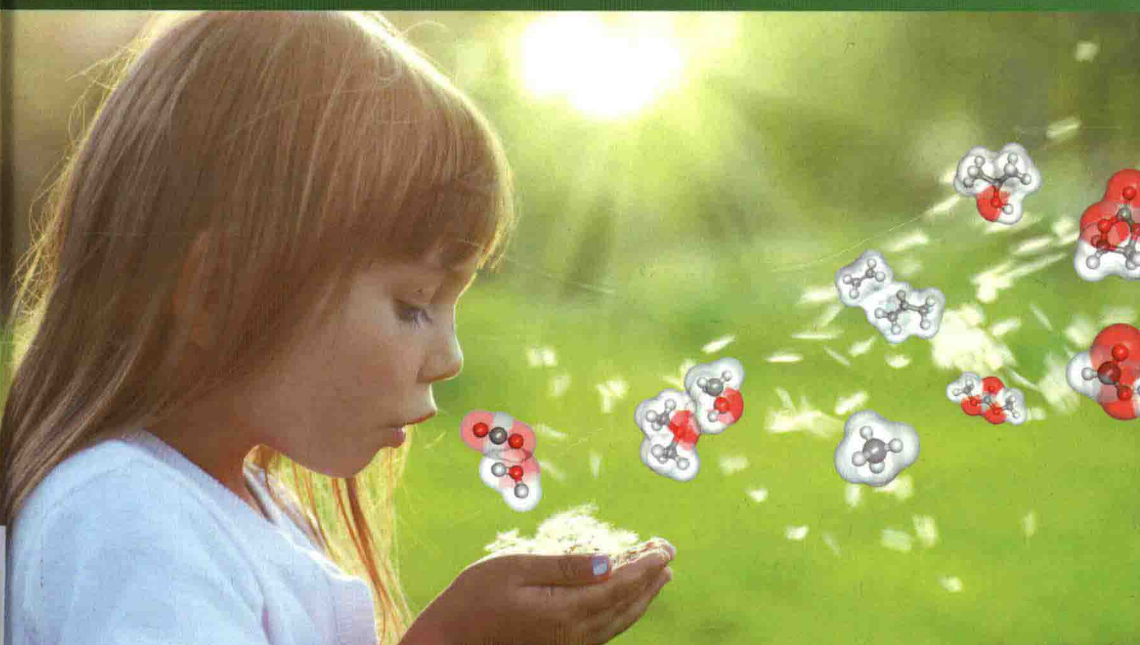
GREEN CARBON DIOXIDE

Advances in CO_2 Utilization

EDITED BY
GABRIELE CENTI • SIGLINDA PERATHONER



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PREFACE

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 (CO_2) to produce fuels and chemicals is the common factor in these grand challenges as an effective solution to contribute to their realization. Reusing CO_2 not only addresses the balance of CO_2 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 CO_2, 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 CO_2 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 CO_2-economy in which it will be possible to achieve full-circle recycling of CO_2 using renewable energy sources, analogous to how plants convert CO_2 to sugar and O_2, using sunlight as a source of energy through photosynthesis. Capture and conversion of CO_2 to chemical feedstocks could thus provide a new route to a circular economy.

There is thus a new vision of CO_2 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 CO_2 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. CO_2 is a raw material for the production of base chemicals (such as light olefins), advanced materials (such as CO_2-based polymers), and fuels (often called solar fuels).

There are many opportunities and needs for fundamental R&D to realize this new CO_2 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 CO_2. 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_3O species or the formation of CH_3O 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 ($\lambda > 420$ 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.

The editors are very grateful to all the authors for their authoritative participation in this book. A special thanks goes to Dr. Maria D. Salazar-Villalpando, formerly of the National Energy Technology Laboratory (NETL-DoE, US), who originally initiated this book, inviting all authors to contribute the different chapters.

The Editors
G. CENTI AND S. PERATHONER
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