Heterogeneous Catalysis

Advancing Critical Chemical Processes for a Sustainable Future: Challenges for Industry and the Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis (FUNCAT)

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Dedicated to Dr. Wolfgang Schmidt on the occasion of his 60th birthday

Abstract: Catalysis is involved in around 85% of manufacturing industry and contributes an estimated 25% to the global domestic product, with the majority of the processes relying on heterogeneous catalysis. Despite the importance in different global segments, the fundamental understanding of heterogeneously catalysed processes lags substantially behind that achieved in other fields. The newly established Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis (FUNCAT) targets innovative concepts that could contribute to the scientific developments needed in the research field to achieve net zero greenhouse gas emissions in the chemical industries. This Viewpoint Article presents some of our research activities and visions on the current and future challenges of heterogeneous catalysis regarding green industry and the circular economy by focusing explicitly on critical processes. Namely, hydrogen production, ammonia synthesis, and carbon dioxide reduction, along with new aspects of acetylene chemistry.

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1. Introduction and Vision of FUNCAT

Catalysis plays an essential role for our civilization from societal, economic, and ecological viewpoints. Catalysis is not only the heart of the chemical industry, but also involved at some point in the processing of around 85% of all manufactured substances and products. Nearly everything in our daily life depends on a catalytic process or catalyst. This includes toothbrushes and toothpaste, pharmaceuticals, most parts of automobile production and exhaust catalytic converters, synthetic fuels (e.g., gasoline, diesel, and biofuel), paper and plastic production, and many textiles, including the clothes that we are wearing. In these cases, catalysis not only facilitates the manufacturing of many goods in a more economical way, but it also makes processes and production more sustainable by reducing energy, by-products, and waste. In the future, it is predicted that catalysis will have an even wider impact by considering the urgent societal need for reliable clean water, sustainable energy, and greater resources, such as food supplies.[1] Among others, we believe that development of sustainable technologies and catalysts for green hydrogen (H_2) production, ammonia (NH_3) synthesis, carbon dioxide (CO_2) reduction, and acetylene chemistry could have substantial impacts on our future landscape.

Recently, we established the Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis (FUNCAT) by bringing together expertise in the Max Planck Gesellschaft—specifically in the Max Planck Institute for Chemical Energy Conversion (CEC), the Fritz Haber Institute of the Max Planck Gesellschaft (FHI), and the Max-Planck-Institut für Kohlenforschung (KOFO)—with the Cardiff Catalysis Institute (CCI) in the UK to tackle grand challenges in heterogeneous catalysis. As shown in Figure 1, the structure of the Centre is organized around three main scientific themes: i) from single site to particle, ii) acetylene as a feedstock for chemical production, and iii) the importance of dynamics where we use our complementary expertise to establish a new approach to study heterogeneous catalysis. The synergy of the involved institutions will add scientific value for i) development of advanced synthetic methods for the synthesis of controlled nanostructures, ii) advancing novel theoretical tools in cooperation between theoreticians and experimentalists to

guide the synthesis of advanced solid catalysts, and iii) in-depth understanding of the role of catalyst dynamics in real-world catalysis by application of in situ and operando techniques.

Professor Michael (Mike) Bowker is a senior member of the UK Catalysis Hub network and the Cardiff Catalysis Institute. He has been involved in research across a spectrum of activities in heterogeneous catalysis, nanoscience, and surface imaging/reactivity, ranging from selective oxidation catalysis and photocatalysis, studies of adsorption and catalysis on well-defined surfaces, and atomic resolution imaging, to nanofabrication. He has an h-index of 68 and over 300 papers and patents in the field.

Serena DeBeer is a Professor and Director at the Max Planck Institute for Chemical Energy Conversion. She is also an Adjunct Professor in the Department of Chemistry and Chemical Biology at Cornell University, an honorary faculty member at Ruhr University in Bochum, and the group leader of the PINK Beamline at the Energy Materials In-Situ Laboratory at Helmholtz Zentrum in Berlin. Her group focuses on development of advanced X-ray spectroscopic tools for understanding key mechanisms in biological, homogeneous, and heterogeneous catalysis.

Nicholas F. Dummer is a Research Fellow at Cardiff University (CU). He obtained his PhD in 2005 at CU. In 2012, he was appointed Special Ass. Prof. in the Catalysis Research Center of Hokkaido University, Japan. In 2013, he was awarded a Senior Research Fellowship at Wollongong University, Australia. He returned to CU in 2015 and is the local FUNCAT coordinator for the Max-Planck Centre in CU. He has co-authored over 65 articles on heterogeneous catalysts in a range of processes, including selective methane oxidation, biomass valorisation, and hydrogenation.

Graham Hutchings is Regius Professor at Cardiff University. He studied chemistry at University College London and got his PhD in 1975. His early career was in industry with ICI and AECI Ltd. In 1984, he moved to academia and has published over 900 papers and patents. He was elected Fellow of the Royal Society in 2009 and a Member of Academia Europaea in 2010. He was awarded the Davy Medal of the Royal Society in 2013, the ENI Award for Advanced Environmental Solutions in 2017, a CBE in the Queen's Birthday Honours List in 2018, and the Michel Boudart Award in 2021.

Matthias Scheffler is director of the NOMAD (Novel Materials Discovery) Laboratory in Berlin at the FHI of the Max Planck Society and IRIS Adlershof of the Humboldt-Universität. He works in condensed-matter theory and materials science. A focus is on density functional theory and many-electron quantum mechanics, and on development of multi-scale approaches. In recent years, his work is largely concerned with data-centric scientific concepts and methods and the goal that materials-science data must become "Findable and Artificial Intelligence (AI) Ready".

Ferdi Schüth studied Chemistry and Law in Münster and received his PhD in Chemistry in 1988. After his Habilitation in 1995, he was appointed as Full Professor at Frankfurt University. In 1998, he became a Director at the Max-Planck-Institut für Kohlenforschung. He has received several awards, including the Gottfried Wilhelm Leibniz-Prize and the Heisenberg-Medal. He served as Vice President of the Max-Planck-Society between 2014 and 2020. His research interests include the fundamentals of the formation of solids, catalysis, nano-structured materials, and mechanochemistry.

Stuart Taylor completed his PhD at the University of Liverpool in 1994, and then took up an academic position at Cardiff University School of Chemistry in 1997 and was promoted to Professor in 2013. Currently he is the Director of Research for the School and has over 330 publications in the field of heterogeneous catalysis. He has wide-ranging expertise in experimental studies of catalysis, with his work exploiting preparation techniques for fundamental catalyst understanding and design. His work impacts on chemicals, fuels, sustainability, energy, and the environment.

Harun Tüysüz obtained his PhD degree in chemistry at the Max-Planck-Institute für Kohlenforschung (MPI-KOFO) in 2008 and then did a postdoc at the University of California, Berkeley. In 2012, he was appointed head of the group of Heterogeneous Catalysis and Sustainable Energy at the MPI-KOFO. He is the local FUNCAT coordinator in Germany. His research deals with development of nanoscale materials for sustainable energy-related catalytic applications. He has been awarded several prizes, including the Jochen-Block-Prize 2016 and the DECHEMA Prize 2019.
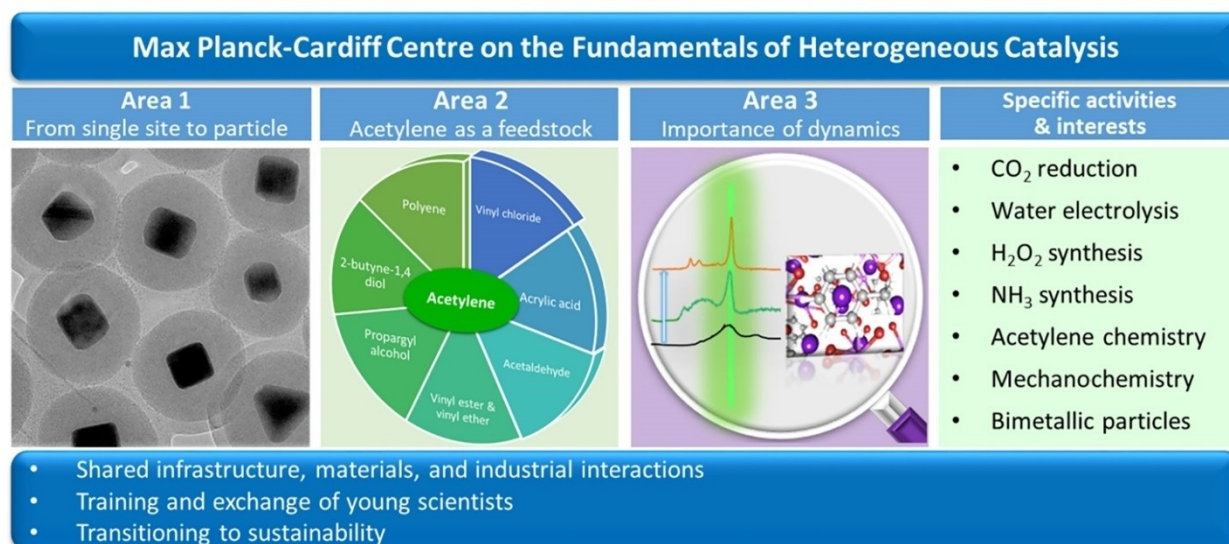
Figure 1. Areas of interest and activities of the Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis (FUNCAT).

Specific activities related to the main themes within the Max Planck–Cardiff Centre involve selective hydrogenation and hydrochlorination of acetylene, CO_2 hydrogenation, direct hydrogen peroxide synthesis, and Cooperative Redox Enhancements (CORE) over bimetallic nanoparticle catalysts. Furthermore, we are interested in development of transition-metal-based electrocatalysts for water electrolysis towards green H_2 production, and implementation of mechanochemistry for solid catalyst preparation and mechanochemical transformation, such as in NH_3 synthesis. These activities are often supported, or in some cases led, by a complementary team performing calculations on the energetics of reaction pathways and nanoparticle structures, and catalyst characterisation with advanced techniques such as atomic-scale electron microscopy, X-ray adsorption, and in situ or operando approaches to surface species determination. Each aspect of these research activities allows for enhanced collaboration, training, and development of sustainable routes to establish new catalytic processes, as illustrated in Figure 1. The combined scientific and structural added value will lift catalysis research in the participating institutions to a new level and will provide a great platform for shared infrastructure and other shared activities, including training of young scientists. The vision of FUNCAT is to lead and coordinate catalytic science in the Cardiff Catalysis Institute and three Max Planck Institutes, and to achieve maximum impact for the design of solid catalysts and challenging catalytic systems.

This Viewpoint Article elaborates on recent developments and our thoughts on the challenges in heterogeneous catalysis that need to be overcome to achieve a sustainable future, with a focus on key industrially relevant processes, such as green H_2 production, NH_3 synthesis, hydrogenation of CO_2, and acetylene chemistry.

2. Industry Transition Roadmap Towards a Zero-Greenhouse Gas Footprint and the Role of Heterogeneous Catalysis

It is evident that much of the present, large scale, commercially led chemical industry must change so as to transition to a net-zero greenhouse gas footprint with reduced use of energy and of non-renewable feedstocks. Commercial chemical production to supply intermediates or final products for a vast number of applications have catalysis at the heart of the processes. This is the reason why it is appropriate to look to catalysis to facilitate a much-needed net-zero greenhouse gas future. On a commercial scale, several issues that limit progress are evident. Firstly, capital investment in new plants and/or processes is economically unattractive when existing plants are available, unless the new plant/process is significantly better. Secondly, using suitable renewable feedstocks is typically more costly than non-renewable feedstocks in many parts of the world, and this is a major roadblock to transitioning. Furthermore, these renewable feedstocks must result in the same product profile without extensive pre- and post-treatment cleaning or abatement. The use of renewable feedstocks must also be assessed economically and politically within the context of the food versus fuel debate.[2] Thirdly, political boundary conditions are often not stable, so that investment in new processes, which rely on political involvement such as CO_2 taxation, is often precarious.

The Haber–Bosch process is commonly used as an example of a chemical process that is both a great benefit to the global community and one that can be considered harmful. The Haber–Bosch process uses around 1 % of the total global energy demand and outputs 1.2 % of global anthropogenic CO_2 emissions.[3] To put this into context, it is estimated that the Haber–Bosch process produces a CO_2 output comparable to total global passenger and freight

aviation (estimated 1.9 %), while sustaining a global population of approximately 7 billion people. Therefore, changes to this process in terms of energy reduction would be felt on a global scale. The Haber–Bosch process is one of the oldest commercial examples of catalysis technology, having begun at the start of the 20th century, it is still in place today. While improvements to this process have been sought for much of this time (see Section 4 for further details), the NH_3 synthesis step remains largely unchanged since its initial discovery. The single most important advance in making the Haber–Bosch process more sustainable would be the replacement of H_2 production based on fossil fuels by H_2 production from renewable energy, such as by electrolysis with renewable electricity.

Another large-scale chemical process, where improvements in design and engineering over time have resulted in more efficient outcomes, is ethylene oxidation (EO). From commercialization in 1925 to the present, the direct EO synthesis process over Ag-based catalysts has evolved to a global production of in excess of 5 Mtpa. Prior to this direct synthetic route, the earlier two-step process involved the production of ethylene chlorohydrin, where high chlorine use and an effluent stream that requires clean-up were phased out in the mid-20th century.[4] The demand for EO continues to grow and progressing to a renewable source of ethylene should be a priority.

On a smaller scale, a drop-in replacement for mercury-based catalysts was developed in collaborative partnership between Cardiff University and Johnson Matthey for the hydrochlorination of acetylene used in production of vinyl chloride monomer (see Section 6 for further details).[5] The advanced, atomically dispersed gold catalyst used in this example provides a secondary but crucially important environmental benefit: the reduction of harmful Hg emissions. The use and release of Hg and Hg compounds were the subject of the Minamata Convention, a UN treaty signed in 2013. In this case, replacement of Hg reduced the emission of the harmful metal into the local environment. Despite the higher cost of Au, further benefits to this drop-in replacement are realized through enhanced catalyst lifetime and the opportunity to recover the gold component.

Successfully reducing harmful emissions, energy usage, and non-renewable feedstocks at the commercial scale will require many stakeholders to work together. For example, academic research on significantly more active catalysts cannot often translate to the increased scale and capital investment of commercial operations. Thus, increased collaboration between commercial and academic sectors with clear targets is required, although governments must play a role. The complex and often inconsistent global landscape of subsidies paid to both production and consumption of non-renewables is not ideal to reduce reliance on fossil fuels. However, subsidies for clean energy are catching up to those of non-renewables; for example, in the UK subsidies for clean energy are approaching 30 bn British pound sterling (GBP). However, government financial support for fossil fuels stands at over 40 bn GBP since Jan 2020.[6] Globally, the total governmental subsidies to non-renewable energy stands at 423 bn United States dollars (USD) each year, slowing the transition to cleaner energy.[7]

Overall, as important as the design of new solid catalysts is, sustainable technological development, availability and usage of the renewable energy sources and feedstocks are the crucial factors that are going to be critical to achieve a greenhouse gas footprint of zero. Accessibility to competitive electricity from renewable energies is going to be essential for the reduction of CO_2 in the chemical industry. It should also be kept in mind that it can take an extended period of time to implement new technologies at scale; thus, deployment of more sustainable industrial processes must be accelerated. This holds even if they may not be competitive in the beginning because operational experience at a global scale is mandatory for the full transition to a renewable system. We believe that sustainable H_2 will be a key energy vector of the future, which will be elaborated on in the next section.

3. Status Quo of H_2 and Its Production

H_2 has a high gravimetric energy density of about 120 MJ kg^{-1}, which is 2.5 to 3 times higher in comparison with other common fuels such as gasoline and natural gas.[8] Volumetric storage density, on the other hand, is much lower, even in compressed or liquefied form. As such, H_2 can potentially be used as a feedstock or source of power for different sectors, including as a feedstock in industry, mobility and transportation, heating, and power generation (Figure 2). Therefore, H_2 is considered as a key strategic component in the change to a sustainable future as a potentially 100 % clean energy source and carrier. However, over 95 % of the world's current H_2 is still produced using fossil fuels through the steam methane (CH_4) reforming process (SMR) and variants thereof.[9] The remainder of the H_2 produced is mainly generated as a by-product, from chlorine electrolysis and the coke oven gas of the steel industry. Although H_2 itself is fundamentally non-polluting when it is used as an energy source, there is a large CO_2 footprint associated with its production through these conventional pathways. A pure H_2 demand of about 90 Mt in 2020—produced mainly from fossil fuels—resulted in around 900 Mt of CO_2 emissions.[10] Thus, there is an urgent need to reduce this CO_2 footprint and dramatically increase production of H_2 with a zero-CO_2 footprint.

Green H_2 (Figure 2) can be generated via different pathways, such as water electrolysis using sustainable electricity or direct photocatalytic, photovoltaic-assisted electrochemical, and photoelectrochemical water-splitting systems using solar energy.[11] There are other ways of producing H_2 in a more or less sustainable manner, often indicated by different "colour codes" but, in the long run, the "green" routes appear to be the most promising, and thus, the discussion will focus on these.[12] Among the solar-light-driven methods, the photovoltaic-assisted electrolyzer is the most promising, which has reached solar-to-H_2 energy conversion efficiencies of 30 % at the laboratory scale. This record-holding cell consists of two polymer electrolyte
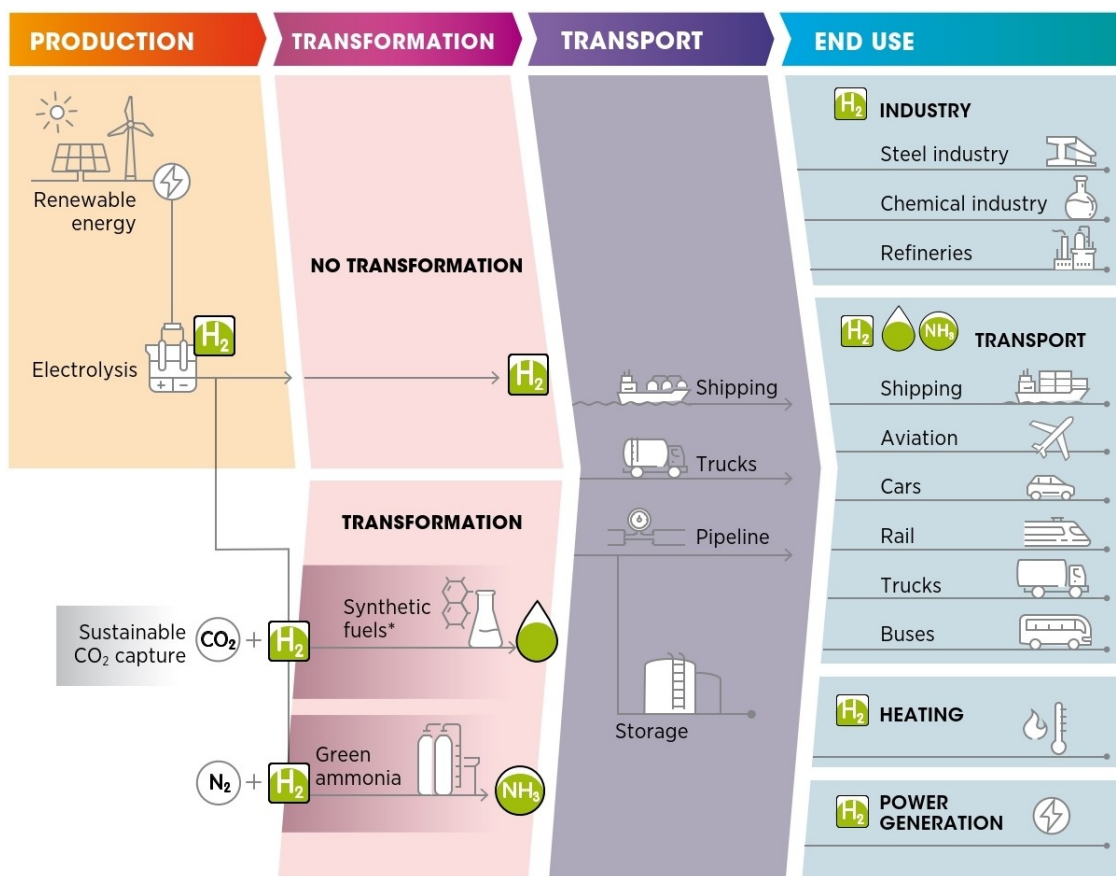
Figure 2. Production of green H_2 and its utilization across different energy schemes. Copyright IRENA (2020), green hydrogen: a guide to policy making, International Renewable Energy Agency.

membrane electrolysers and a triple junction solar cell made of InGaP/GaAs/GaInNAsSb.[13] Although this system is promising from a scientific point of view, its implementation in large-scale applications is not feasible and also very costly. However, systems using standard silicon-based solar cells could also have overall efficiencies of close to 15 %. Photocatalytic solar water splitting that uses a simple powdered semiconductor shows notably lower solar-to-H_2 energy conversion efficiencies of around 1 %, despite 50 years of research effort.[14] On the other hand, direct photocatalytic water splitting can deliver advantages in lower costs and scalability.[15] Recently, Domen and co-workers reported solar H_2 production on a 100 m^2 array of panel reactors comprised of a co-catalyst-decorated $SrTiO_3$:Al photocatalyst; the system was active over several months with autonomous separation of H_2 from the gas product mixture using a commercial polyimide membrane. Even though this is considered a promising system, it could only reach a maximum solar-to-H_2 energy conversion efficiency of 0.76 % due to the poor light harvesting ability of the photocatalyst.[16] The separation of H_2 and O_2, and associated safety regulations, make the process very challenging for larger scale commercial applications.

Within the existing class of materials and technologies, electrochemical water splitting has the greatest potential for large-scale green H_2 production.[17] There are four main

types of electrolyser: alkaline, polymer electrolyte membrane (PEM), anion exchange membrane (AEM), and solid oxide electrolysers. While alkaline and PEM electrolysers are commercial processes,[18] AEM and solid oxide electrolysers are still at the laboratory scale. Alkaline electrolysers have the simplest design and are operated with concentrated KOH as an electrolyte, Ni-coated stainless steel as the working electrode, and ZrO_2 as a diaphragm. One drawback, however, is that the intermixing of produced H_2 and O_2 limits the power-operating range and pressure of the electrolyser cell. These problems are less significant for acid electrolyzers, but the commercial catalysts for both half reactions (hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)) are mainly based on non-abundant noble elements like Ru, Ir, and Pt.[19] Thus, there is a necessity for development of more active, durable, sustainable, economical, and ecological catalysts by taking into account a holistic design concept for a material, especially for the more challenging OER.[20] Some research activities of FUNCAT are dedicated to development of effective electrocatalysts and understanding of the alkaline water electrolysis process by using spectroscopic tools.[17a,21]

PEM electrolyzers use a thin Nafion membrane and electrodes that can be operated at pressures of up to 70 bar with high efficiency. The acidic environment of the membrane and harsh oxidative environments limits the composi-

tional choice of the electrocatalysts.[18] PEMs are also very sensitive to water impurities, which could be problematic by considering that globally billions of people face challenges with access to clean water. Overall, both commercial technologies have their own advantages and limitations, which leaves room for further parallel innovation and improvement to make green H_2 production more cost effective.[22]

Production of H_2 from renewable energy sources is still not very significant, although the global capacity of electrolysers that produce green H_2 has doubled over the last five years and reached around 300 MW capacity by mid-2021. Nevertheless, the progress thus far is very encouraging as there are many ongoing projects, developments, and constructions that could increase the production capacity up to around 90 GW by 2030. However, if all the intended projects are accomplished as planned, green H_2 production from electrolysers will only just exceed 8 Mt by 2030. Although, this is a significant amount, it is still below 10 % of the current global H_2 production and it is far away from the 80 Mt target to reach net-zero CO_2 emission by 2050.[23] Thus, the production capacity of electrolysers needs to be increased radically to achieve this target. Alternatively, "blue" H_2, produced from CH_4 with CO_2 capture and storage, could provide H_2 with a lower CO_2 footprint, at least for a transition period.

Among all the challenges of water electrolysis, availability and cost of renewable electricity are the main bottlenecks holding back large-scale production and cost reduction of green H_2. Using Germany as an example, in 2021 about 225 TWh of electricity was produced from renewable sources like wind energy (113,5 TWh), photovoltaics (48.4 TWh), biomass (43 TWh), and hydropower (19.4 TWh). The amount of produced renewable electricity was only 45.7 % of the total electricity production. This amount was almost 6 % less than 2020 due to the fluctuation of solar and wind power.[24] Despite massive investments in renewables, Germany is still not capable of producing a sufficient amount of renewable electricity for routine consumption. The demand for renewable electricity will significantly increase for green H_2 production and decarbonization of some key industrial processes, like Haber–Bosch NH_3 synthesis (see Section 4). Hence, there will be a significant need for more affordable renewable electricity in order to realize a sustainable future. Fortunately, electricity does not need to be generated in countries with less sunshine and wind power. Alternatively, renewable energy could be harvested in sun-rich countries—such as Spain, Australia, and North Africa—converted to H_2 (or other chemicals more amenable to transport and storage, like NH_3 or methanol), which could then be shipped by various means to the consumption centres, although some of the energy will be lost during the conversion and transportation.

4. Status Quo of Traditional NH_3 Synthesis and Alternative Technologies

The synthesis of NH_3 is arguably one of the most important catalytic processes currently in operation. Without the NH_3 made available by this process for the production of fertilizers, the world could not be fed—at least not at the cost at which food is available today. Globally, approximately 170 Mt of NH_3 are produced per year, and with an average energy requirement in modern plants of 27–36 GJ/t $_{NH_3}$.[25] This corresponds to about 1 % of the global primary energy consumption (170 Mt/a × 32 GJ/t = 5.44 EJ/a, total energy consumption 2020: 557 EJ). The real consumption is even higher, since not all plants are at the highest technical standard. Thus, NH_3 production is a substantial contributor to global warming. At the same time, NH_3 is being discussed as an element of a future energy infrastructure.[26] This is because NH_3 provides a means to transport H_2 over long distances and it can also be used directly as a fuel (e.g., in shipping), which would increase the amounts needed even further. Therefore, although the Haber–Bosch process has been in operation for over 100 years and can rightfully be considered a mature technology, research on NH_3 synthesis, especially with the goal to make it more sustainable, is only now proceeding at a highly increased pace, following different lines of development.[27]

The key contributor to the CO_2 footprint in NH_3 synthesis is H_2 production via natural gas reforming.[28] Classical Haber–Bosch synthesis can therefore be developed to be more sustainable by integrating electrolysis for H_2 production in the process. However, from a sustainability point of view, the use of electrolysis H_2 only makes sense if the electricity for the electrolysis is provided from renewable energy, such as photovoltaics or wind. Beyond sustainable H_2 generation, though, there are other factors in the classical Haber–Bosch process that could be improved. Conditions, (i.e., temperatures around 500 °C and pressures around 200 bar), are essentially unchanged compared to the time when the process was invented, and the same also holds for the catalyst.[27b] The only major innovation was the introduction of Ru catalysts, which are highly active at somewhat lower pressure than the Fe system.[29] There have been additional improvements in the catalyst; for instance, by supporting Ru on strongly electron-donating supports, such as electrides and other materials,[30] which not only work for Ru but also improves the performance of other metals like Co.[31] However, the lower NH_3 partial pressures reached at lower total pressure makes downstream separation more difficult, and thus, a new catalyst would also require changes to the separation stage, which is a substantial obstacle. Commercially, Ru-based catalysts are only used in some plants in the final reactor downstream of the main, Fe-catalysed conversion. There are also other important elements in NH_3 plants that contribute to the CO_2 footprint, such as blowers and heaters, which are powered by gas in most cases. Replacing steam turbines for compression by electric compressors, and gas heating by electric heating, could further reduce the CO_2 emissions from the Haber–

Bosch synthesis, provided the electrical energy is renewable energy. A detailed analysis of the potential in improving the Haber–Bosch process has recently been published, and assuming published CO_2 footprints for renewable electricity, the specific CO_2 emissions of an electrified NH_3 synthesis could be brought down by about 80% compared to the natural-gas-based process.[28]

While there is great potential in making the Haber–Bosch process more sustainable, it is also worth exploring other alternatives. The H_2 for NH_3 synthesis can be supplied by water electrolysis (see above Figure 2). Going one step further, direct cathodic hydrogenation of nitrogen to NH_3 in an electrochemical process is possible. A significant fraction of the publications on NH_3 synthesis from the last five years are focused on such electrochemical approaches, with electrocatalysts using the single-atom-catalyst concept probably being the most original approach. However, the results have to be taken with care in many cases,[32] and the verified productivities remain very low,[33] so that it appears questionable whether such electrocatalytic processes will be able to compete with an electrified Haber–Bosch-type process even in the future.

Other approaches for NH_3 synthesis rely on different ways of introducing energy, such as by mechanochemistry,[34] photocatalysis,[35] or different plasma processes.[25] At present, all of these are far from being practically applicable and will most probably not contribute to solving the problems associated with NH_3 synthesis over the next decades. FUNCAT is also working on development of alternative catalysts and methods for NH_3 synthesis. The team based at the Max-Planck-Institut für Kohlenforschung recently demonstrated that a mixture of solid iron and cesium can mechanocatalytically drive NH_3 formation from its elements at room temperature and atmospheric pressure (Figure 3).[34a] The cesium-promoted iron catalysts could produce NH_3 at concentrations of more than 0.2 vol% for over 50 hours, which has been found to be very pressure dependent (Figure 3b).

Plasma-driven reactions could become (again) an interesting, but indirect, alternative to Haber–Bosch synthesis. Essentially, the world is not so much interested in NH_3 per se, but rather in nitrogen fertilizer, which could also be provided in the form of nitrates. Before the Haber–Bosch-process entered the scene for fertilizer production, the Birkeland–Eyde process, an arc process converting nitrogen and oxygen to NO_x, and finally nitric acid, was used in the early years of the 20th century.[36] At that time, the process suffered from very low energy efficiency. However, with the knowledge and technology available nowadays, energy efficiency might be increased, and if renewable electrical energy were to be available at low cost in parts of the world, the process might deserve renewed exploration. The benchmark for such a plasma process would not be the Haber–Bosch process alone, but the combination of it with the Ostwald process, since only the combination of the two results in nitric acid production.[36]

Although significant efforts have been devoted to developing more sustainable NH_3 synthesis through electro- and photochemistry, mechanochemical, and biochemical routes, no catalyst and process have been discovered that could fulfil the activity, selectivity, and stability requirements for commercial applications. When we consider electrochemical N_2 reduction as an example, all discovered electrocatalysts show a large overpotential and very low selectivity toward NH_3; most protons and electrons are consumed in H_2 evolution. Though the required overpotential could be decreased with new catalytic systems, the selectivity still remains a main issue.[37] As an alternative, molecular catalysts and enzymes typically have better selectivity toward NH_3 synthesis; however, their stabilities and low turnover numbers are problematic.[38]

Overall, NH_3 synthesis will remain important for the decades to come, and possibly become even more important if NH_3 becomes part of our energy infrastructure. Given the high energy demand and the CO_2 footprint of NH_3 synthesis, however, NH_3 needs to be considered anew. Thus, intensified research efforts in NH_3 synthesis are urgently needed, with full electrification probably being one of the most promising directions.
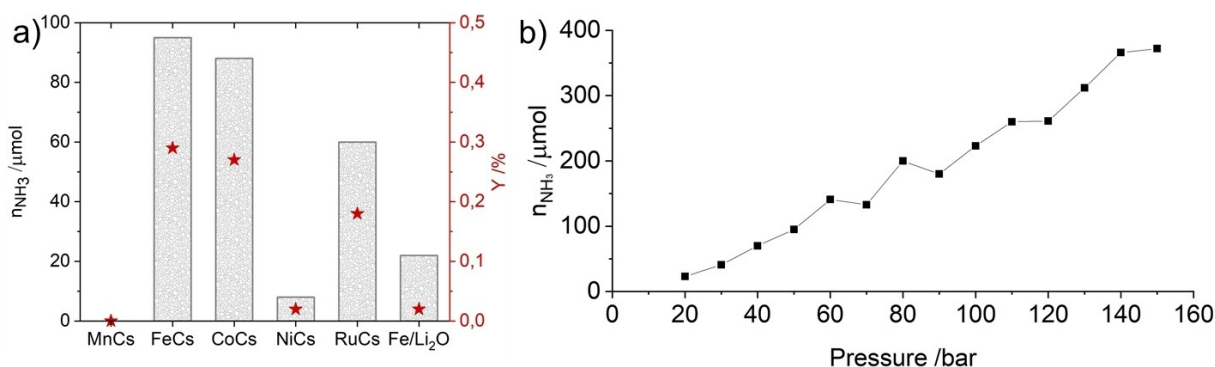
Figure 3. a) Mechanocatalytic room-temperature synthesis of NH_3 from its elements over different catalysts, b) pressure-dependency of the mechanocatalytic NH_3 formation over optimized FeCs mixed catalyst. Reprinted with permission ref. [34a] Copyright 2021, Wiley-VCH Verlag GmbH & Co.

5. CO₂: A Threat or Potential Feedstock?

Global CO_2 emissions are dominated by burning fossil fuels for power generation, heat, and transport, and current global CO_2 production from the energy sector alone is around 36 billion tonnes per annum.[39] This continuing CO_2 emission to the atmosphere has resulted in a concentration rise to nearly 420 ppm from the steady state of 270 ppm, and most of this has happened in recent times (an increase of around 100 ppm since 1960).[40] The resulting global warming is a big problem for the biota of the earth and requires short term solutions in conjunction with longer term cultural changes to tackle the immense challenge.

To reduce CO_2 emissions, we ultimately need to move away from reliance on fossil fuels and replace them with sustainable technologies, but more immediately, we also need other solutions. CO_2 capture and storage is an option that has received a lot of attention for long-term sequestration. However, there is often a disconnection between locations and scales of CO_2 production and geological reservoirs. CO_2 capture and utilization is expected to operate on a smaller scale than storage; nevertheless, conversion of CO_2 to useful fuels and chemicals will be a significant contributor to reducing CO_2 emissions.[41]

A promising technology to aid in this is green H_2 production from water electrolysis using renewable electricity (see Section 3) with subsequent conversion of CO_2 to hydrogenated compounds. This would serve to increase the H_2 density for storage, transportation, and application purposes. One of the ways of achieving this is production of a liquid fuel, such as methanol, by the hydrogenation of CO_2 employing a suitable catalyst.[42] Methanol can be used directly, or the H_2 can be re-extracted from it. A small-scale demonstration plant for methanol synthesis has been built (Figure 4), converting CO_2 from a coal-fired power station in Germany,[43] and CO_2 is effectively the carrier for H_2. A traditional $Cu/ZnO/Al_2O_3$ catalyst has been used for methanol synthesis from CO_2,[42b] but long-term stability is unclear, and alternative catalysts are required. Unlike the current route from fossil fuels, in which CO is hydrogenated to methanol, a direct route from CO_2 produces equimolar amounts of water, and so steam-resistant, stable catalysts need to be developed. In particular, supported PdZn alloy catalysts,[44] or indium-based systems are promising alternatives,[45] and developing more active catalysts that operate at lower temperatures, and even in the liquid phase, has the potential to increase methanol equilibrium yields. It is also likely that these developments will have to be linked to a reverse water–gas shift catalyst at the front end to produce CO, so that a traditional mix can be used into the methanol plant, and hence, will not produce water in that part of the process.

Methanol is a starting material for production of a range of chemicals and thus also has potential to replace the usual fossil fuel feedstocks derived mainly from oil. For instance, the now well-established catalytic MTO (methanol-to-olefins) process provides a route into a wide variety of desirable and valuable chemical products,[46] while in other
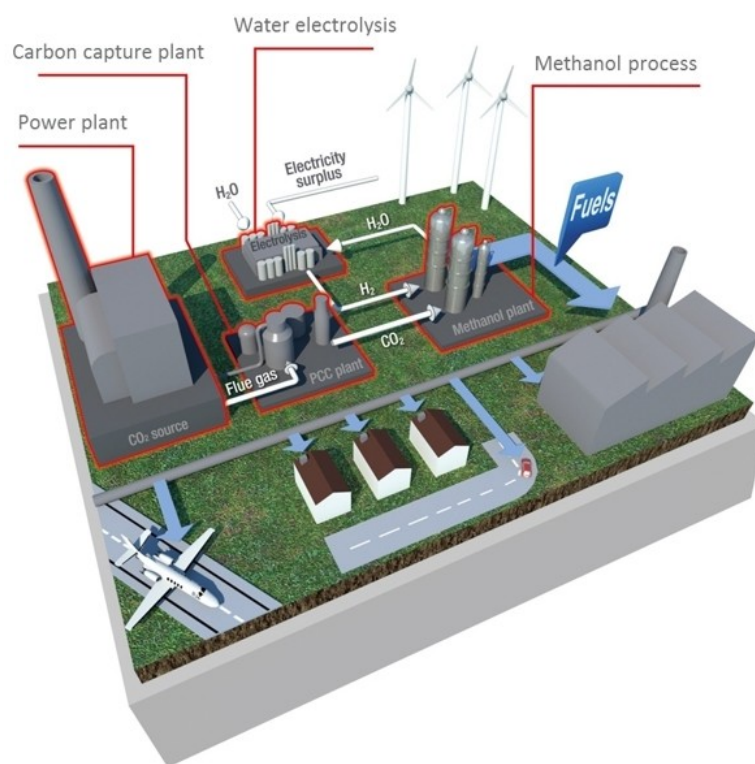
Figure 4. Diagrammatical representation of the 500 t/y mefCO₂ plant built at Niederaussem in Germany to convert CO_2 from the power plant to methanol using H_2 from renewable electricity. Reprinted from ref. [43] courtesy of Ange Sanchez Diaz at i-deals, Madrid.

examples methanol can also be readily converted into aromatics[47] and formaldehyde[48] using existing catalysts. Against this background, CO_2 can be converted into green chemical building blocks for many uses, including polymers, pharmaceutical, platform chemicals, and intermediates.

Much of the catalytic technology required for chemical conversion of CO_2 is in place and is well-developed, but there is still plenty of opportunity to make improvements in catalyst design to enhance activity, selectivity, and stability. Efficient processes for CO_2 utilization will need combinations of innovative technologies merged with old ones to produce new, efficient routes to the molecules on which humankind relies so heavily. Hence, CO_2 can be viewed as an important chemical feedstock rather than a problem; the challenge will be to source and condition CO_2 streams of sufficient concentration and purity for economic processing.

Catalysis is at the heart of these new processes, from Cu catalysts of improved stability for methanol synthesis from CO_2, to CO production via the reverse water–gas shift reaction, to combining methanol conversion catalysts with CO_2 hydrogenation catalysts to produce a range of products with enhanced yield directly from a CO_2 feed. There is no doubt that conversion of CO_2 into useful chemicals and fuels is going to be an important process, combining security of chemical feedstocks with reducing CO_2 emissions to combat global warming. FUNCAT is working on many of these aspects, especially focusing on understanding and developing the next generation of catalysts for direct CO_2 conversion and artificial-intelligence-driven discovery of catalyst genes with application to CO_2 activation on semiconductor oxides,[49] as well as CO_2 hydrogenation to metabolic intermediates in the context of the origin of life.[50]

## 6. Can Acetylene Processes Play a Role in a Sustainable Future?

Acetylene is a highly reactive molecule that has great potential as a chemical intermediate in a future sustainable chemical industry. Acetylene chemistry was well developed over a century ago, but it was displaced as a central chemical intermediate by the ready availability of ethene from oil. Consequently, acetylene chemistry is currently a largely unexplored field. Acetylene is primarily produced by either the partial oxidation of natural gas or as a coproduct from the steam cracking of ethylene.[51] In countries with abundant coal reserves, acetylene is produced from the hydrolysis of calcium carbide.[52] This is not only an energy-intensive process but also suffers from poor atom efficiency, since calcium hydroxide is the by-product. Although much of the chemical industry is based on petroleum-based feedstocks, acetylene is still used for the production of trichloroethylene, vinyl chloride, perchloroethylene, acrylonitrile, acetic acid, and acetaldehyde.

Looking to the future and the need for the development of a sustainable chemical industry that is not based on fossil carbon, it seems that acetylene can play a vital role in this endeavour. The availability of CH_4 from biogas or as a by-product from CO_2 hydrogenation, together with access to renewable energy, will enable acetylene production using high-temperature partial oxidation or arc processes. This will open up the possibility of exploring the chemistry of acetylene with renewed activity and new approaches—something that has lain dormant for about 70 years. Acetylene is a reactive chemical intermediate with the potential to be used in very selective reactions and can, therefore, play a vital role in new sustainable green chemical processes. This is an area where the Max Planck–Cardiff Centre FUNCAT will seek to develop a new program of work combining the expertise of high-pressure acetylene catalysis developed at the Max-Planck-Institut für Kohlenforschung and the low-pressure acetylene catalysis developed at the Cardiff Catalysis Institute.

Nowadays, the synthesis of acetylene from CH_4 is possible by coupling in renewable electrical energy, either in an electric arc furnace at short residence time or in plasma reactors. In addition to producing acetylene, such plants could have a load-levelling function in renewable electricity systems. However, in addition to its technical relevance, acetylene is a highly interesting molecule from a fundamental point of view: it is the smallest hydrocarbon with a carbon–carbon bond and thus theoretically easily traceable; it has high electron density in the C≡C triple bond, which provides one point of attack in reactions, and the proton is very acidic (for a hydrocarbon), so that reasonably stable metal acetylides or carbides are known. The acidity provides quite a different mode of reactivity than the electron-rich C–C bond. However, the reactivity of acetylene has hardly been explored over the last several decades, despite the tremendous achievements in terms of catalytic materials.[53] One reason for this lack of activity is that not many laboratories have the infrastructure for handling acetylene in a safe manner. However, the groups at the Cardiff Catalysis Institute and the Max-Planck-Institut für Kohlenforschung are two notable exceptions with their infrastructure to handle acetylene under low and high pressure; combined with materials synthesis expertise and the theoretical approaches available in the Max Planck Centre, unique research directions can be pursued.

Acetylene has the potential to be a central chemical intermediate (Figure 5).[53] The initial key reaction is acetylene hydrochlorination to produce vinyl chloride monomer (VCM).[5b] This process is an environmentally benign alternative to the Hg-catalysed reaction, which is implemented on a very large commercial scale predominantly in China. A gold on carbon catalyst is being commercially operated in China, and it is known that well-dispersed Au cations are the active species.[54] It is unclear whether this holds also for Au on other supports for reactions of acetylenes. The methods envisaged in the centre to selectively create specific Au structures on different supports, combined with theoretical approaches to understand catalytic behaviour, could clarify this question and provide fundamental knowledge on the reactivity of acetylene on different Au species. A second, highly interesting system for which the expertise of the different partners is required, is selective hydrogenation of acetylene in
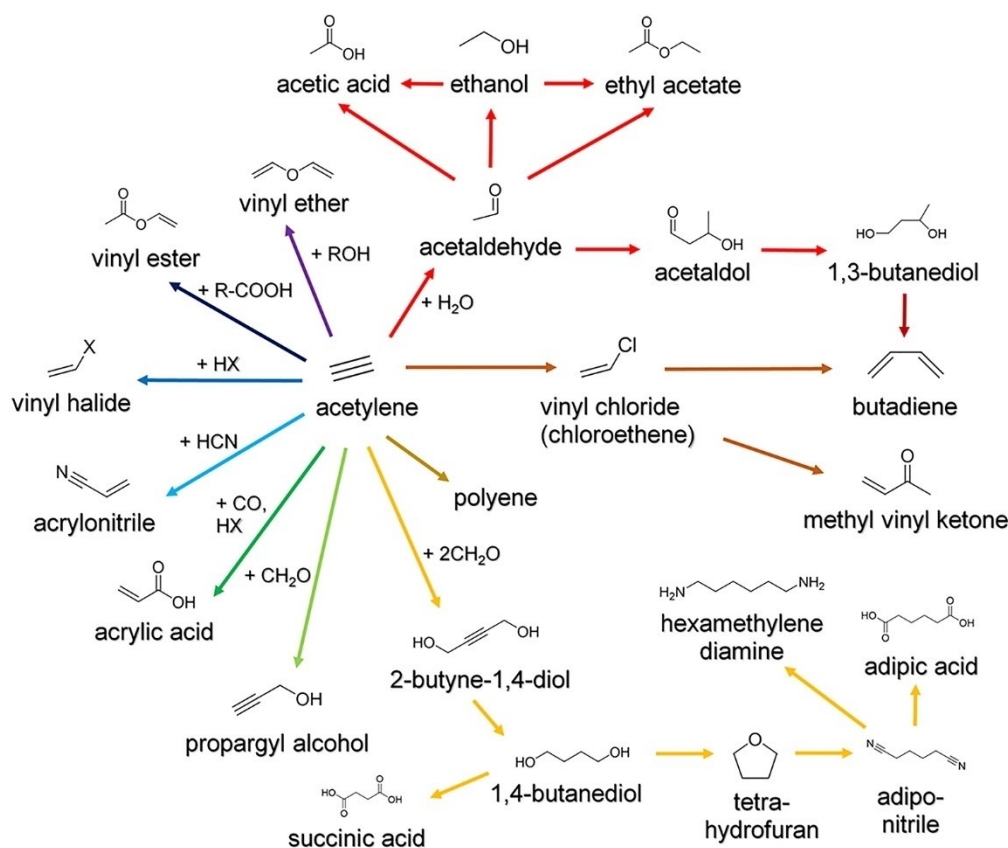
Figure 5. Acetylene can be the starting point for the production of many chemicals.

ethylene. For polyethylene synthesis, this is an industrially relevant reaction, since acetylene traces poison the polymerization catalyst.[54] However, the reaction could become even more important if ethylene is synthesized in a plasma process from CH_4, where high amounts of acetylene can be formed as well. For this reaction, theoretical approaches using simple descriptors have been published, and there are also many experimental studies but at low acetylene concentrations.[55] Knowledge about the interaction of acetylene and ethylene with different surfaces should guide the exploration of new catalysts and systems. Of special importance is the avoidance of uncontrolled oligomerization reactions of acetylene, since this leads to the formation of so-called "green oil" and "red oil", which deactivate the catalysts.[53]

Controlled oligomerization of acetylene can open new avenues where research activity is desired. Zeolite-based catalysts can give relatively high yields (around 35%) of C_4 compounds from an acetylene/H_2 feed at elevated pressures.[56] Understanding this reaction theoretically, starting from the initial experimental findings, would be an important step to increase the yields of such reactions and would help to steer the reaction towards the most desirable C_4 compounds. FUNCAT's team at the Max-Planck-Institut für Kohlenforschung and Cardiff Catalysis Institute are also dealing with catalyst development and diverse aspects of

acetylene chemistry to provide alternative chemical intermediates.

7. Road Ahead

The greatest barrier towards a sustainable future is availability of affordable renewable electricity that can assist efforts to reach zero-CO_2 emission targets. Many industrial processes need to be de-carbonized and green H_2 can play an essential role in this transition. However, green H_2 is currently two to three times more expensive than grey H_2 (SMR or gasification), and there are still obstacles associated with the capital and electricity costs for green H_2 production from water electrolysis. Additionally, there are technical issues and limitations with the existing infrastructure and with end users, which will require significant investments to be able to use green H_2 as a feedstock and fuel in industry, transportation, and for heat and power generation. On the other hand, while the cost of green H_2 is expected to decrease substantially, fossil-based H_2 will become more expensive due to increasing CO_2 penalties, so that eventually green H_2 may even be the more cost competitive choice in the near future.

How can heterogeneous catalysis contribute towards a sustainable future? Control over the structure of catalysts and atom economy can make chemical processes more

efficient and sustainable by involving all atoms in reactions to produce targeted products.[57] Atom economy and recycling of the used catalysts will be essential for a sustainable chemical industry. In particular, if we keep using our resources in the present manner, we will have serious supply shortages of many elements in the near future. Furthermore, control over the catalytically active sites to optimize activity and stability is going to be essential to achieve a sustainable future. Development of new sustainable technologies and concepts are also going to be critical. For instance, renewable-energy-driven electro- and mechanochemical cycling and transformation could play an important role. The development of innovative electrocatalytic processes for selective hydrocarbon functionalization could open a new industrial path for fine chemical and petrochemical production with a lower CO_2 footprint. However, this will require scientific and technological breakthroughs.

Artificial intelligence (AI) may capture the catalytic progression better than previous theoretical/computational methods because it targets correlations and does not assume an underlying physical model. However, at present AI strategies for heterogeneous catalysis are hindered because i) we are lacking big data, in particular data from in situ and operando techniques at reaction conditions, ii) the characterization of available data in terms of metadata is often insufficient, and iii) the number of good catalysts is very small in comparison to the number of all possible materials.[58] To release the full potential of data-centric research in heterogeneous catalysis, some elaborate work is necessary, but the first promising steps have already been taken:

- New tools are already being invented; for example, for fitting data, removing noise from data, learning rules that are behind patterns in data and identifying "statistically exceptional" subgroups of data.[59] With such rules, it will be possible to identify "materials genes"; i.e., physical parameters that are related to the underlying processes that trigger, facilitate, or hinder the catalyst activity, selectivity, or stability.[60] We are confident that these methods will be advanced and more methods will be developed in the near future to help the discovery and optimization of industrial catalysts.
- FAIR (findability, accessibility, interoperability, and reusability) data repositories need to be advanced,[59] they need to be used, and the publication culture should change. The concept of "clean data"—that is, data that are comprehensively annotated—is being developed.[61] This is much more elaborate than it sounds, and publications that "just" present and describe such comprehensively characterized data should be appreciated by the community as much as a standard publication in a high-impact journal.

Observing interactions between catalyst, reactant, and product, and understanding reaction mechanisms and deactivation pathways are crucial for the implementation and further development of catalysts. In particular, operando methods performed as close as possible to real-world working conditions are essential for understanding the transformation of a catalytically active site during the course of a reaction. Here, a combination of multiple complementary techniques (e.g., X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), Raman and infrared (IR) spectroscopies, etc.) is highly desirable in order to achieve a more holistic picture of the transformations that occur.[62] We note, however, as the catalytically active sites may represent a minor component of the material under study, experimental approaches that enable added spatial, temporal, and/or electronic selectivity are often needed to elucidate the true active site. Furthermore, it is important to emphasize that the optimization of a catalyst goes beyond the active site alone and changes which occur from the atomic scale to the macroscale (e.g., on the level of the reactor) must be understood in order to optimize the full catalytic system. Looking toward the future, it is clear that combining the knowledge gained from a wide range of operando studies together with AI approaches will assist in the design and development of more effective catalysts for a wide range of essential energy-converting processes.

Evidently, our society is going through an energy-transition phase to reach net-zero emissions. Our vision is that the discovery of new catalysts lies at the heart of our quest to achieve net-zero emissions. Our intention—as we have set it out in this Viewpoint Article—is to focus on key areas we have identified. Each represents significant challenges and we aim to address these accordingly, but we would also like to inspire others to take up the challenge to identify the new catalysts that we certainly now need. In particular, to achieve CO_2 neutrality, all contributors to greenhouse-gas emissions need to be evaluated in detail and potential for improvements needs to be assessed. Heterogeneous catalysis can play an essential role in this transition by making chemical processes and transformations more economical and sustainable. There is still the need for discovery of more effective catalysts for key reactions, such as electrochemical water splitting, NH_3 synthesis, and CO_2 reduction. Most importantly, the availability of sustainable electricity and green H_2 are going to be the bottlenecks for a sustainable future.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analysed in this study.

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