GREEN CARBON DIOXIDE
Advances in CO₂ Utilization

EDITED BY
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WILEY
GREEN CARBON DIOXIDE
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Mitigating climate change, preserving the environment, using renewable energy, and replacing fossil fuels are among the grand challenges facing our society that need new breakthrough solutions to be successfully addressed. The (re)use of carbon dioxide (CO₂) to produce fuels and chemicals is the common factor in these grand challenges as an effective solution to contribute to their realization. Reusing CO₂ not only addresses the balance of CO₂ in the Earth’s atmosphere with the related negative effects on the quality of life and the environment, but represents a valuable C-source to substitute for fossil fuels. By using renewable energy sources for the conversion of CO₂, it is possible to introduce renewable energy into the production chain in a more efficient approach with respect to alternative possibilities. The products derived from the conversion of CO₂ effectively integrate into the current energy and material infrastructure, thus allowing a smooth and sustainable transition to a new economy without the very large investments required to change infrastructure. As a longer-term visionary idea, it is possible to create a CO₂-economy in which it will be possible to achieve full-circle recycling of CO₂ using renewable energy sources, analogous to how plants convert CO₂ to sugar and O₂, using sunlight as a source of energy through photosynthesis. Capture and conversion of CO₂ to chemical feedstocks could thus provide a new route to a circular economy.

There is thus a new vision of CO₂ at the industrial, societal, and scientific levels. Carbon dioxide is no longer considered a problem and even a waste to be reused, but a key element and driving factor for the sustainable future of the chemical industry. There are different routes by which CO₂ can be converted to feedstocks for the chemical industry by the use of renewable energy sources, which also can be differentiated in terms of the timescale of their implementation. CO₂ is a raw material for the production of base chemicals (such as light olefins), advanced materials (such as CO₂-based polymers), and fuels (often called solar fuels).

There are many opportunities and needs for fundamental R&D to realize this new CO₂ economy, but it is necessary to have clear indications of the key problems to be addressed, the different possible alternative routes with their related pro/cons, and their impact on industry and society. The scope of this book is to provide to managers, engineers, and chemists, working at both R&D and decision-making levels, an overview of the status and perspectives of advanced routes for the utilization of CO₂. The book is also well-suited to prepare advanced teaching courses at the
Masters or Ph.D. level, even though it is not a tutorial book. Over a thousand references provide the reader with a solid basis for deeper understanding of the topics discussed.

It is worthwhile to mention that this book reports perspectives from different countries around the world, from Europe to the US and Asia. CO$_2$ is becoming, in fact, a primary topic of interest in all the countries of the world, although with different priorities, which are reflected here.

Chapter 1 introduces the topic with a perspective on producing solar fuels and chemicals from CO$_2$ after having introduced the role of CO$_2$ (re)use as an enabling element for a low-carbon economy and the efficient introduction of renewable energy into the production chain. Two examples are discussed in a more detail: (i) the production of light olefins from CO$_2$ and (ii) the conversion of CO$_2$ to fuels using sunlight. The final part discusses outlook for the development of artificial leaf-type solar cells, with an example of a first attempt at a photoelectrocatalytic (PEC) solar cell to go in this direction.

Chapter 2, after introducing some background aspects of CO$_2$ characteristics and the photocatalytic chemistry on titania, focuses the discussion on the analysis of photo- and electrochemical pathways for CO$_2$ conversion, discussing in detail the role of free radical-induced reactions related especially to the mechanism of methane (and other products) formation from CO$_2$ during both photo- and electro-induced processes.

Chapter 3 also provides a critical analysis of the possible reduction pathways for synthesis of useful compounds from CO$_2$, with a focus especially on photo- and electrocatalytic routes. This chapter not only offers the readers a general overview of recent progress in the synthesis of useful compounds from CO$_2$ but provides new insights in understanding the structure-component-activity relationships. It highlights how new nanostructured functional materials play an important role in photo- and electrocatalytic conversion of CO$_2$, with a series of examples showing how rather interesting results could be obtained by tuning the catalysts’ characteristics.

Chapter 4 focuses the discussion on the analysis of the reaction mechanisms of heterogeneous catalytic hydrogenation of CO$_2$ to produce products such as methane, methanol, and higher hydrocarbons. In CO$_2$ methanation, CO$_{ads}$ is the key intermediate for methanation. In methanol synthesis, two possible pathways are discussed in detail: (i) direct hydrogenation of CO$_2$ via formate and (ii) the reduction of CO$_2$ to CO with subsequent hydrogenation to methanol. Depending upon the partial pressure of CO and CO$_2$, either the hydrogenation of CH$_3$O species or the formation of CH$_3$O can be rate-limiting for methanol formation. The mechanism of formation of higher alcohols may proceed through the reaction of CO insertion with hydrocarbon intermediates (RCH$_n$–) or through a direct nondissociative hydrogenation of CO$_2$. In the hydrogenation of CO$_2$ through a modified Fischer–Tropsch synthesis (FTS) process, the different effects of carbon dioxide on Co- and Fe-based catalysts are analyzed, showing also how the nature of the catalyst itself changes, switching from CO to CO$_2$ feed. This
chapter thus gives valuable insights on how to design new catalysts for these reactions.

Chapter 5 analyzes in detail the recent developments in the metal oxide catalysts for the direct synthesis of organic carbonates such as dimethyl carbonate (DMC) from alcohol and CO\(_2\). Ceria, zirconia, and related materials can catalyze the reaction with high selectivity under the conditions of the reaction without additives. Surface monodentate monoalkyl carbonate species are important intermediates. The yield is generally very low because of the equilibrium limitation. Combination of the reaction with organic dehydrating agents such as nitriles has been applied in order to overcome the equilibrium control. About 50% maximum methanol-based yield of DMC can be obtained when benzonitrile is used as a dehydrating agent. This chapter also analyzes future challenges for the design of catalysts and for the use of dehydrating agents to suppress the catalyst deactivation and the side reactions involving the dehydrating agents and the hydrated products.

Chapter 6 discusses in detail the theory and application of the STEP (solar thermal electrochemical production) process for the utilization of CO\(_2\) via electrosynthesis of energetic molecules at solar energy efficiency greater than any photovoltaic conversion efficiency. In STEP the efficient formation of metals, fuels, and chlorine and carbon capture is driven by solar thermal-heated endothermic electrolyses of concentrated reactants occurring at a voltage below that of the room temperature energy stored in the products. As one example, CO\(_2\) is reduced to either fuels or storable carbon at solar efficiency over 50% due to a synergy of efficient solar thermal absorption and electrochemical conversion at high temperature and reactant concentration. Other examples include STEP iron production, which prevents the emission of CO\(_2\) occurring in conventional iron production, STEP hydrogen via efficient solar water splitting, and STEP production of chlorine, sodium, and magnesium.

Chapter 7 analyzes the electrochemical reduction of CO\(_2\) in organic solvents used as the electrolyte medium, with a focus on understanding the effects of various parameters on electrolytic conversion of CO\(_2\): Electrode materials, current density, potential, and temperature are examined, with methanol as electrolyte. A methanol-based electrolyte shows many advantages in the electrocatalytic reduction of CO\(_2\) over other aqueous and nonaqueous solvents. CO\(_2\) is completely miscible with methanol, and its solubility in methanol is five times higher than in water. The concentration of CO\(_2\) can be increased as liquid CO\(_2\) is made in a methanol electrolyte by increasing the electrolytic pressure. The faradaic efficiency of reduction products mainly depends on nature of the electrolyte. The strategy for achieving selective formation of hydrocarbons is also discussed.

Chapter 8 analyzes the conversion of CO\(_2\) to synthetic fuels via a thermochemical process, particularly the reforming of CO\(_2\) with hydrocarbons to form syngas. Aspects discussed include catalyst selection, possible operation, and potential application. In addition, research approaches for the conversion of syngas to methanol, DME, and alkane fuel (which is commonly known as gas-to-liquid or GTL) are also analyzed.
Chapter 9 discusses in detail the photocatalytic reduction of CO$_2$ with water on TiO$_2$-based nanocomposite photocatalysts. In particular, it is shown how the rate of CO$_2$ conversion can be improved by several means: (i) incorporation of metal or metal ion species such as copper to enhance electron trapping and transfer to the catalyst surface; (ii) application of a large-surface-area support, such as mesoporous silica, to enhance better dispersion of TiO$_2$ nanoparticles and increase reactive surface sites; (iii) doping with nonmetal ions such as iodine in the lattice of TiO$_2$ to improve the visible light response and charge carrier separation; and (iv) pretreatment of the TiO$_2$ catalyst in a reducing environment like helium to create surface defects to enhance CO$_2$ adsorption and activation. Combinations of these different strategies may result in synergistic effects and much higher CO$_2$ conversion efficiency. The final section also provides recommendations for future studies.

Recent updates on the photocatalytic mechanism of CO$_2$ reduction, with focus on novel carbon-based AgBr nanocomposites, are discussed in Chapter 10. Aspects analyzed include the efficiency of photocatalytic reduction of CO$_2$ and stability under visible light (λ > 420 nm). Carbon-based AgBr nanocomposites were successfully prepared by a deposition-precipitation method in the presence of cetyltrimethylammonium bromide (CTAB). The photocatalytic reduction of CO$_2$ on carbon-based AgBr nanocomposites irradiated by visible light gives as main products methane, methanol, ethanol, and CO. The photocatalytic efficiency for CO$_2$ reduction is compared with that of AgBr supported on different materials such as carbon materials, TiO$_2$, and zeolites.

While Chapters 1–10 look mainly in a medium-long term R&D perspective, it is necessary to have practical solutions also for the short term, because the climate changes associated with the increase in greenhouse gas (GHG) emissions have already started to become an issue in several countries, with an intensification of extreme weather events. Chapter 11 thus is focused on a topic different from those discussed in the other chapters. It provides an analysis of the state of the art in enhanced oil recovery (EOR) and carbon capture and sequestration (CCS) and their role in providing a stable energy supply and reduction in CO$_2$ emissions. EOR increases oil production by using CO$_2$, thus achieving both a stable energy supply and CO$_2$ reduction simultaneously. In contrast, CCS reduces CO$_2$ emissions even for non-oil producers. This chapter provides the background, fundamental mechanisms, and challenges associated with EOR and CCS, and shows that there are still several issues that need to be resolved, including recovery or storage efficiency, the cost of CO$_2$ capture, transport, and injection, and the CO$_2$ leakage risk. More research is required on fundamental mechanisms of the dynamics of EOR and CCS to allow significant improvements in the efficiency and safety of these techniques.

This book thus provides an overview on the topics of CO$_2$ (re)use from different perspectives, with strong focus on aspects related to industrial perspectives, catalyst design, and reaction mechanisms. Most of the contributions are related to photo- and electrocatalytic conversion of CO$_2$, because these are considered the new directions for achieving a sustainable use of CO$_2$, and the basis for realizing over the long term artificial leaf-type (artificial photosynthesis) devices.
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1.1 INTRODUCTION

The last United Nations Climate Change Conference (COP17/CMP7, Durban, Dec. 2011) and the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report under preparation [1], two of the actual reference points regarding the strategies for the reduction of greenhouse gas (GHG) emissions, are still dedicating minor attention to the question of using CO₂. We discuss here how using CO₂ is a key element in strategies for a sustainable development as well as a nonnegligible mitigation option for addressing the issue of climate change. There is a somewhat
rigid separation between the discussion on the reduction of the emissions of GHG, based mainly on the introduction of renewable or alternative sources of energy and on the increase of efficiency in the use/production of energy, and the strategies for cutting current GHG emissions, based essentially only on the carbon capture and sequestration (CCS) option. The use of carbon dioxide as a valuable raw material is considered a minor/negligible contribution for the issue of climate change and thus not a priority to address.

The World Energy Outlook 2010 [2] report prepared by the International Energy Agency (IEA) has discussed different options and scenarios for GHG emissions, proposing a reduction of CO₂ emissions in the 2.3–4.0 Gt·y⁻¹ range within one decade (by the year 2021) and in the 10.8–15.4 Gt·y⁻¹ range in two decades (by the year 2031) with respect to the business-as-usual scenario. About 20% of this reduction would derive from CCS. According to this estimation, about 400–800 Mt·y⁻¹ of CO₂ in a decade and about 2100–3000 Mt·y⁻¹ of CO₂ in two decades will be captured. The McKinsey report [3] estimated the global potential of CCS at 3.6 Gt·y⁻¹ and the potential in Europe at 0.4 Gt·y⁻¹ — around 20% of the total European abatement potential in 2030.

With these large volumes of CO₂ as raw material at zero or even negative cost (the reuse of CO₂ avoids the costs of sequestration and transport, up to about 40–50% of the CCS cost, depending on the distance of the sequestration site from the place of emission of CO₂) soon becoming available, there are clear opportunities for the utilization of CO₂. In addition to direct use, many possibilities exist for its conversion to other chemicals, in addition to already-existing industrial processes.

A number of recent articles, reviews, and books have addressed the different options for converting CO₂ [4–15]. Scientific and industrial initiatives toward the chemical utilization of CO₂ have increased substantially over the last few years [6a], and there is increasing attention to the use of CO₂ to produce

- Advanced materials (for example, a pilot plant opened at Bayers Chempark in Leverkusen, Germany in February 2011 to produce high-quality plastics—polyurethanes— based on CO₂ [16]);
- Fine chemicals [5,10,11,14] (for example, DNV is developing the large-scale electrochemical reduction of carbon dioxide to formate salts and formic acid [17]);
- Fuels [6,9,15] (for example, Carbon Recycling International started in September 2011 in Svartsengi, Iceland, a plant for producing 5Mt·y⁻¹ of methanol from CO₂ using H₂ produced electrolytically from renewable energy sources—geothermal, wind, etc. [18]).

The chemical transformation of CO₂ is a dynamic field of research, in which many industrial initiatives also thrive, even if it is not always straightforward to grasp the real opportunities and limitations of each option. CO₂ utilization as a raw material is expected in a short- to medium-term perspective to continue its progression, with several new products coming onto the market (e.g., polycarbonates). In the long term, CO₂ recycling can become a key element of sustainable
carbon-resource management in chemical and energy companies, combined with curbing consumption. CO₂ can also become a strategic molecule for the progressive introduction of renewable energy resources into the chemical and energy chain, thus helping to slowly lessen our consumption of fossil fuels. Thus the prospects for large-scale utilization [6a] indicate that CO₂ recycling can become an important component of the strategy portfolio necessary for curbing CO₂ emissions (with an estimated potential impact of hundred millions of tons of CO₂ recycling, similar to the impact of CCS) and at the heart of strategies for sustainable chemical, energy, and process industries, for a resource and energy efficiency development, for example, as a key enabling technology and backbone for the resource-efficient Europe flagship initiative of the Europe 2020 Strategy [19].

The concept of “Green Carbon Dioxide” [20], considering CO₂ not a “devil” molecule (a problem or even a possible reuse of a waste) but a key element for sustainable strategies of energy and chemical companies, is thus the new emerging vision that we emphasize in this chapter, because the new strategies toward resource and energy efficiency development need to be advanced in both the industrial and scientific communities. The concept of solar fuels is a key part of this vision [21–26], but we will not limit the discussion on the state of the art and perspectives to this area, because CO₂ recycling is an enabling element for a low-carbon economy and the efficient introduction of renewable energy in the production chain. This chapter thus analyzes these aspects and describes the opportunities offered by CO₂ recycling and solar fuels in this more general vision and context.

1.1.1 GHG Impact Values of Pathways of CO₂ Chemical Recycling

For a correct evaluation of the real impact of recycling CO₂ via chemical conversion with respect to alternative options such as storage (CCS) or even direct use in applications such as enhanced oil recovery (EOR), which, however, can be applied only in specific locations, food use, and intensive agriculture (to enrich the atmosphere in greenhouses), etc. it is necessary to discuss the impact value of the chemical recycling of CO₂.

The GHG impact value (GIV) indicates the effective amount of CO₂ eliminated from contribution to the GHG effect (over a given time frame, for example, 20 years) on a life-cycle assessment (LCA) basis. For example, for CO₂ storage (CCS) the energy necessary for the recovery, transport, and storage of CO₂ must be calculated for each ton of stored CO₂. GIV for CCS clearly depends on a number of factors, from the type and composition of the emissions, to the distance of the capture site from the storage site, the modalities of transport, etc. Detailed studies are not available, but on average, it is a realistic estimate that around 0.5–0.6 tons of CO₂-equivalent energy is necessary for the capture, transport, and storage of 1 ton of CO₂ sequestrated [21,27]. In fact, capture with the amine-absorption technologies (the most used today) accounts for about 0.2 tons of CO₂ and transport/storage accounts for an additional 0.3–0.4 tons of CO₂ (per ton of CO₂ sequestrated). These are average values, because in many places, such as in various areas of Europe, it is necessary to transport CO₂ for over 150–200 km and pipelines are not available.
The storage will be long term, and thus over a time frame of 20 years the average GIV for CCS will be around 0.4–0.5.

There are different options for the reuse of CO$_2$. We may roughly distinguish two main routes for reusing CO$_2$ to produce commercially valuable products, apart from the routes involving bacteria and microorganisms:

1. Those reactions incorporating the whole CO$_2$ moiety in organic or inorganic backbones;
2. Those involving the rupture of one or more of the C–O bonds.

This classification is important in term of energy balance and applications. The first class of reactions (both organic and inorganic) is not energy intensive and sometimes may also occur spontaneously, although with low kinetics, as in the production of inorganic carbonates. The second class, reactions involving the cleavage of the C–O bond, is energy intensive and requires the use of reducing agents, typically H sources such as H$_2$. For a CO$_2$ resource- and energy-efficient management, the energy necessary for these reactions should derive from renewable (solar, wind, geothermal energy, etc.), or at least from non-carbon-based (nuclear energy) sources or, eventually, waste-energy sources.

There are two typical potentially large-scale examples for the first class of reactions [6a], the production of saleable precipitated carbonate and bicarbonates or carbonates from minerals and the production of polymers incorporating CO$_2$ units. An example of the first case is the mineralization via aqueous precipitation (MAP) process developed by Calera [28] in a 10MW demonstration unit in Moss Landing, California (US) and followed by an Australian demonstration project in Latrobe Valley, Victoria (Australia). The flue gas from fossil fuel combustion is reacted with alkaline solutions heavy in calcium and/or magnesium, such as certain minable brines, to form a stable carbonate solid with a by-product of relatively fresh water that would be suitable for desalination. When suitable brines are not readily available, an alkaline solution of sodium hydroxide must be manufactured via, for example, chemical electrolysis. Once the CO$_2$ has been absorbed into a bicarbonate solution, it can be stored underground or transformed into a carbonate (building material). A full LCA does not exist, and also in this case the exact value depends on the specific process characteristics (the alkalinity sources, for example) and use of the final product [29]. The production of the alkaline solution is the energy-intensive step, and energy estimation indicates a GIV value of about 0.6–0.8 [30] for the production of building materials (with thus a lifetime over 20 years). This average value is similar for the other CO$_2$ mineralization technologies, where, for example, the critical energy-intensive step is the mining and crushing of the minerals (for example, olivine) used as the raw material.

For the production of CO$_2$-based polymers, correct LCA assessments also do not exist, and the GIV value depends on specific process characteristics that have not yet been developed on a commercial scale, apart from Asahi Kasei’s phosgene-free process to produce aromatic polycarbonate starting from ethylene epoxide, bisphenol-A, and CO$_2$ [31]. Polypropylene and polyethylene carbonate as
well as polyhydroxyalkanoate (PHA) from CO₂ and linear epoxides are currently developed by Novomer on a pilot-plant scale [32], while Bayer is developing on a pilot scale a process for producing polyurethane from polyether polycarbonate polyols, as already cited [16]. These are the more relevant examples of CO₂-based polymers, but additional examples also exist [6a].

The difference with respect to inorganic carbonates is that these polymers will substitute for polymers derived from fossil fuel sources, although it must be noted that the weight content of CO₂ ranges from about 17%wt. for aromatic polycarbonate to about 30%wt. for polyurethane and about 50%wt. for polypropylene carbonate. In addition, the use of these polymers will bring further benefits. For example, polyurethane foams are one of the most efficient insulation materials on the market today for roof and wall insulation, insulated windows and doors, and air barrier sealants. Spray polyurethane foams can cut yearly energy costs upwards of 35% with respect to alternative insulation material, but their use is still limited by their cost. The expansion of their market through larger availability at low cost from production using CO₂ as raw material will thus have direct benefits in terms of use of CO₂ as raw material and reduction of the use of fossil fuels and indirect benefits in terms of energy saving. Polycarbonate multiwall structures also offer a real advantage in thermal insulation. As clear as glass, polycarbonate has superior characteristics as to energy savings, safety, and practicality for civil and industrial buildings, with the use of panels in structures that need reduced weight, abundant light, and high resistance to atmospheric agents. The indirect impact on energy saving is difficult to estimate, because it will depend on market development, incentives for energy saving, etc. It may be thus given only a very approximate estimation. We consider realistic a conservative average GIV value (the lifetime of these CO₂-based polymers is over 20 years) of about 2–4.

Production of fuels from CO₂, which involves the rupture of one or more of the C–O bonds and thus the need to supply renewable energy to make the conversion sustainable, is a different case. In fact, CO₂ recycling via incorporating renewable energy introduces a shorter path (in terms of time) to close the carbon cycle compared to natural cycles and an effective way to introduce renewable energy sources in the chemical/energy chain. In addition, it will reduce the use of fossil fuels for these chemical/energy uses. Let us consider the simple case of methane production from CO₂, although as discussed below this is not the ideal energy vector into which carbon dioxide can be transformed. However, it is the simplest example for considering the fuel life cycle and the related GIV. If we capture CO₂ from the emissions deriving from the combustion of methane, we must spend energy in the capture (similar to the CCS case), but if we use renewable energy for the conversion of CO₂ to methane (as discussed below), the net effect is that we introduce renewable energy into the energy chain. Considering that (i) 0.2 tons of CO₂ are necessary for capturing each ton of CO₂ (in terms of CO₂-equivalent energy), (ii) 0.2 tons of CO₂ are associated with the loss of energy in the conversion process, and (iii) 0.1–0.2 tons of CO₂ are necessary to produce the renewable energy necessary for the conversion of CO₂ to fuels, we have still a positive value of saving about 0.4–0.5 tons of CO₂. We must note that the carbon footprints for the different renewable
resources are different and on the average not negligible, but to simplify the discussion we consider only an average value. When an excess of energy is used in the transformation, for example, to store the excess of energy in the form of chemical fuel, the impact value could be even better. Each time that a cycle is completed (capture of CO₂, conversion of CO₂ to CH₄, for example, by using H₂ produced from a renewable energy sources—photovoltaic, wind, etc., storage/transport of methane, use of methane to produce energy and CO₂), there is a saving of at least 0.4–0.5 tons of CO₂ per amount of CO₂ sequestrated. However, the cycle could be repeated several times. In a 20-year time frame, a single molecule of CO₂ is recycled virtually several thousand times, with thus a continuous mechanism of reintroduction of renewable energy. From a practical aspect, the number of cycles will depend on the cost differential with respect to use of fossil fuels, incentives in limiting GHG emissions, carbon taxes, technology development, etc. It is thus quite difficult to estimate a correct GIV, but we consider a conservative average a GIV value of about 10–12 over 20 years. There is thus a large amplification of the impact value of chemical utilization of CO₂ to produce polymers or fuels, with respect to the CCS or mineralization cases, even within the limits resulting from the absence of more specific studies.

Figure 1.1 summarizes the discussed average impact value on GHG for the different routes of chemical CO₂ recycling with respect to CCS and CO₂ mineralization. It may be noted that this concept is the opposite of that used in the IPCC report [33] which indicated that “the lifetime of the chemicals produced is too short with respect to the scale of interest in CO₂ storage. Therefore, the contribution of industrial uses of captured CO₂ to the mitigation of climate change is expected to be small.” This statement is not correct, because the chemicals/fuels produced from

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Figure 1.1 Average indicative impact values estimated for the different routes of chemical CO₂ recycling with respect to CCS and CO₂ mineralization.