p.A.
Buonsanti	Raffaella	École Polytechnique Fédéral de Lausanne
Burdyny	Thomas	Delft University of Technology
Cantat	Thibault	CEA CNRS Université Paris Saclay
Carmo	Marcelo	Forschungszentrum Juelich GmbH
Centi	Gabriele	ERIC aidbl and University of Messina
Cerioti	Michele	École Polytechnique Fédéral de Lausanne
Chan	Karen	Technical University of Denmark
Chorkendorff	Ib	Technical University of Denmark
Clot	Eric	University of Montpellier
Crema	Luigi	Fondazione Bruno Kessler
De Coninck	Eric	ArcelorMittal
De Corte	Simon	Ghent University
de Groot	Huub	Leiden University
de Jongh	Petra	Utrecht University
De Leeuw	Nora	Cardiff University
De Roeck	Frederik	Ghent University
De Touzalin	Aymard	European Commission
De Vos	Dirk	Katolieke Universiteit Leuven
DeBeer	Serena	CEC, Max Planck Society
Dekeukeleire	Stijn	Ghent University
Dickens	Colin	Stanford University
Dobrée	Joey	Stamicarbon
Draxl	Claudia	FMP und Humboldt University of Berlin
Dufour	Elena	European Energy Research Alliance
Einsle	Oliver	Albert-Ludwigs-Universität Freiburg
El Gammal	Adel	European Energy Research Alliance
Ellis	Peter	Johnson Matthey

Escudero-Escribano	María	University of Copenhagen
Faber	Carina	Katolieke Universiteit Leuven
Fleischer	Maximilian	Siemens AG
Förster	Andreas	DECHEMA e.V.
Friedrich	K. Andreas	German Aerospace Center
Frondel	Manuel	RWI - Leibniz-Institut für Wirtschaftsforschung
Galvita	Vladimir. V.	Ghent University
Garcia	Hermenegildo	University of Valencia
Gascon	Jorge	King Abdullah University of Science and Technology (KAUST)
Gazzani	Matteo	Utrecht University
Geerlings	Hans	Shell / Delft University of Technology
Geisbauer	Andreas	Clariant Produkte (Deutschschland) GmbH
Ghiringhelli	Luca	FHI, Max Planck Society
Gläser	Roger	University of Leipzig
Glaum	Robert	University of Bonn
Goetheer	Earl	TNO/Delft University of Technology
Gonsalvi	Luca	Consiglio Nazionale delle Ricerche - Istituto di Chimica dei Composti Organometallici
Granger	Pascal	Université de Lille
Grimaud	Alexis	Collège de France
Grimbergen	Reinier	TNO
Groppi	Gianpiero	Politecnico di Milano
Growitsch	Christian	Fraunhofer IMWS
Grunwald	Armin	Karlsruhe Institute of Technology
Grunwaldt	Jan-Dierk	Karlsruhe Institute of Technology
Guarneri	Elena	Technical University of Denmark
Guell	Berda M.	SINTEF
Hansen	John B.	Haldor Topsøe A/S
Haustermans	Luc	Yara International
Hautier	Geoffroy	Katolieke Universiteit Leuven
Hensen	Emiel J.M.	Eindhoven University of Technology
Herranz	Juan	Paul Scherer Institut
Herrero	Enrique	University of Alicante
Higuera Cebrian	Esther	European Commission
Hu	Xile	École Polytechnique Fédéral de Lausanne
Hutchings	Graham	Cardiff Catalysis Institute
Iaquaniello	Gaetano	Nextchem – Marie Tecnimont
Jacobsen	Karsten W.	Technical University of Denmark
Janáky	Csaba	University of Szeged
Jensen	Anker D.	Technical University of Denmark
Jongsma	Tjeerd	ISPT
Joss	Lisa	University of Manchester
Junker	Helle	Innovation Fund Denmark
Khodakov	Andrei Y.	CNRS-University of Lille
Kintrup	Juergen	Covestro Deutschland AG
Kofoed	Niels Peter	NPK Erhverv
Koper	Marc	University of Leiden
Koroidov	Sergey	Stockholm University

Kresse	Georg	University of Vienna
Krtil	Petr	J. Heyrovsky Institute of Physical Chemistry
Kuchta	Kerstin	Hamburg University of Technology
Kulesza	Pawel	University of Warsaw
Latimer	Allegra	Stanford University
Lauritsen	Jeppe	Aarhus University
Leitner	Walter	CEC, Max Planck Society
Lercher	Johannes A.	Technical University of Munich
Lloret Fillol	Julio	Institute of Chemical Research of Catalonia
Lopez	Nuria	Institute of Chemical Research of Catalonia
Magnuson	Ann	Uppsala University
Makepeace	Joshua	University of Oxford
Mamyrkhanova	Aizhan	European Energy Research Alliance
Margraf	Johannes	Technical University of Munich
Marin	Guy	Ghent University
Martens	Johan	Katolieke Universiteit Leuven
Matejak	Ivan	European Energy Research Alliance
Mazzotti	Marco	ETH Zürich
Mitchell	Sharon	ETH Zurich
Moser	Peter	RWE Power AG
Moses	Poul Georg	Haldor Topsoe A/S
Mougin	Julie	CEA Grenoble
Muhler	Martin	Ruhr University Bochum
Müller	Sabrina A.	DECHEMA
Nielsen	Kathrine B.	Technical University of Denmark
Nilsson	Anders	Stockholm University
Nolan	Steven P.	Ghent University
Nørskov	Jens K.	Technical University of Denmark
Olsbye	Unni	University of Oslo
Ostuni	Raffaele	Casale SA
Palkovits	Regina	RWTH Aachen University
Pacchioni	Gianfranco	Universita' degli Studi Milano-Bicocca
Paredis	Erik	Ghent University
Perathoner	Siglinda	ERIC aidbl and University of Messina
Perraud	Simon	CEA
Presofeam	Antonin	Ghent University
Prieto	Gonzalo	ITQ Institute of Chemical Technology (CSIC-UPV)
Quadrelli	Elsje A.	CPE Lyon -CNRS- University of Lyon
Rabaey	Korneel	Ghent University
Repo	Timo	University of Helsinki
Requate	Till	Kiel University
Rettig	Rainer	Covestro Deutschland AG
Reuter	Karsten	Technical University of Munich
Rezabek	Pavel	Czech Power Company ČEZ
Rinke	Patrick	Aalto University
Risch	Marcel	Helmholtz Zentrum Berlin
Robert	Marc	University Paris Diderot
Roger	Anne-Cécile	University of Strasbourg
Roldan Cuenya	Beatriz	FHI, Max Planck Society

Romano	Matteo C.	Politecnico di Milano
Rossmeisl	Jan	University of Copenhagen
Rutkowska	Iwona	University of Warsaw
Rutkowska-Zbik	Dorota	Jerzy Haber Institute of Catalysis and Surface Chemistry
Saeys	Mark	Ghent University
Sauer	Jörg	Karlsruhe Institute of Technology
Scheffler	Matthias	FHI, Max-Planck Society
Schild	Philippe	European Commission
Schlögl	Robert	FHI, Max Planck Society
Schmidt	Christoph M.	RWI - Leibniz-Institut für Wirtschaftsforschung
Schouten	Klaas Jan	Avantium
Schreiber	Moritz	Total Research & Technology
Seeberg	Inger	Copenhagen Airports
Skúlason	Egill	University of Iceland
Stanev	Yoan	European Energy Research Alliance
Stephens	Ifan E.L.	Imperial College London
Strasser	Peter	Technical University Berlin
Sutter	Daniel	Climeworks AG
Symes	Mark	University of Glasgow
Thybaut	Joris	Ghent University
Tromp	Moniek	University of Groningen
Trunschke	Annette	FHI, Max Planck Society
Tsampas	Michail	Differ
Urakawa	Atsushi	Delft University of Technology
Van Geem	Kevin M.	Ghent University
Van Speybroeck	Veronique	Ghent University
Vegge	Tejs	Technical University of Denmark
Vermeiren	Walter	Total
Vesborg	Peter	Technical University of Denmark
Wass	Duncan	Cardiff University
Waser	Jérôme	École Polytechnique Fédéral de Lausanne
Weckhuysen	Bert	Utrecht University
Witko	Małgorzata	Jerzy Haber Institute of Catalysis and Surface Chemistry
Worrell	Ernst	Utrecht University
Zabukovec Logar	Natasa	National Institute of Chemistry and University of Nova Gorica

Appendix D

Energy-X overview

The EU-funded ENERGY-X project (Horizon 2020 Grant Agreement N° 820444) aims at building a strategic roadmap towards a large-scale research initiative addressing the efficient conversion of solar and wind energy into chemical form. It includes 13 partners across Europe.

Coordinator:

Jens K. Nørskov (Technical University of Denmark)

Core partners:

Technical University of Denmark

Ib Chorkendorff

DECHEMA

Kurt Wagemann

Andreas Förster

CEA

Alain Bengaouer

Julie Mougin

Thibault Cantat

Fritz Haber Institute of the Max Planck Society

Robert Schlögl

Annette Trunschke

Utrecht University

Bert Wechhuysen

University of Essen

Christoph Schmidt

Technical University of Valencia

Hermenegildo Garcia

Avelino Corma

Ghent University

Guy Marin

European Research Institute of Catalysis, University of Messina

Gabriele Centi

EERA

Adel El Gammal

Czech Academy of Sciences

Petr Krtil

ETH Zurich

Javier Perez-Ramirez

Sharon Jan Mitchell

Polish Academy of Sciences

Malgorzata Witko

Dorota Rutkowska-Zbik