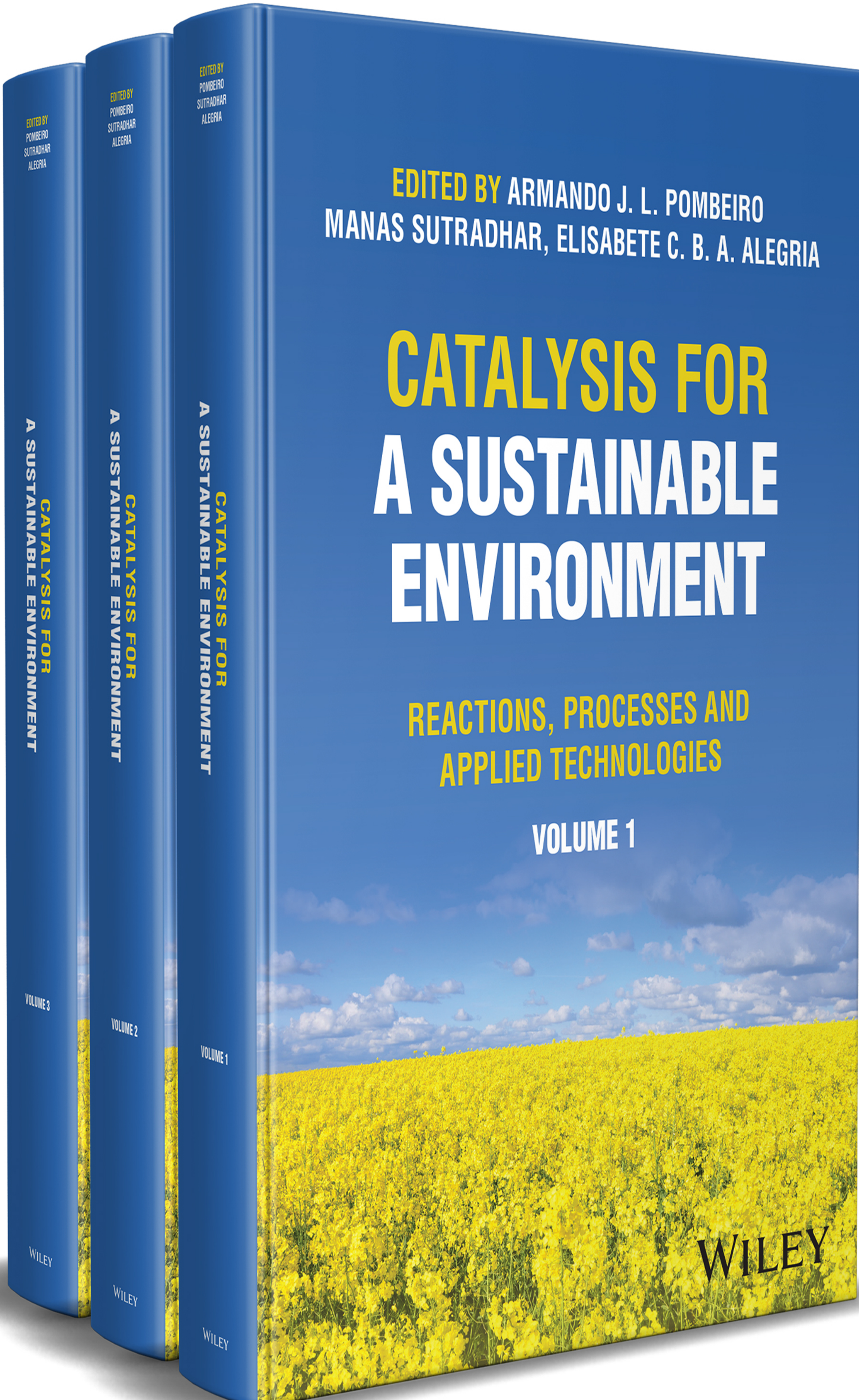

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MANAS SUTRADHAR, ELISABETE C. B. A. ALEGRIA
CATALYSIS FOR
A SUSTAINABLE
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REACTIONS, PROCESSES AND
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VOLUME 1
VOLUME 2
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Catalysis for a Sustainable Environment

Catalysis for a Sustainable Environment

Reactions, Processes and Applied Technologies

Volume 1

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He has authored or edited 10 books, (co-)authored *ca*. 1000 research publications, and registered *ca*. 40 patents. His work received *over*. 30,000 citations (over 12,000 citing articles), h-index *ca*. 80 (Web of Science).

Among his honors, he was awarded an Honorary Professorship by St. Petersburg State University (Institute of Chemistry), an Invited Chair Professorship by National Taiwan University of Science & Technology, the inaugural SCF French-Portuguese Prize by the French Chemical Society, the Madinabeitia-Lourenço Prize by the Spanish Royal Chemical Society, and the Prizes of the Portuguese Chemical and Electrochemical Societies, the Scientific Prizes of ULisboa and Technical ULisboa, and the Vanadis Prize. Special issues of Coordination Chemistry Reviews and the Journal of Organometallic Chemistry were published in his honor.

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Preface

Aiming to change the world for the better, 17 Sustainable Development Goals (SDGs) were adopted by the United Nations (UN) Member States in 2015, as part of the UN 2030 Agenda for Sustainable Development that concerns social, economic, and *environmental sustainability*. Hence, a 15-year plan was set up to achieve these Goals and it is already into its second half.

However, the world does not seem to be on a good track to reach those aims as it is immersed in the Covid-19 pandemic crisis and climate emergency, as well as economic and political uncertainties. Enormous efforts must be pursued to overcome these obstacles and chemical sciences should play a pivotal role. *Catalysis* is of particular importance as it constitutes the most relevant contribution of chemistry towards sustainable development. This is true even though the SDGs are integrated and action in one can affect others.

For example, the importance of chemistry and particularly catalysis is evident in several SDGs. Goal 12, addresses “Responsible Consumption and Production Patterns” and is aligned with the circularity concept with sustainable loops or cycles (e.g., in recycle and reuse processes that are relevant within the UN Environmental Program). Goal 7 addresses “Affordable and Clean Energy” and relates to efforts to improve energy conversion processes, such as hydrogen evolution and oxygen evolution from water, that have a high environmental impact. Other SDGs in which chemistry and catalysis play an evident role with environmental significance include Goal 6 (“Clean Water and Sanitation”), Goal 9 (“Industry, Innovation and Infrastructure” 13 (“Climate Action”), Goal 14 (“Life Below Water”), and Goal 15 (“Life on Land”).

The book is aligned with these SDGs by covering recent developments in various *catalytic processes* that are designed for a *sustainable environment*. It gathers skilful researchers from around the world to address the use of catalysis in various approaches, including homogeneous, supported, and heterogeneous catalyses as well as photo- and electrocatalysis by searching for innovative green chemistry routes from a sustainable environmental angle. It illustrates, in an authoritative way, state-of-the-art knowledge in relevant areas, presented from modern perspectives and viewpoints topics in coordination, inorganic, organic, organometallic, bioinorganic, pharmacological, and analytical chemistries as well as chemical engineering and materials science.

The chapters are spread over seven main sections focused on Carbon Dioxide Utilization, Transformation of Volatile Organic Compound (VOCs), Carbon-based Catalysts, Coordination, Inorganic, and Bioinspired Catalysis, Organocatalysis, Catalysis for the Purification of Water and Liquid Fuels,and Hydrogen Formation, Storage, and Utilization. These sections are gathered together as a contribution towards the development of the challenging topic.

The book addresses topics in (i) activation of relevant small molecules with strong environmental impacts, (ii) catalytic synthesis of important added value organic compounds, and (iii) development of systems operating under environmentally benign and mild conditions toward the establishment of sustainable energy processes.

This work is expected to be a reference for academic and research staff of universities and research institutions, including industrial laboratories. It is also addressed to post-doctoral, postgraduate, and undergraduate students (in the latter case as a supplemental text) working in chemical, chemical engineering, and related sciences. It should also provide inspiration for research topics for PhD and MSc theses, projects, and research lines, in addition to acting as an encouragement for the development of the overall field.

The topic Catalysis for Sustainable Environment is very relevant in the context of modern research and is often implicit, although in a non-systematic and disconnected way, in many publications and in a number of initiatives such as international conferences. These include the XXII International Symposium on Homogeneous Catalysis (ISHC) that we organized (Lisbon, 2022) and that to some extent inspired some parts of this book.

In contrast to the usual random inclusion of the topic in the literature and scientific events, the applications of catalytic reactions focused on a sustainable environment in a diversity of approaches are addressed in this book.

The topic has also contributed to the significance of work that led to recent Nobel Prizes of Chemistry. In 2022, the Nobel Prize was awarded to Barry Sharpless, Morten Meldal, and Carolyn Bertozzi for the development of click chemistry and bioorthogonal chemistry. The set of criteria for a reaction or a process to meet in the context of click chemistry includes, among others, the operation under benign conditions such as those that are environmentally friendly (e.g., preferably under air and in water medium). In 2021, the Nobel Prize was awarded to Benjamin List and David W.C. MacMillan for the development of asymmetric organocatalysis, which relies on environmentally friendly organocatalysts.

The book illustrates the connections of catalysis with a sustainable environment, as well as the richness and potential of modern catalysis and its relationships with other sciences (thus fostering interdisciplinarity) in pursuit of sustainability.

At last, but not least, we should acknowledge the authors of the chapters for their relevant contributions, prepared during a particularly difficult pandemic period, as well as the publisher, John Wiley, for the support, patience, and understanding of the difficulties caused by the adverse circumstances we are experiencing nowadays and that constituted a high activation energy barrier that had to be overcome by all of us… a task that required rather active catalysts.

We hope the readers will enjoy reading its chapters as much as we enjoyed editing this book.

Armando Pombeiro
Manas Sutradhar
Elisabete Alegria

Introduction

Armando J.L. Pombeiro[1], Manas Sutradhar[2], and Elisabete C.B.A. Alegria[3]

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The relevance of catalysis in our lives is well-documented by its involvement in the industrial production chain for the manufacture of most products, such as petrochemicals, fine chemicals for pharmaceuticals, polymers, fertilizers, and bio-produced materials. Catalysis is also prominent in many biological transformations and connects several areas of chemical and related sciences from different perspectives (e.g. chemistry and energy, chemistry and the environment, Chemistry at the Interface of Biology, pharmacology and medicine, functional biomaterials, materials sciences, and chemical engineering).

Catalysis plays a key role in achieving the United Nations (UN) Sustainable Development Goals (SDGs), namely those of *environmental* significance as mentioned in the Preface of this book. With the aim of ending poverty, protecting the environment and promoting prosperity, the UN embraced 17 SDGs in 2015 and encouraged countries, industries, and organizations around the world to adopt these goals. These actions include, for example, the development of sustainable forms of energy and its storage, the application of green chemistry principles in industrial processes, the recycling of resources, orientation towards a circular economy, the use of low-cost raw materials and of carbon from biomass, the conversion of CO_2 and CO from flue gases, and the mitigation of air pollution.

The Covid-19 pandemic forced a long period of reflection about the value of human relations and of human interactions with the environment. The pandemic provided a unique opportunity to join efforts towards achieving the above aims of the UN 2030 Agenda that includes the SDGs. However, efforts concerning direct human interactions do not seem to be paving a promising path. Let us hope that the harmonization of human actions with the need for a healthy and *sustainable* environment will be more successful despite of the difficulties already experienced by initiatives such as the UN Paris Agreement on Climate Change that aims to limit global warming by reducing greenhouse gas emissions.

One major environmental concern is pollution. Control of this pollution is a main objective that can be accomplished by work that can be described as environmental catalysis. For example, work

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in this field aims to contribute towards the reduction of emissions of environmentally unacceptable compounds such as CO_2, volatile organic compounds (VOCs), nitrogen oxides (NO_x), sulfur oxides (SO_x), and CO. It involves the use of catalytic cleanup technologies for this purpose, as well as the conversion of VOCs, liquid and solid waste treatment, and the conversion of greenhouse gases. It also addresses, for instance, the application of catalysis under eco-friendly conditions, the use of catalytic technologies for waste minimization, catalyst recycling, and the development of new catalytic routes for selective synthesis of valuable products. Additional important developments of environmental interest include the use of energy-efficient catalytic processes (which are assisted by low power microwave radiation or ultrasound), catalysis in the reduction of the environmental impact, and catalysis to produce clean fuels.

Sustainability is a relevant concern for all of these and green chemistry routes that protect or are compatible with protecting the environment should be pursued. Sustainable processes should replace conventional chemical syntheses and transformations by minimizing the formation of by-products or waste and bypassing the use of conventional and polluting organic solvents under eco-friendly reaction conditions. Working for a sustainable future is a current challenge and *Catalysis for a Sustainable Environment* can aid in these efforts.

Structure of the Book

This book brings together researchers whose contributions to the development of environmentally sustainable catalytic processes are well recognized. Throughout the chapters, the authors give their perspectives on state-of-the-art approaches and address innovative methodologies in relevant areas of homogeneous, supported, and heterogeneous catalysis, as well as photo-, electro- and magnetocatalysis from a sustainable viewpoint.

The book consists of 38 chapters spread over 7 sections (Parts) as follows: (I) Carbon Dioxide Utilization, (II) Transformation of Volatile Organic Compounds (VOCs), (III) Carbon-based Catalysis, (IV) Coordination, Inorganic, and Bioinspired Catalysis, (V) Organocatalysis, (VI) Catalysis for the Purification of Water and Liquid Fuels, and (VII) Hydrogen Formation, Storage, and Utilization. The book has an interdisciplinary character illustrating relevant areas in coordination, inorganic, organic, organometallic, bioinorganic, and pharmacological chemistry, as well as nanochemistry, chemical engineering, and materials science.

As addressed in **Part I**, the use of renewable carbon sources such as biomass and CO_2 (Chapter 2) for the manufacture of chemicals such as acetic acid or urea (Chapters 3 and 7), and fuels (Chapters 2 and 5) is a highly active field of research and a step towards a circular carbon economy. Recently, efforts focused on combining CO_2 with bio-based resources has highlighted the importance of catalysis in the process viability of converting inactive substrates (Chapter 2). Hybrid catalysis, based on the integrated use of robust and selective chemocatalysts, stands out as one of the important trends for CO_2 conversion to added-value chemicals (Chapter 2). The formation of cyclic carbonates by catalytic reactions of CO_2 with promising bio-based resources (epoxides, carbohydrates, and diols) is analysed (Chapter 4). The methanation of CO_2 (Sabatier reaction) to produce electricity is also addressed, with an emphasis on the performance of zeolite-supported catalysts and on structure-reactivity relations (Chapter 5).

The application of Fischer-Tropsch catalysis to convert green H_2 and sustainable carbon into kerosene range hydrocarbons for aviation fuels is presented, with one of the indirect routes involving the conversion of CO_2 plus green H_2 into CO and water via the reverse displacement of water gas shift (Chapter 6).

The elimination of nitrogen oxides (NO_x) (Chapter 8) and VOCs (Chapters 8 and 9), critical precursors for ozone and particle matter, is an important research topic that is treated in **Part II**. From this perspective, the most promising NO_x and VOCs treatment technologies are highlighted, including catalytic ozonation of NO (Chapter 8) and advanced oxidation processes for VOCs (Chapter 9). Apart from the elimination of aromatic VOCs (Chapter 9) and saturated hydrocarbons (cyclohexane) (Chapter 10), the selective functionalization of these compounds to added-value organic products is discussed.

Carbon-based materials have been successfully applied to specific reactions, either as catalysts or as catalyst supports and various synthetic strategies are available, as illustrated in **Part III**. The versatility of carbon materials is related to their capacity to maximize surface area and be easily functionalized by replacing carbon atoms with heteroatoms such as S, N, O, P, or B, allowing control of their electronic properties (Chapter 11). Methodologies for the introduction of these heteroatoms into carbons and synthetic methods for nanostructured carbons are reviewed and their use as catalysts is discussed in the context of sustainable production of fuels and chemicals, energy conversion, and environmental protection (Chapter 11). State-of-the-art approaches focussed on metal-free carbon-based catalysts for gas-phase industrial oxidation processes (H_2S oxidation to sulphur and alkane dehydrogenation) are presented (Chapter 12). The application of emerging eco-sustainable carbon-metal oxide (nano)catalysts as electrocatalysts, as catalysts for biomass valorization, and as (photo)(electro)catalysts for water and wastewater treatment is covered (Chapter 13).

The use of metal-based coordination compounds for the development of sustainable catalytic protocols is discussed mainly in **Part IV** for many (technological) processes of organic synthesis. These include hydroformylation (Chapter 14), synthesis of ethylene copolymers by incorporation of sterically encumbered olefins and cyclic olefins (Chapter 15), depolymerization of plastic waste (catalytic hydrogenation, hydrogenolysis, hydrosilylation, and hydroboration) (Chapter 16), tandem reactions (Chapter 20), carbene transfer from diazocarbenes to C–H and C–C π-bonds (Chapter 21), synthesis of organic scaffolds of pharmaceutical importance (Chapter 22), oxidation reactions (Chapters 23–25), cross-coupling reactions (Chapter 26), and Friedel Crafts acylation (Chapter 27). The contribution of pincer complexes to the development of environmentally friendly systems, particularly in hydrogenation and dehydrogenation reactions or in the transformation of CO_2 into valuable products such as methanol, is highlighted (Chapter 18). The synergistic cooperation of metals in heterometallic complexes is also emphasized for various homogeneous catalytic processes (Chapter 19). Rules governing the regio- and stereoselectivity of catalytic functionalizations in the presence of biologically-inspired transition metal-based catalysts are addressed to provide mechanistic insights into selective bioinspired C-H oxygenations, halogenations, and azidations of steroids and terpenoids (Chapter 17). Several chapters address the significance of particular components of reactions. The significance of Au nanoparticles as catalysts in oxidation reactions (e.g. of CO and VOCs) and in the water-gas shift is described (Chapter 23). The use of platinum (Pt) complexes in water and in micellar catalysis is also highlighted illustrating the lowering of the E-factor in various organic transformations (Chapter 24). The importance of using water for enhanced activities and selectivities at any level (chemo, regio, or enantio) is shown in a range of catalytic reactions (Chapter 25). The significance of speciation chemistry in the optimization of catalysts for the Suzuki-Miyaura coupling and towards the development of greener catalysts is shown (Chapter 26). The contribution of structure-property relationships for a better design of zeolite catalysts in Friedel Crafts acylation reactions is also treated (Chapter 27).

Other important reactions catalysed by coordination compounds are also treated in previous (e.g. Chapters 9 and 10) or following (e.g. Chapters 34, 35, and 38) parts in different contexts.

In **Part V**, recent advances in green and sustainable organocatalysis are addressed, focussed on the reduction of energy consumption, increasing efficiency and selectivity, reducing wastes, and optimizing resource use. Industrial (Roche Pharmaceutical Division) design of sustainable new routes to drugs involving a diversity of catalytic processes is addressed (Chapter 28).

The advantages brought by organocatalytic reactions using immobilized catalysts for asymmetric synthesis of fine chemicals and the effectiveness of relevant organocatalysts that have been used in recent years are discussed (Chapter 29).

Syntheses of long-chain aliphatic polyesters, especially by condensation polymerization (of dicarboxylic acids with diols) and acyclic diene metathesis polymerization are described, and the closed-loop chemical recycling (and upcycling) is highlighted (Chapter 30).

The development of noble metal-free organic photocatalysts as potential electron sources and as an alternative to hazardous alkali metals is challenging, and an overview, combining organic photocatalysis with electrolysis in organic synthesis, is provided (Chapter 31).

The combination of chiral organocatalysis with photoredox chemistry can allow the development of novel enantioselective reactions and softening of reaction conditions, and different modes of organocatalytic activation combined with photocatalysis are addressed (Chapter 32).

Catalytic processes for purification of water and liquid fuels are described in **Part VI**. For example, water is susceptible to pollution by a large number of contaminants from various sources and the application of sustainable materials and technologies for wastewater treatment is addressed, with a focus on the photocatalytic route (Chapter 33).

There has been growing concern about the environmental impact of the emission of carbon dioxide and other pollutants. The most successful desulphurization technologies involving functional materials are described (Chapters 34 and 35).

Part VII concerns the formation (and storage) of hydrogen in different contexts. Examples are given of homogeneous metal-catalysed reactions with paraformaldehyde used as a source of hydrogen in water for transfer hydrogenation reactions, including the reduction of C=C, C=O, –CC–, and –CN bonds (Chapter 36).

Energy storage is a shortcoming of the use of renewable fuels and the storage of chemical energy using hydrogen batteries is discussed (Chapter 37). Readily available and chemically stable storage materials, as well as solvents and catalysts, are relevant for the long-term and large-scale storage of hydrogen (Chapter 37).

Finally, a brief overview is given on the replacement of fossil fuels by hydrogen as a synthetic fuel. Although water splitting for high purity H_2 production is tempting, the associated high energy consumption hampers its application. The potential significance of low-cost mono- and bimetallic metal-organic frameworks/coordination polymers (MOFs/CPs) as bifunctional electrocatalysts is addressed in terms of hydrogen evolution (HER) and oxygen evolution (OER) reactions (Chapter 38).

Final Remarks

Catalysis provides key tools for the development of a sustainable environment and towards the promotion of quality of life, as illustrated herein. This can be pursued by developing innovative catalytic materials and technologies to improve resource use and foster sustainable processes and products.

The preparation of this book was initiated during the Covid-19 pandemic, a period favourable to a meditation assessing the interrelationship between humans and the environment. The book covers several recent catalytic studies that are aimed at improving environmental sustainability. Its contents are intended to give a vision of the challenges and future directions for the development of efficient and eco-sustainable catalytic processes. We hope that it will also serve as an inspiration and an incentive to the *application of catalysis towards environmental sustainability*.

Part I

Carbon Dioxide Utilization

2

Transition from Fossil-C to Renewable-C (Biomass and CO_2) Driven by Hybrid Catalysis

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2.1 Introduction

Moving to a de-fossilized economy is a must for our society, which is in need of reducing the impact of anthropogenic activities on climate to avoid a point of non-return [1–7] that may cause multiple disasters. The use of fossil-C over the last two centuries for feeding the chemical and power industries has produced a continuous release of waste heat and greenhouse gases (GHGs) into the atmosphere and CO_2 has been attributed a central role in driving the climate change. The direct heating of the atmosphere (only an average 33% of the chemical energy of fossil-C is used in the conversion into electric or mechanical energy, the rest being lost to the atmosphere as heat in the temperature range 150–900+ °C) has caused an increase in the concentration of water vapor, a GHG more powerful than CO_2. The two GHGs together with others such as methane, nitrogen oxides (NO_x), and chlorofluorocarbons (CFCs) are reinforcing the natural greenhouse effect, contributing to an increase of the average planet temperature that should be maintained below 2 °C above the average temperature of 1990 to prevent irreversible changes to our planetary ecosystem. Since 1981, the temperature of oceans and land has increased at a rate of 0.18 °C/decade, more than doubling the increase observed during the previous century (1880–1980) of 0.08 °C/decade [8]. Such climate change is causing sudden, violent meteorological events all over the world, while the rise of the level of the oceans, caused by the transfer of water from land to the seas (melting of ice), is a serious menace for coastal areas that could be submersed [9].

In the last three decades, the capture of CO_2 from point sources has been considered as a way to reduce climate change, but this has had no effect and therefore the only way to save our planet is to drastically reduce the extraction and use of fossil-C in all its forms to simultaneously lower the discharge of heat, water vapor, and GHGs to the atmosphere.

Such big change requires a global agreement and action. The Conference of Parties (COP) 2016 through the Paris Agreement has provided the basis for common action that, after some initial important uncertainties, seems now to have the convinced cooperation of all major actors based on developments at the COP in Glasgow in 2021.

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The need is impellent for implementation of the agreement by all industrialized societies to meet the target as demonstrated by action taken to prevent the enlargement of the ozone hole, which banned over 200 ozone-depleting substances (ODS; mainly CFCs and hydro-CDCs [HCFCs]) [10]. Various policy measures have been introduced to limit or phase out the consumption of ODSs since this agreement was reached. As a result, global consumption of ODSs declined by 98.5% between 1986 and 2018, meaning that the release of 343,000 ozone-depleting potential tonnes was avoided between 1986 and 2002 [11]. With the committed participation of all countries, the damage has started to be repaired in three decates. This was possible because substitutes of CFCs were developed, meaning that the delivery of dangerous species to the atmosphere was stopped. This problem has a dimension that is not equivalent to that of fossil-C, which is larger by several orders of magnitude.

However, substitutes for fossil-C must be found rapidly, even if this is not so easy considering the dimension of the problem. Time plays a key role in such change; the sooner we start finding and adopting solutions, the more quickly solutions will be implemented and start to become effective. But first, let us consider how much fossil-C we use currently to illustrate the magnitude of the problem.

2.2 The Dimension of the Problem

As of 2018, our society has consumed 13,978 Mt_{oileq} (Mt_{oileq} means that all the energy consumed is expressed as oil burned). Table 2.1 shows that only the Confederation of Independent States (CIS) has shown an apparent decrease of energy consumption (figures in parentheses) over the period of 1990–2018, during which time CIS varied in composition. However, an increase of 20% in energy consumption is observed for the CIS from 2000 to 2018. Whereas North America, Europe, and Japan were the major consumers of energy until the 2000s, the highest increase since that time has been observed for developing countries with India, China, the Middle East, and Africa leading the world in growth of energy consumption.

Table 2.2 shows the contribution of various forms of fossil-C to the overall energy budget by region or country.

It is obvious that solving the energy source problem is much more complex than substituting ODSs and an efficient solution will be effective only if the following conditions are met:

- Global cooperation is implemented.
- There is global agreement upon an effective defossilization of the energy and chemical sectors.

If there is random national engagement in limiting the causes of climate change, the effects will be very limited or zero.

2.3 Substitutes for Fossil-C

How and where will it be possible to find substitutes for fossil-C? The main targets involve the use of perennial energy sources such as solar, wind, hydro, and geothermal (SWHG) as well as biomass. The latter is considered to be renewable carbon, but alone cannot cover the parts of applications that cannot be decarbonized. Whereas we can imagine decarbonizing the energy sector, it will not be possible to decarbonize the chemical industry, the polymer industry, and part of the fuel sector as our current way of life is based on carbon.

However, biomass alone cannot cover the need of carbon-based goods and fuels. As a consequence, an additional source of carbon will be necessary. This is CO_2, the most abundant

Table 2.1 Total energy consumption as $Mt_{oilequivalent}$ by region or country.and its segmentation by countries and regions.

Country	China	India	USA	Russia	Germany	Japan	South Africa	South Korea	Poland	Turkey	Australia	Indonesia
Mt/y COAL	3770	982	624	234	217	189	186	150	129	125	113	109

Country	Europe	Asia	North America	Latin America	Pacific	Middle East	CIS	Africa
Bcm LNG	538	787	976	243	50	539	671	151
Mt/y OIL	168	349	935	432	Na	1496	691	398

Bcm: billion cubic meters.

Table 2.2 Yearly production of coal, gas, and oil in the various parts of the world (2018).

Country	China	India	USA	Russia	Germany	Japan	South Africa	South Korea	Poland	Turkey	Australia	Indonesia
Mt/y COAL	3,770	982	624	234	217	189	186	150	129	125	113	109

Country	Europe	Asia	North America	Latin America	Pacific	Middle East	CIS	Africa
Bcm LNG	538	787	976	243	50	539	671	151
Mt/y OIL	168	349	935	432	Na	1496	691	398

Bcm: billion cubic meters.

source of carbon we have at hand (ca. 830 Gt_C are available in the atmosphere). The wise use of perennial energies (SWHG) and renewable-C (biomass and CO_2) will sustain our society development in future years. The former will represent the inexhaustible reserve of primary energy, whereas the second will represent the source of carbon for dedicated uses. We do not believe that fossil-C will go down to zero in near or far future, but we believe that its use will be sensibly reduced (perhaps to one-fourth of actual by 2050) with a greatly beneficial impact on our environment, even if the decrease is not very rapid.

In 2020, SWHG covered approximately 29% of the total amount of electric energy consumed in the world, representing a 2 point increase with respect to 2019 (27%). During this time, the use of other fuels decreased. Bioenergy use in industry grew 3%, but the lower oil demand due to the Covid-19 pandemic caused a decline in biofuels used to blend oil-derived fuels.

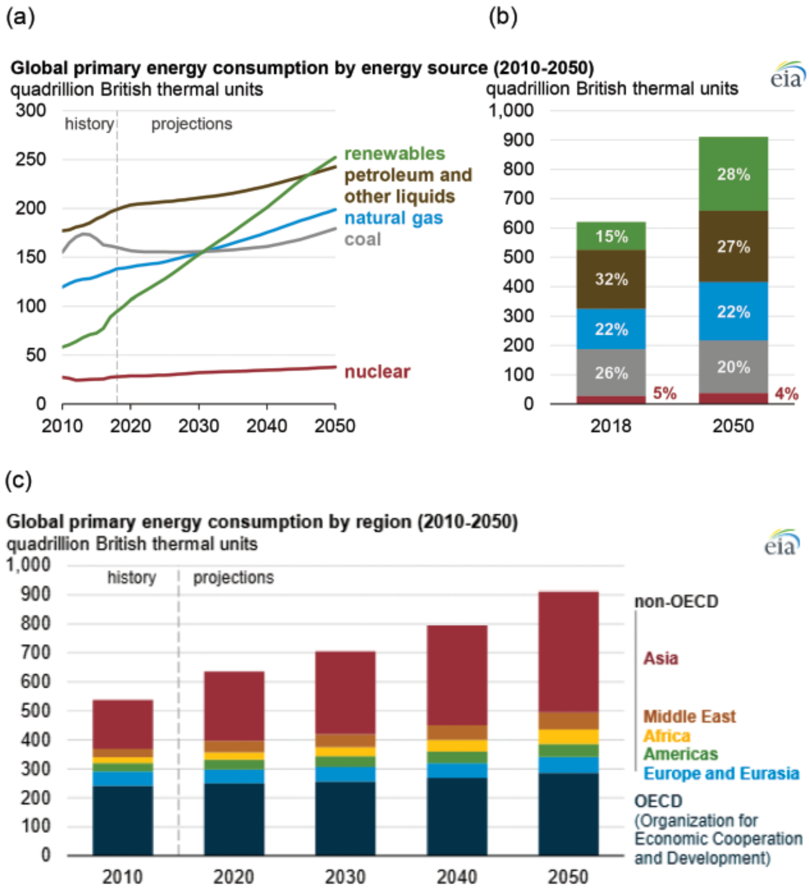
In 2021, electricity from perennial sources was set to expand by more than 8% to reach 8 300 TWh, the fastest year-on-year growth since the 1970s. China alone should account for almost half of the global increase, followed by the United States of America (USA), the European Union (EU), and India. Photovoltaic (PV) and wind are set to contribute two-thirds of such growth [12].

The perennial sources will deliver electrons [13] and, thus, will contribute to electricity production. But electricity alone will not solve all problems of the human society. Electrons will be distributed through dedicated lines to industries, cities, public buildings, and private houses. They will be also used in applications such as electrified transport (trains) or city-aerial electric buses and even in cars using batteries. Electrons will be used to produce H_2 from water (electrolysis). And hydrogen can be used in transport (H_2-fuelled cars). However, some important transport sectors (such as maritime transport and aviation) and some industrial sectors (fine chemicals, polymers, goods used daily, and similar products) will remain out of reach.

Therefore, one can foresee that our society will use a blend of energy sources and vectors by 2050 in which fossil-C will have a decreased share. Our forecast is that fossil-C will decrease from actual 81% of global consumption to perhaps 20%. This will cause the decrease of direct fossil-CO_2 emission from actual 37 Gt/y to 8–9 Gt/y. Various scenarios can be found in the literature and not all agree on the future role of fossil-C. Claims range from a total defossilization to a continued use of fossil-C, but at a reduced rate. Scheme 2.1 shows the transformation of energy consumption expected in coming years as illustrated by the U.S. Energy Information Association (EIA-USA) [14], including the roles of perennial and renewable energy sources.

The major contribution to the growth of use of energy and goods will be given by developing countries in which economic growth will drive the demand for energy. Therefore, Asia (China and India), the Middle East, and Africa will be major actors. One can expect that different sources will be exploited in different regions according to the local reserves and availability of SWHG energy. Perennial energy sources should be preferentially exploited everywhere for reducing climate impacts. Despite some very optimistic scenarios that foresee zero emissions, the EIA scenarios show that fossil-C will still be significantly in use even in 2050. Therefore, a realistic scenario is depicted in Scheme 2.2 with the use of various sources of energy and vectors by application.

As shown in Scheme 2.2, the intensity of use of fossil-C will decrease in all sectors and specially in the production of thermal energy, chemicals for industry, special fuels, and materials. The field of major interest for this chapter is the change of raw materials in the chemical industry, special fuels, and materials, where the big shift will take place as depicted in Scheme 2.3. This shift will require new catalysts able to convert raw materials richer in oxygen and innovative technologies [15]. For this purpose, hybrid catalysis will play a major role.



Scheme 2.1 Expected growth of energy consumption by 2050 (a), the contribution by the various energy sources (b), and the use by selected regions worldwide (c). (EIA data).

Chemicals	Electric Energy Industry-Civil-Land transport	Thermal Energy	Special Fuels Avio-Maritime	Materials
Fossil-C	Fossil-C	Fossil-C	Fossil-C	Fossil-C
Biomass	Biomass	Biomass	Biomass	Biomass
Ren-C	Ren-C	Ren-C	Ren-C	Ren-C
	SWGH	SG		

Scheme 2.2 Correlation of the intensity of use of primary sources of energy according to end users (Ren-C=Renewable-carbon; S=Solar, W=Wind, G=Geothermal, H=Hydro).

2.4 Hybrid Catalysis: A New World

Innovation in catalysis will be a necessity and this will be the major driver of the change in the chemical industry. In fact, moving from fossil-C to renewable carbon (ren-C) as source of raw materials will introduce the use of substrates richer in oxygen (hydrocarbons [HCs] and synthesis gas [syngas] will be substituted by carbohydrates and CO_2) (Scheme 2.3). This will result in a growing demand for green-H_2, unless a major change is made to move closer to nature by using water and CO_2 as source of a myriad of chemicals. Such a great step will require new technologies and new catalysts. Hybrid catalysis is able to combine biotechnology and chemical processes using enzymatic- and chemo-catalysis and this will be the solution. Learning from nature and combining innovation with existing solid knowledge of chemical processes will provide a new attitude to developing new catalytic systems able to use the new substrates.

Hybrid catalysis (Figure 2.1) is the integration of chemo-, electro-, and biotec(enzymatic)-processes. The integration can concern either two sectors at one time (chemo-electro catalysis, bio-electro catalysis, or bio-chemo catalysis), or even all three sectors (bio-chemo-electro catalysis).

In following sections, the advantages of such integration will be discussed with some examples. The basic principle is that in the integration *one technique will do what the other(s) cannot do or will do it better (more selectively or faster or with higher conversion).*

The overall target is to develop innovative processes based on ren-C that are more economical on all levels (atoms, energy, infrastructure, operational, raw materials, etc.) in the short or medium term with respect to fossil-C based processes that have had over one century of optimization before arriving at today's cost levels. Fulfilling such a goal would mean reducing waste (solid-liquid) production and CO_2 emission to the atmosphere. Currently, the chemical industry produces over 90% of the goods used by our society by using catalysts, and over 40% of the entire world economy depends on catalysis [16, 17].

The process integration is not trivial, due to the peculiar properties of chemo- and enzymatic-systems (or microorganisms) and the complexity of their mutual interaction (deactivation of

From Hydrocarbons-HC	$H(CH_2)_nH$	to	Carbohydrates	$R(HCOH)_nR'$
From Carbon Monoxide	CO	to	Carbon Dioxide	CO_2

Scheme 2.3 Major changes in raw materials composition in the chemical industry as ren-C (biomass and CO_2) takes the place of fossil-C and synthesis gas (syngas) derived from it) (Red=Today, Blue=Future).

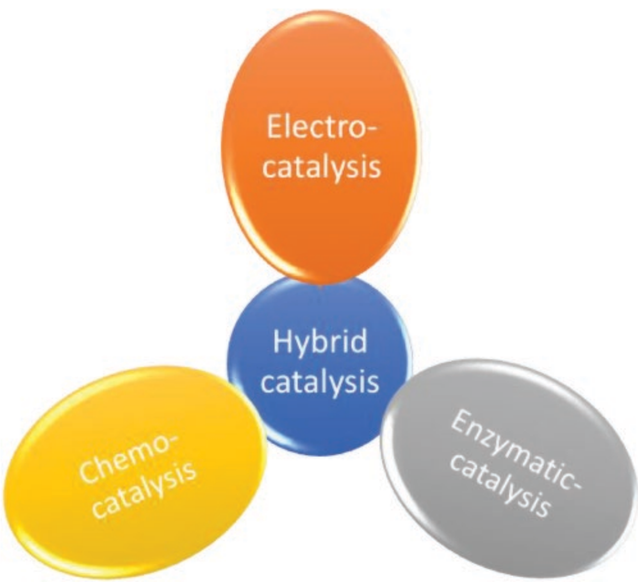


Figure 2.1 Hybrid catalysis: integration of chemo-, electro-, and enzymatic catalysis.

enzymes) and interaction with electrons (energetics). The integration of enzymes (microorganisms) and chemo-catalysts offers the opportunity of combining the stereospecificity and selectivity of the former with the versatility of the latter, while taking advantage of the modular acid-base, redox, and nucleophilic-electrophilic character that will drive the interaction of the substrates.

In fact, enzymes are superior to chemo-catalysts (homogeneous catalysts, essentially) in the synthesis of optically active compounds with high selectivity towards one of the isomers. Although the use of asymmetric ligands makes homogeneous catalysts prone to the production of a high excess of one of the isomers, nevertheless enzymes are much more effective due to their structure.

How easy will it be and how long will it take to realize such integration at the application level, with a simultaneous reduction of investment costs (CAPEX), reduction in operational costs (OPEX), and increase in selectivity and rate of production? The timing is not exactly predictable, but it is time now to invest resources (personnel and financial) in this field. It must be pointed out that a real hybrid catalyst should act in a single pot. So far, examples of combinations of catalytic stages were used in which two different catalytic systems act in two separate, consequent stages, reaching a result that each alone would not be able to touch. These are cases of combined more than integrated catalytic systems.

Notably, hybrid catalysis has mostly been applied to the conversion of bio-sourced molecules since its appearance, which is more complex than steps used in chemical processes and, this is increased to reduce the impact of chemo-catalysis, even due to the spent catalyst disposal and recovery. The reader will not be surprised if the examples discussed in the next section are based on the conversion of bio-sourced substrates.

In following paragraphs, the state of the art (SotA) and perspective applications will be discussed, highlighting the power and potential of hybrid catalysis.

2.5 Hybrid Catalysis and Biomass Valorization

Land biomass is in general a solid material made of a variety of single molecules and linkages. It can be classified by large as cellulosic and oily biomass, the former formed by cellulose (35–50%), hemicellulose (20–30%), and lignin (10–25%) and the latter formed by long chain fatty esters of glycerol. Sugars, amines, aminoacids, organic aromatic and aliphatic moieties, polymeric species, esters (with long- and short-chain acids), and ethers (aliphatic and aromatic) are among the species most frequently present in various kinds of biomass. This means that the raw-biomass conversion implies the interaction of the catalyst with a variety of linkages, such as: C–C, C–O, C–N, C–H, O–H, N–H, C–S, S–O, S–N, P–C, P–O, O–E, and C–E (where E is an element different from C, H, N, O, P, S).

Chemical catalysts are designed to be quite specialist and may act on a specific bond, leaving the others unaltered. Chemo-catalysts (homogeneous, supported, and heterogeneous) have been developed and are used in the chemical industry primarily for carrying out a defined linkage cleavage/formation targeting selectivity in processes such as: the conversion/valorization of hydrocarbons to bulk or fine chemicals, the conversion of syngas to Cn species (Fischer-Tropsch reaction), the hydrogenation of/addition to unsaturated C–C (double and triple) bonds, and C–C coupling, working in a liquid or gaseous phase.

Chemo-catalysts primarily act singularly on individual molecules and are less able to attack compact structures. The use of multifunctional catalysts or assembled catalysts might guarantee a concerted action on the complex system, but the effect could reduce selectivity and result in the formation of a variety of products. A recent example of such catalytic activity on solid systems is plastics depolymerization [18], an infrequent and difficult process.