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David S.A. Simakov

Renewable Synthetic Fuels and Chemicals from Carbon Dioxide

Fundamentals, Catalysis, Design Considerations and Technological Challenges

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Contents

Introduction

The purpose of this book is to provide the reader with a general scientific and technological background in the broad area of the carbon dioxide (CO_2) conversion to renewable synthetic fuels and chemicals. Thermocatalytic, electrochemical, photocatalytic and biological routes are discussed, with a particular emphasis on sustainability. The readers who are interested in more details are referred to a number of excellent reviews throughout the text. The book is written in such a way that no specialized background is required. For each type of the CO_2 conversion pathway, the reader is first introduced to basic principles, followed by more elaborated discussion on reaction mechanisms and design considerations. A specific emphasis is made on technological challenges and practical realization potential.

Following the industrial revolution and accelerating growth of the human population, the emission of CO_2 in the atmosphere became a significant factor contributing to the global warming. Currently, the world energy market mainly relies on the combustion of fossils, a low energy conversion efficiency process, which leads to large emissions of CO_2. Heavy dependence on fossil energy also has economic and geo-political consequences. At the same time, alternative, renewable energy sources cannot supply the rapidly growing demand. While it is rather difficult to predict the exact consequences of the anthropogenic climate change in the future, there is a consensus in the scientific community that it is highly desirable to limit the emissions of CO_2.

There are three main approaches to reduce the atmospheric CO_2 concentration: direct reduction of CO_2 emissions, CO_2 capture and storage, and CO_2 utilization via conversion into fuels and platform chemicals. The first approach is mainly based on the improvement of the utilization efficiency of fossil fuels. Indeed, very significant progress has been made in this direction. However, lowering the CO_2 emission via this route is difficult due to the rapidly increasing population and increasing demand for high quality of life in developing countries. Emissions reduction via CO_2 capture and storage, e.g., in geological formations, has a limited capacity due to high capital and operating costs, making the widespread commercialization of this approach rather challenging.

The alternative is CO_2 conversion into synthetic fuels and chemicals using renewable energy to create an artificial carbon cycle. Being a harmful greenhouse gas, CO_2 is also an excellent, non-flammable and non-corrosive, source of carbon. Resources are abundant, including flue gases from coal- and natural gas-fired power plants, biogas and landfill gas (up to 50% CO_2), and off-gas streams in several industrial processes such as ammonia production and fermentation. There are also large resources of CO_2 accompanying natural gas and oil production wells; this CO_2 is normally just vented into the atmosphere.

Conversion of CO_2 into fuels and chemicals requires hydrogen (H_2). In fact, hydrogen, carbon and oxygen are among the most abundant elements in the Universe, as well as simple molecules composed of these elements such as methane (CH_4), water (H_2O) and carbon dioxide (CO_2). On Earth, there is plenty of water which can be used as a source of H_2 for CO_2 hydrogenation. However, H_2 generation from H_2O (a highly oxidized compound) requires energy. If this energy could be provided using renewable sources, such process will create a pathway for the production of renewable synthetic fuels from CO_2.

Apparently, this approach is attractive, since it can reduce greenhouse gas emissions and fossil fuels consumption by providing an alternative, renewable source for carbon-based fuels and chemicals. However, CO_2 is a highly oxidized, stable molecule which conversion requires substantial energy investment, which can make the whole process chain being unsustainable. Also, renewable CO_2 conversions processes should rely on renewable sources of energy, which requires high capital investments. Thus, it is of crucial importance to identify truly sustainable routes for CO_2 conversion into fuels and chemicals. Critical assessment based on fundamental understanding of CO_2 conversion mechanisms combined with techno-economic evaluation is required.

This book outlines most recent progress in CO_2 utilization into useful fuel and chemicals via chemical and biological routes. Various processes and their mechanisms are discusses, including photochemical, electrochemical, thermocatalytic, and biological conversion. The book consists of four chapters, each chapter providing fundamentals, discussing catalysis and design considerations, and outlining resent progress and technological challenges. The book is useful for a broad community of academic and industrial researchers in the fields of chemical reaction engineering, catalysis, reactor design, electrochemistry, and biotechnology.

Chapter 1
Thermocatalytic Conversion of CO_2

Current solutions for CO_2 emissions reduction mainly rely on capturing CO_2 emitted from power stations and its storage. Such processes are based on CO_2 separation via either amine scrubbing, pressure swing adsorption, or membrane separation followed by cryogenic liquefaction. The purified CO_2 is then can be stored in geological formation, or used for enhanced oil recovery. The process is energy intensive, leading to high capital and operating costs. Also, it is not clear what would be the long-term consequences of the CO_2 storage in underground reservoirs. An alternative to CO_2 storage is its chemical transformation into fuels and chemicals that can potentially replace (at least partially) the fossil feedstocks used in chemical industry.

Being a harmful greenhouse gas, CO_2 is also an excellent source of carbon, non-flammable and non-corrosive. Resources are abundant, including flue gases from coal- and natural gas-fired power plants, biogas and landfill gas (up to 50 mol% CO_2), and off-gas streams in several industrial processes such as ammonia production and fermentation. There are also large resources of CO_2 accompanying natural gas and oil production wells (associated petroleum gas); this CO_2 is typically vented into the atmosphere with flare gas.

Conversion of captured CO_2 into synthetic fuels and chemicals is an attractive avenue for reduction of CO_2 emissions and, as such, this topic has attracted the interest of many research groups around the world. Many research efforts have focused on photochemical and electrochemical reduction of CO_2 into a variety of products, including formic acid and methanol, in aqueous environments using water as a source of H_2 for CO_2 reduction. This approach is apparently attractive as it only uses water and CO_2 as the starting materials and the sun or (potentially) renewable electricity as a source of energy. However, photochemical CO_2 reduction has inherent limitations of solar energy utilization, while electro-chemical reduction of CO_2 has low efficiencies of electricity utilization. Both processes are limited by low CO_2 solubility in water and have severe diffusion limitations. An alternative approach is thermocatalytic conversion that combines the use of high temperatures

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with a heterogeneous catalyst, providing fast reaction rates and, therefore, allowing for large volume production.

1.1 Motivation and General Background

The thermocatalytic conversion of CO_2 into fuels and chemicals requires a source of H_2. Hydrogen generation via steam reforming of natural gas is obviously not an option as it will result in the overall positive carbon footprint. However, if the required H_2 is produced via water electrolysis using renewable electricity (solar, wind, or hydro), the resulted synthetic fuel will be renewable. Utilization of the off-peak, surplus electricity, or low carbon footprint electricity (nuclear power) could be also relevant under suitable circumstances. Ultimately, the large-scale thermocatalytic conversion of CO_2 using renewable H_2 can create an artificial carbon cycle recycling the otherwise emitted CO_2 in our energy distribution systems and, therefore, reducing the consumption of fossil fuels.

Several notable thermocatalytic conversion pathways are shown in Fig. 1.1 (endothermic and exothermic processes are marked with blue and red arrows respectively). Methane (CH_4) can be reacted with water in a process of methane steam reforming (MSR) or with CO_2 via methane dry reforming (MDR), producing syngas (a mixture of primarily H_2 and CO). Another way to generate syngas is the reverse water gas shift reaction (RWGS), which is an attractive avenue for CO_2 hydrogenation. Syngas is a valuable chemical feedstock which can be further converted into fuels via Fischer-Tropsch synthesis (FTS) and into a variety of

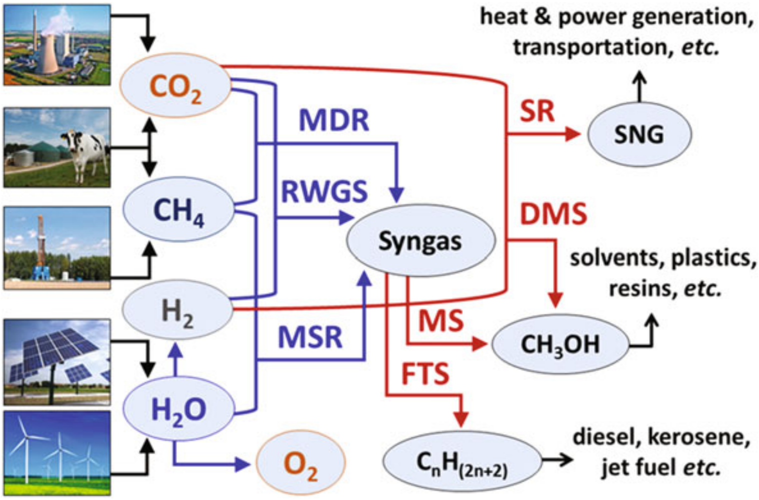


Fig. 1.1 Various pathways for conversion of renewable energy, water and greenhouse gases into synthetic fuels

chemicals via methanol synthesis (MS); methanol can be also generated from CO_2 and H_2 via direct methanol synthesis (DMS). Another route for CO_2 hydrogenation is the highly exothermic Sabatier reaction (SR, also known as CO_2 methanation) that produces synthetic CH_4, frequently referred to as synthetic natural gas (SNG), or renewable natural gas (RNG).

1.2 Conversion Pathways and Major Challenges

Carbon dioxide (CO_2) can be converted to a variety of synthetic fuels and chemical via thermocatalytic routes. The most notable processes that have high potential for industrial scale implementation are the methane dry reforming (MDR) [1], Eq. (1.1), the reverse water gas shift reaction (RWGS), Eq. (1.2), the Sabatier reaction (SR), Eq. (1.3), and the direct methanol synthesis (DMS) [2], Eq. (1.4):

$$CO_2 + CH_4 \rightleftarrows 2CO + 2H_2 \quad \Delta H^{\circ}_{298K} = +247.3 \text{ kJ/mol} \tag{1.1}$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad \Delta H^{\circ}_{298K} = +41.2 \text{ kJ/mol} \tag{1.2}$$

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H^{\circ}_{298K} = -164.9 \text{ kJ/mol} \tag{1.3}$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad \Delta H^{\circ}_{298K} = -49.2 \text{ kJ/mol} \tag{1.4}$$

For processes that involve H_2 as a reactant, Eqs. (1.2)–(1.4), H_2 should originate from a renewable source (e.g., water electrolysis using solar and wind energy), to make the process sustainable. The MDR reaction does not require molecular H_2, utilizing CH_4 as a source of hydrogen instead. All these processes directly incorporate CO_2 into the production chain of synthetic fuels and chemicals. The MDR reaction is highly endothermic, RWGS is mildly endothermic, while SR and DMS are highly exothermic. Therefore, efficient heat supply or removal is among the challenges to be addressed, calling for innovative reactor designs. Another major challenge is catalysis, as in all abovementioned reactions severe catalyst deactivation can occur. Therefore, there is a requirement for novel nanostructured catalysts, highly-active and stable but also inexpensive, to make the process economically viable.

Heterogeneous catalysis is widely used on industrial scale in thermocatalytic processes such as methane steam reforming (MSR), Eq. (1.5), water gas shift (WGS), Eq. (1.6), and CO methanation, Eq. (1.7):

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \quad \Delta H^{\circ}_{298K} = +206.1 \text{ kJ/mol} \tag{1.5}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad \Delta H^{\circ}_{298K} = -41.2 \text{ kJ/mol} \tag{1.6}$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \quad \Delta H^{\circ}_{298K} = -206.1 \text{ kJ/mol} \tag{1.7}$$

Note that WGS is the reversible reaction of RWGS and CO methanation is the reverse process of MSR. Most of H_2 currently produced worldwide is generated via MSR and WGS in large-scale plants. Methanation is used in ammonia synthesis plants to remove traces of CO. Commercial catalysts used in these processes are typically based on low-cost transition metals (e.g., Ni, Cu, Cr, Fe). There are certain similarities between the processes described by Eqs. (1.5)–(1.7) and the pathways for CO_2 utilization represented by Eqs. (1.1)–(1.4). All these routes are based on thermocatalytic conversion using heterogeneous catalysis and involve simple molecules such as CH_4, CO_2, CO, H_2, and H_2O is gaseous phase.

It would be highly desirable if the abovementioned low-cost commercial catalysts could be employed in the thermocatalytic processes for CO_2 utilization. Unfortunately, these catalysts are not suitable for the thermocatalytic CO_2 conversion, for a number of reasons. First of all, the CO_2 molecule is very difficult to activate, thus requiring superior catalytic activity, which cannot be provided by commercial reforming and methanation catalysts. Another major problem is coking. In commercial processes such as MSR and WGS excess steam is used to reduce carbon formation. However, CO_2 hydrogenation reactions cannot be run with excess steam, which is a reaction product, Eqs. (1.2)–(1.4). Since these reactions are reversible, the excess amount of water will drive the equilibrium in the opposite direction towards CO_2 formation, leading to low CO_2 conversions.

With respect to reactor design, there is a number of conceptual solutions which have been successfully employed in the chemical industry for a variety of thermocatalytic processes. Among widely accepted designs are fixed bed (also called packed bed) reactors and fluidized bed reactors [3]. Fixed beds are generally more compact and simple to run but their heat management could be problematic for highly exothermic processes such as the Sabatier reaction (SR) and direct methanol synthesis (DMS). The reason is that heat transfer in packed beds is not very efficient. Fluidized beds, on the other hand, provide better transport characteristics. However, this type of reactor is bulky and restricted to a narrow window of operation in terms of flow rates.

Many challenges remain to be overcome for successful commercialization of the thermocatalytic CO_2 hydrogenation processes. So far, the majority of the work has been done on methanation using coal or dry biomass as a source of carbon, which requires multiple steps of gasification and separation prior to methanation making the entire system inefficient [3]. Direct hydrogenation of CO_2 is much more attractive (given that there is a renewable, low-cost source of H_2) but reactor design is very challenging, especially thermal management. One of the possible directions is the use of multi-functional reactors that combine exothermic and endothermic reactions and integrate reaction and separation steps in a single, highly-efficient catalytic unit. Design of such reactors is challenging and requires modeling and optimization but the potential is huge as such units can provide compact, economically feasible solutions for making synthetic fuels from CO_2. Another aspect of reactor design is incorporation of renewable energy sources into the process, either directly or indirectly. For example, solar energy can be concentrated and used as a source of heat for highly endothermic reactions, storing the energy of solar irradiation in the energy of chemical bonds.

1.3 Catalysis and Catalyst Deactivation

First of all, it should be emphasized that all abovementioned equations, Eqs. (1.1)–(1.7), represent overall reactions. In reality, each reaction consists of a number of elementary steps occurring at the interface between the gas and solid phase. A conventional heterogeneous gas-solid phase catalyst consists of metallic nanoparticles (typically transition metals) dispersed on a ceramic support. Reactants first adsorb and dissociate on the catalytic surface, react, and then desorb, as it is schematically represented on Fig. 1.2 (for the case of methane steam reforming). Some molecules are difficult to activate (such as CH_4 and CO_2) and can only dissociate on metallic or another surface with high catalytic activity. Other molecules, e.g., H_2O, can dissociate even on a ceramic support, especially if the support features redox-active centers.

Possible elementary steps for the conversion of CO_2 to CO, CH_4, CH_3OH, and hydrocarbons are depicted in Fig. 1.3 [2]. In the "formate pathway", the adsorbed hydrogen (*H) reacts with the adsorbed CO_2 (*CO_2) to form adsorbed formate species (*HCOO) that undergo series of elementary steps involving hydrogenation and dissociation to form CH_4 and CH_3OH. In the "RWGS and CO hydrogenation pathway", the initially formed carboxylate species (*HOCO) dissociate to form *CO and *OH species. The *CO intermediate can either desorb as CO or undergo further hydrogenation steps resulting in formation of CH_3OH, CH_4 or other hydrocarbons along the "CO_2-FT pathway" (FT stands for Fischer-Tropsch process). In addition to kinetic requirements of the highly active and selective catalyst to perform one of these conversion pathways, there are also thermodynamic constrains. While methanol synthesis and Fischer-Tropsch are highly exothermic, the

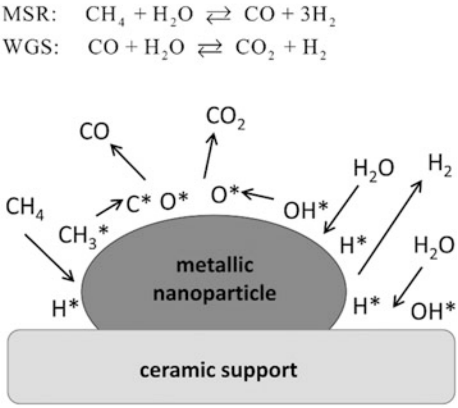


Fig. 1.2 Schematic (oversimplified) representation of the combined MSR–WGS process occurring on the surface of the supported metallic nanoparticle

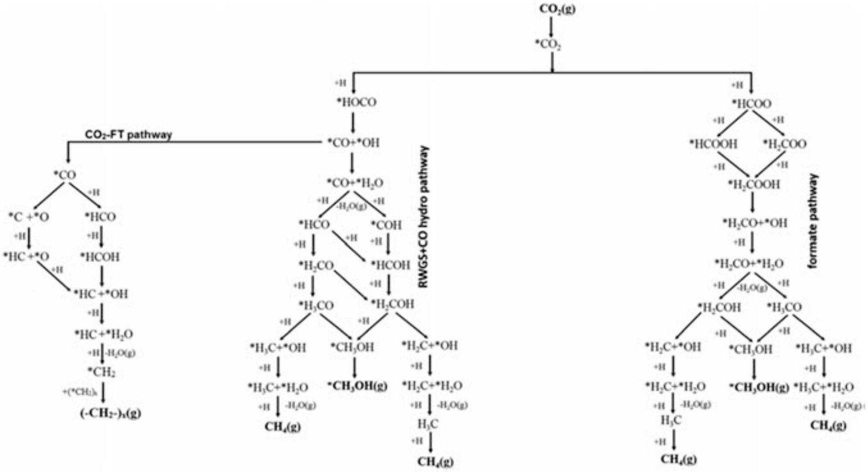


Fig. 1.3 Possible elementary reaction schemes for conversion of CO_2 to CO, CH_3OH, CH_4, and higher hydrocarbons [2]

RWGS reaction is endothermic. Therefore, operating temperature and pressure will be among crucial parameters affecting product distribution [4, 5]. Equilibrium composition of the product gas for the RWGS reaction with an inlet molar ratio of $H_2/CO_2 = 3$ is shown in Fig. 1.4.

As compared to transition metals such as Cr, Fe, Cu, and Ni, platinum group metals (Ru, Rh, Pd, Os, Ir, and Pt) have superior catalytic activity and excellent resistance against coking [1]. However, the cost associated with current platinum

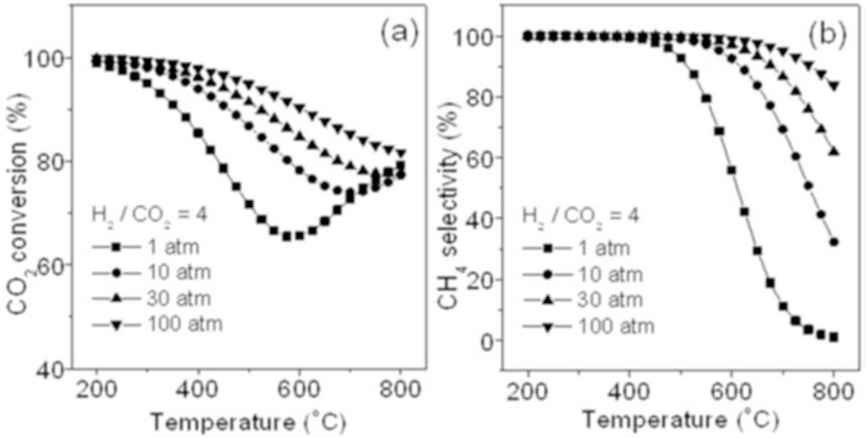


Fig. 1.4 Influence of temperature on the thermodynamic equilibrium of the RWGS (at 1 bar and $H_2/CO_2 = 3$ in the feed) [5]

group metal-based catalyst formulations is prohibitively high because of relatively high metal loadings (1–5 wt%). Loadings have to be reduced drastically for these catalysts to be commercially viable. Fortunately, evidence is mounting that overall catalytic activity is strongly affected not just by the amount of accessible active sites but also by their nature, which is size and shape-dependent [6–9]. This finding opens new avenues for catalyst nano-structuring (e.g., core-shell nano-catalysts, catalytic nano-rods) that can drastically reduce catalyst loadings by at least an order of magnitude [6] and may allow the use of noble metals, at least for some applications. Another, probably more promising approach, is the use of inexpensive emerging materials, such as nano-carbides, transition metal oxides, and bi- and multi-metallic alloys. This direction provides many degrees of freedom and could be guided by the density functional theory (DFT), a first principles computational method that evaluates the energy of a system from the electronic density.

The DFT method can be applied to understand the underlying mechanisms of catalytic reactions and, importantly, to predict the reactivity of heterogeneous catalytic systems [1, 10–13]. Specifically, potential energy diagrams can be readily constructed from the energy profiles of elementary steps for various catalysts (an example is shown in Fig. 1.5 [11]). Such diagrams allow for comparing relative stabilization of intermediates or transitions states for a particular set of reaction conditions. DFT-based predictive modeling can be used to identify materials, including pure metals and their alloys, with high catalytic activity in the CO_2 hydrogenation under relevant conditions. The selected candidates can be then tested

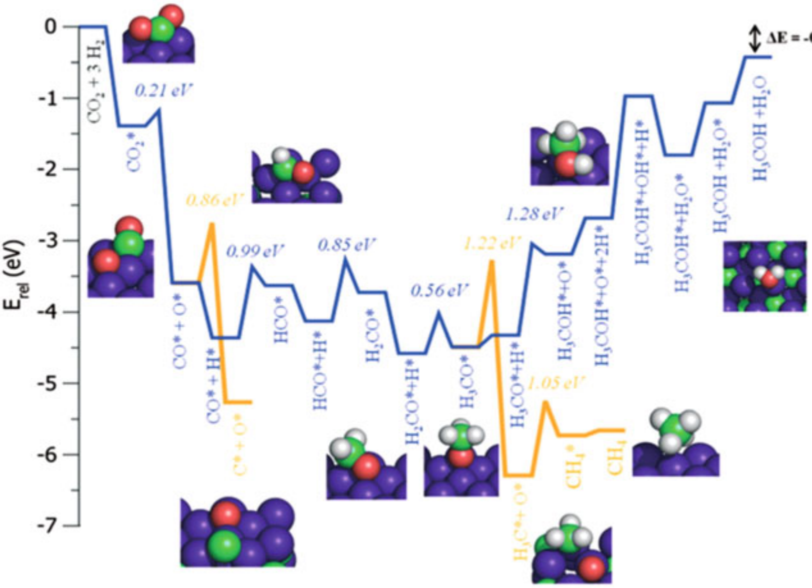


Fig. 1.5 Calculated energy profile for CO_2 hydrogenation to methanol on the clean β-Mo_2C(001)-Mo surface. Purple, green, red, and white balls denote Mo, C, O, and H atoms respectively [11]

experimentally to verify that they indeed have high activity and, importantly, for stability against sintering, oxidation and coking deactivation, sulfur poisoning etc.

With respect to catalyst deactivation, it always will be an issue for catalysts not based on noble metals. Even platinum group metals are susceptible to deactivation under severe conditions and over extended periods of operation. The three main mechanisms for catalyst deactivation are poisoning, sintering and coking. Poisoning occurs in the presence of sulphur compounds in feed gas stream, e.g., H_2S in biogas, due to the loss of catalytically active sites which are deactivated by strong chemisorption of sulphur, as it is schematically shown in Fig. 1.6 [14]. Poisoning deactivation can be prevented through upstream desulfurization treatments. Though such pretreatment increases capital and operational costs, it is rather necessary as sulphur poisoning can deactivate the catalyst rapidly and irreversibly.

Along with poisoning, sintering can be also an important factor contributing to catalyst deactivation. Sintering is a process of loss of the catalytically active surface area as a result of the growth and coalescence of supported metallic nanoparticles. The growth of nanoparticles is due to nanoparticle migration and coalescence, or Ostwald ripening that is the growth of larger nanoparticles at the expense of smaller ones due to the differences in surface energy. When the temperature high, metallic nanoparticles can actually migrate on the support surface and interact via either coalescence or Ostwald ripening when the nanoparticles come in close proximity to each other, Fig. 1.7 [15]. The eventual result of the catalyst deactivation by sintering is reduction of the conversion rate per catalyst weight due to the overall reduction of the catalytically-active surface available for reaction. However, once sintering has occurred to a certain extent, the sintering rate slows down, simply because larger nanoparticles growth slower, because of the reduced surface energy. Therefore, catalyst sintering typically does not lead to complete catalyst deactivation, as poisoning normally does.

If the process is operated with a proper upstream pretreatment to remove sulphur and at moderately high temperature, the problems of catalyst poisoning and sintering could be resolved, at least to a significant extent (except for highly endothermic MDR, Eqs. (1.8)–(1.10) that requires temperatures above 1100 K [1]). Unfortunately, this is not the case with the catalyst deactivation by coking that can occur by several pathways in different temperature regimes. The deposition of

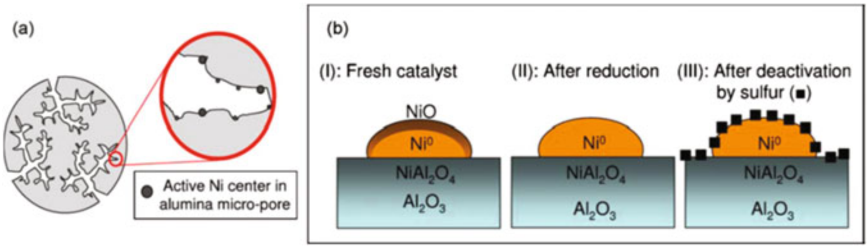


Fig. 1.6 Schematic representation of the sulphur poisoning mechanism of the Ni/Al_2O_3 catalyst [14]

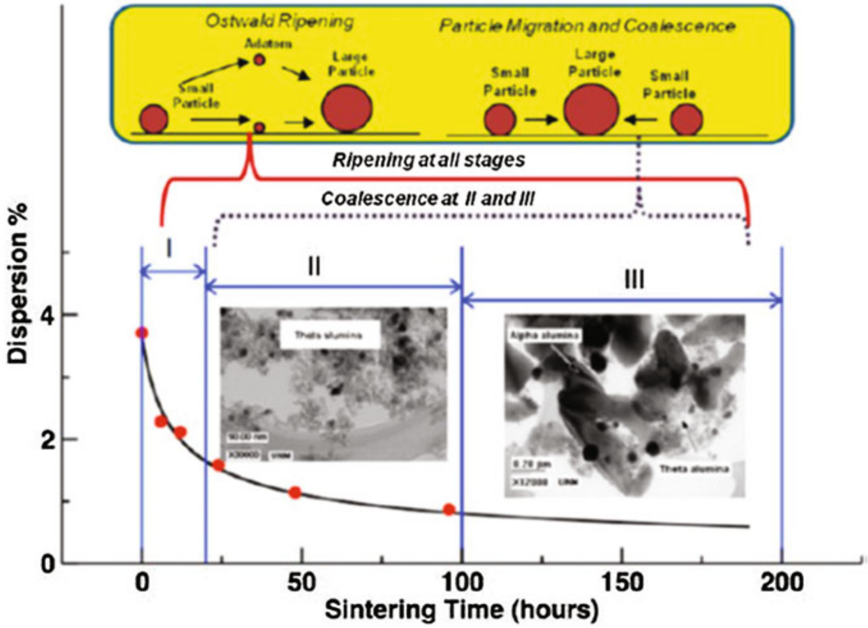


Fig. 1.7 Sintering of catalytic nanoparticles via Oswald ripening and migration/coalescence [15]

carbon deactivates the catalyst by fouling the catalyst surface, blocking catalyst pores and disintegrating the catalyst support. The three major forms of deposited carbon are encapsulating hydrocarbon films formed by polymerization, whiskerlike (filamentous) carbon, and pyrolytic carbon. An example of the extensive formation of filamentous carbon on the Ni/MgO catalyst is shown in Fig. 1.8. The most thermodynamically probable reactions involved in carbon deposition in CO_2 hydrogenation processes are CH_4 cracking, Eq. (1.8), Boudouard reaction, Eq. (1.9), and CO reduction (reverse gasification), Eq. (1.10) [1]:

$$CH_4 \rightleftarrows C + 2H_2 \quad \Delta H^{\circ}_{298K} = +74.8\ \text{kJ/mol} \tag{1.8}$$

$$2CO \rightleftarrows C + CO_2 \quad \Delta H^{\circ}_{298K} = -173.3\,\text{kJ/mol} \tag{1.9}$$

$$CO + H_2 \rightleftarrows C + H_2O \quad \Delta H^{\circ}_{298K} = -131.3\,\text{kJ/mol} \tag{1.10}$$

Carbon deposition by CH_4 cracking dominates at relatively high temperatures as this reaction is endothermic. On the other hand, carbon formation via Boudouard reaction and reverse gasification will mainly occur at relatively low temperatures, as these reactions are highly exothermic. The Boudouard and reverse gasification reactions, Eqs. (1.9) and 1.10), require CO as a source of carbon. Therefore, al low CO partial pressures and for temperatures above 700 K coking is expected to be predominantly caused by CH_4 cracking, Eq. (1.8). Importantly, all three reactions

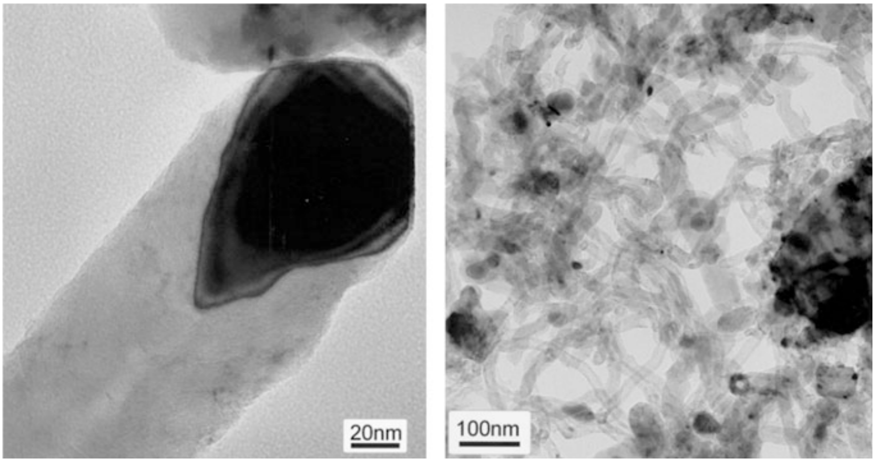


Fig. 1.8 TEM micrographs showing extensive formation of filamentous carbon (whisker carbon) during methane dry reforming over a Ni/MgO catalyst [10]

are reversible. The H_2-induced gasification, the reverse reaction in Eq. (1.8), is expected to be the predominant process for carbon removal at relatively low temperatures which are in general favorable for exothermic CO_2 hydrogenation reactions. The reactions of carbon gasification by H_2O and CO_2, the reverse reactions in Eqs. (1.9) and (1.10), can potentially occur as well, because CO_2 is a reactant and H_2O is a product in the CO_2 hydrogenation reactions. However, these gasification reactions are highly endothermic, as compared to the mildly exothermic carbon gasification by H_2, and are not expected to have a significant contribution at lower temperatures, in particular when H_2 is supplied in excess.

1.4 Reactor and System Design

Alongside the development of highly active, selective and stable catalysts, reactor design is another crucial aspect of process development. Methanol synthesis is clearly a well-developed, industrial scale technology with the well-established solutions for the reactor design. However, the industrial methanol synthesis uses syngas (a mixture of CO and H_2) as a feed. Utilization of CO_2 mixed with H_2 as a feed will require some fine tuning. Although the overall process will be still exothermic, the difference in the reaction heat should be properly addressed when redesigning methanol synthesis reactors for direct CO_2 conversion. A significant progress has been achieved in the design of methanation reactors. However, these systems were predominantly designed for conversion of CO, or mixtures of CO and CO_2, to synthetic natural gas (SNG) [16]. Although historically methanation systems were designed for conversion of synthesis gas generated by coal or biomass gasification, concentrated CO_2 streams were also recently considered as a feedstock for methanation. From the point of view of reactor design, fixed beds (also called packed beds) or fluidized beds were conventionally used in such systems.

Both reactor designs have its own advantages and disadvantages with respect to performing the CO_2 conversion reaction. Fixed beds are more compact but their heat management is problematic, while fluidized beds provide better transport characteristics, but are bulky and restricted to a narrow window of operation. Despite the fact that these conceptual configurations were suggested decades before, many challenges remain to be overcome for successful commercialization, with design requirements varying significantly depending on a source of carbon and hydrogen. So far, the majority of the work in the field has been done on methanation using coal or dry biomass as primary sources (coal or biomass gasification followed by gas cleaning and conditioning with subsequent methanation and upgrading). Recently, methanation was considered as one of the intermediate steps for the power-to-gas technology in which H_2 is first generated by water electrolysis and then reacted with CO_2 to produces SNG [3]. In addition to the conventional fixed bed and fluidized bed configurations, other reactor designs were suggested, such as three-phase slurry reactors, monolith reactors, and microchannel reactors. Thermal management remains one of the most challenging problems in the design of reactors for the thermocatalytic CO_2 conversion. A comprehensive overview of the reactor design concepts is available in the literature [3].

Due to the highly exothermic nature of the CO_2 hydrogenation processes such as the Sabatier reaction, Eq. (1.3), and direct methanol synthesis, Eq. (1.4), it is nearly impossible to operate the reactor adiabatically due to the hot spot formation. Exceedingly high temperatures created at the location of the hot spot lead to rapid catalyst deactivation by sintering and coking and even mechanical disintegration. The primary approach to resolve this drawback was to use cascades of adiabatic reactors (typically 2–6) with intermediate cooling and gas recirculation. A multi-stage methanation system including 3–4 adiabatic packed bed reactors with internal cooling and gas recirculation was developed by Haldor Topsøe, Fig. 1.9 [3]. In this commercially available Topsøe Recycle Energy-Efficient Methanation (TREMP) system, gas recirculation is used for temperature control of the first methanation reactor, keeping the reactor temperature below 700 °C. The effluent gas exiting from the first reactor is cooled by a heat exchanger and fed into the subsequent methanation stages in order to maximize methane production. The exact process configuration and number of reactors will depend on a specific application. A number of other methanation systems based on multiple packed bed reactors with intermediate cooling were suggested. However, the widespread commercialization of this concept has not been achieved, mainly due to the high capital investment and high operating costs associated with the use of multiple reactors, recycle compressors, and heat exchangers.

An alternative approach is to use a single pass, actively cooled reactor instead of multiple adiabatic reactors. The idea is to optimize heat removal in such a way that the hot spot formation is avoided and nearly uniform temperature distribution is

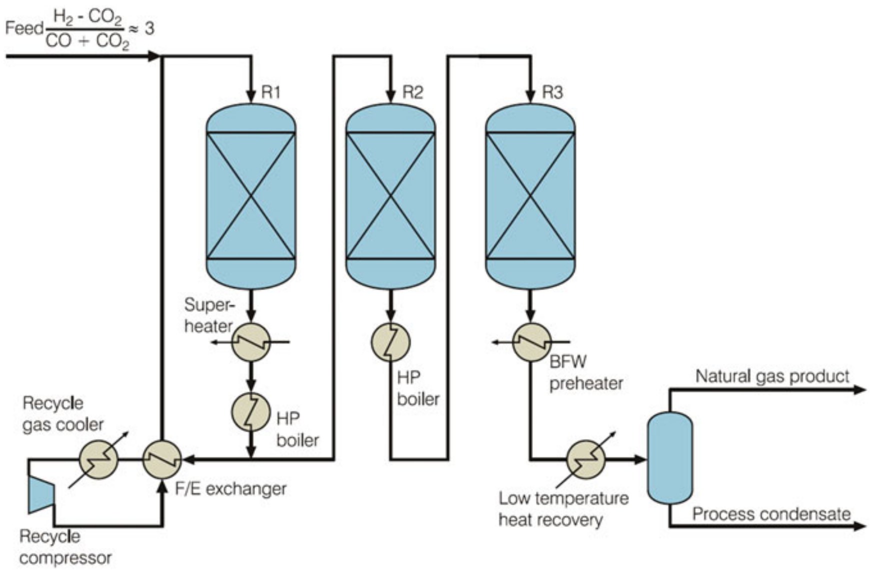


Fig. 1.9 Methanation system based on multiple packed-bed reactors with intermediate cooling and gas recirculation (TREMP^{TM}) [3]

achieved. Several alternative reactor designs aimed to achieve such nearly isothermal reactor conditions have been suggested, including a heat-exchanger type packed-bed reactor with cooling tube bundles embedded in the catalytic bed, a structured microchannel reactor, and a honeycomb design [3]. While isothermal operation simplifies process control significantly by reducing the number of reactors and system complexity, the reactor itself becomes much more expensive. This is particularly true for structured reactors because of the complicated catalyst deposition on the metallic microchannel or ceramic honeycomb structure and, particularly, the difficulty of replacing the deactivated catalyst. Also, heat removal optimization to avoid the hot spot formation is a difficult task.

Another option is to use a fluidized bed. Fluidized bed reactors are widely accepted as nearly isothermal reactors due to their excellent transport characteristics, allowing for the use of a single pass reactor and a relatively simple process to control, Fig. 1.10 [16]. However, catalyst attrition remains one of the major obstacles toward implementation of fluidized beds. Another disadvantage is that fluidized-bed reactors can only be operated in a narrow range of operating conditions dictated by the fluidization velocity, restricting reactor throughputs. Another concept is a three-phase methanation reactor, such as the slurry reactor illustrated in Fig. 1.11 [17]. Such reactors provide excellent heat transfer characteristics, allowing isothermal operation, but are restricted to a narrow operating window dictated by solvent/heat transfer fluid properties. Other major drawbacks are the gas-to-liquid mass transfer resistance and the fluid decomposition and evaporation.

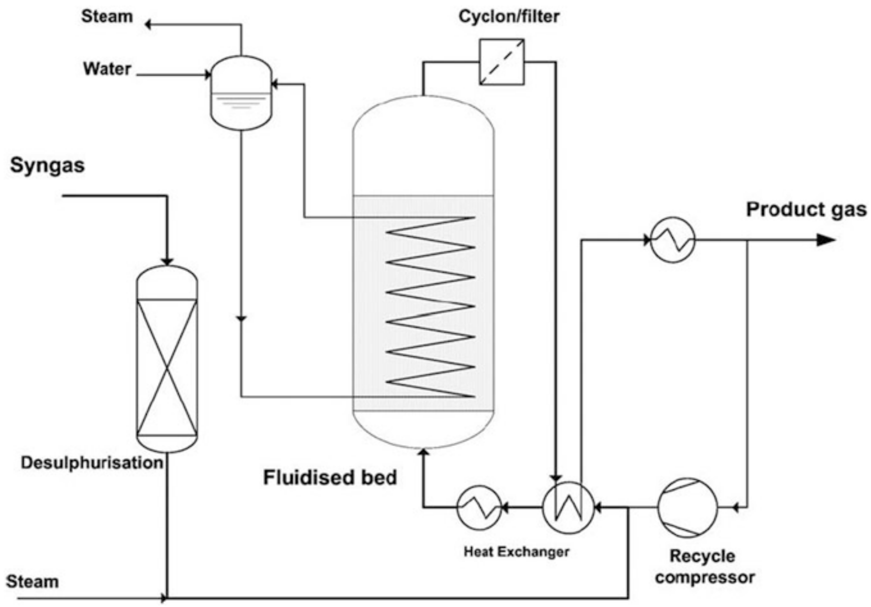
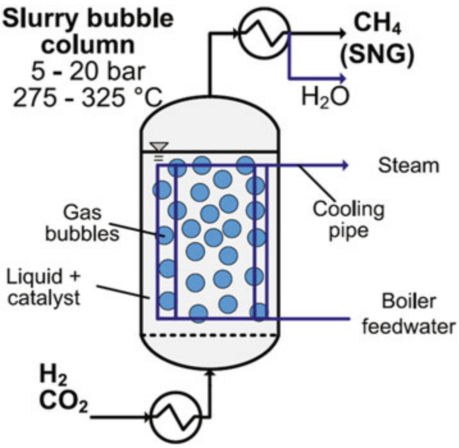


Fig. 1.10 A flow diagram of the methanation system based on a single fluidized bed reactor [16]

Fig. 1.11 Three-phase CO_2 methanation reactor [17]



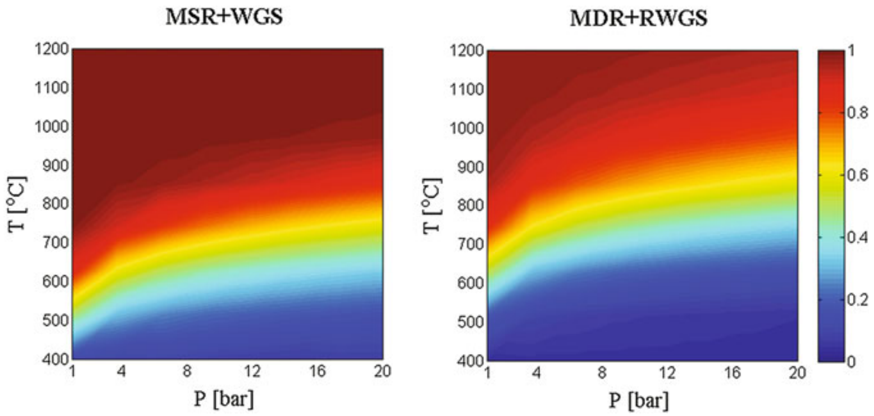


Fig. 1.12 Equilibrium CH_4 conversion for the combined MSR and WGS (*left side*) and MDR and RWGS (*right side*) processes, shown in the parametric domain of temperature and pressure. For MSR, the feed steam-to-carbon ratio of H_2O/CH_4 = 3 was used [1]

1.5 Methane Dry Reforming

Methane dry reforming (MDR),

$$CO_2 + CH_4 \rightleftarrows 2CO + 2H_2 \quad \Delta H^\circ_{298K} = +247.3 \text{ kJ/mol} \tag{1.1}$$

though a very well-known reaction, has a lot of challenges, mainly associated with catalyst deactivation and efficient heat supply. MDR is highly endothermic, significantly more endothermic than methane steam reforming (MSR), 247 kJ/mol versus 206 kJ/mol:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \quad \Delta H^\circ_{298K} = +206.1 \text{ kJ/mol} \tag{1.5}$$

In industrial reforming units heat is typically supplied by burning a certain fraction of the natural gas fed. Since the MDR reaction results in increase of number of moles, high CO_2 conversion is thermodynamically favored at low pressures. On the other hand, elevated pressures are required for large scale installations; industrial reformers are typically operated at 3–25 bar. Therefore, temperature should be kept as high as possible in order to achieve reasonably high CO_2 conversions. Thermodynamic analysis shows that temperatures above 1200 K are required to achieve CO_2 conversions above 80% even at moderately elevated pressures, Fig. 1.12 [1].

At such exceedingly high temperatures, catalyst deactivation by coking becomes a huge problem. Under the conditions of MDR, carbon deposition may occur at the catalytic surface by several reaction pathways, namely methane cracking, Boudouard reaction, and reverse gasification, Eqs. (1.8)–(1.10). Carbon can be deposited in different forms, either encapsulating the catalytic surface, or diffusing

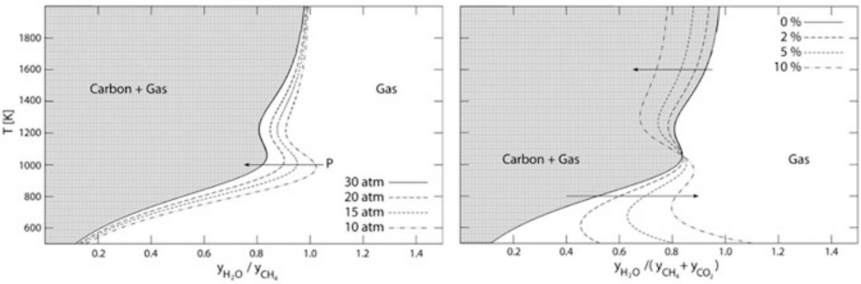


Fig. 1.13 Carbon formation equilibrium for a steam-methane system (*left side*) and for a steam-methane-carbon dioxide system (*right side*). The shaded area refers to the carbon formation zone at 30 atm. Limiting curves for different pressures (*left side*) and for different $CO_2/(CO_2 + CH_4)$ ratios (*right side*) are also shown [1]

into the metallic catalytic phase and forming filamentous carbon (so-called whiskers). Growth of carbon whiskers eventually results in mechanical disintegration of the catalyst pellets into finer particles, drastically increasing the pressure drop along the reformer.

Thermodynamically speaking, carbon formation is less favorable at low temperatures and high steam-to-carbon ratios. In Fig. 1.13, the thermodynamic analysis of the limiting conditions for carbon formation is shown, plotted in a temperature vs. steam-to-carbon ratio plane [1]. The shaded areas on the left of the limiting curves represent conditions under which carbon formation occurs. For both systems (MSR and MDR), at high temperatures the limiting steam-to-carbon ratio tends to 1, while higher pressures slightly shift the carbon formation boundary towards lower steam-to-carbon ratios. Industrial steam reformers are typically fed with steam-to-carbon ratios close to 3, which are far away from the carbon formation boundary. Such ratios are needed because commercial Ni-based catalysts are susceptible to fast deactivation by coking even when operating at steam-to-carbon ratios which are thermodynamically outside of the carbon formation regime. The use of high steam-to-carbon ratios effectively prevents coking, but results in less efficient operation because of increased energy demand for excess steam heating and reactive stream dilution.

In MSR water is used as oxidant, thus excess steam in the feed can be used to prevent coking without negative consequences on the process conversion. Unfortunately, this is not the case of MDR in which CO_2 is used as oxidant. Upon addition of substantial amount of steam to the feed CH_4 will predominantly react with H_2O, not with CO_2, as MSR is significantly less endothermic. As a result, the H_2/CO ratio of 2, which is characteristic of the MDR reaction, will be shifted towards $H_2/CO = 3$, which is typical for the MSR reaction. This ratio is too high for synthesis of hydrocarbons via the Fischer-Tropsch process. The ideal ratio for the Fischer-Tropsch process is actually $H_2/CO = 2$, which can be potentially provided by MDR but only if a catalyst that can withstand temperatures above 1200 K over long periods of operation without severe deactivation by coking could be developed.

1.6 Methanol Synthesis via CO_2 Hydrogenation

Methanol is an important feedstock for the chemical industry, primarily used for the manufacture of chemicals, e.g., formaldehyde, and a variety of products including plastics, paints and explosives. Methanol can be also used as a fuel or converted to other fuels through the methanol to gasoline (MTG) and methanol to olefins (MTO) processes. As a relatively low-cost feedstock, methanol can partially replace petroleum, avoiding the pollution associated with the extensive use of petroleum-based feedstocks. Currently, methanol is predominantly produced from synthesis gas:

$$CO + 2H_2 \rightleftarrows CH_3OH \quad \Delta H^{\circ}_{298K} = -90.8 \text{ kJ/mol} \tag{1.11}$$

The process is exothermic, therefore, requires cooling. Some heat can be recovered and used for other processes. Since the methanol synthesis reaction is exothermic, reversible and results in decrease in the total number of moles, high methanol yields are thermodynamically favored at lower temperatures and higher pressures. In industrial installations, methanol synthesis is typically carried out at 473–573 K and pressures as high as 50–100 bar over a $Cu/ZnO/Al_2O_3$ catalyst. The synthesis gas (syngas, a mixture of CO and H_2) is produced from natural gas via methane steam reforming (MSR), Eq. (1.5). The methanol synthesis requires the H_2/CO ratio of 2, Eq. (1.11). However, the MSR reaction, Eq. (1.5), produces the H_2/CO ratio of 3. The excess hydrogen is usually subtracted and burnt to provide heat for other processes, e.g., MSR. Another option is to inject CO_2 into the methanol synthesis reactor, where CO_2 reacts with excess H_2 to form methanol:

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad \Delta H^{\circ}_{298K} = -49.2 \text{ kJ/mol} \tag{1.4}$$

The use of CO_2 captured from industrial, residential and agricultural waste streams (combustion flue gas, landfill gas, biogas) mixed with H_2 generated via renewable routes (e.g., electrolysis using photovoltaic electricity) is a sustainable alternative to the use of natural gas-based syngas. In this case, not only the emission of CO_2 is reduced, but a valuable chemical feedstock (renewable synthetic methanol) is produced. There is a huge technological advantage in pursuing this direction, as there are many similarities with the conventional methanol synthesis with respect to catalysis, reactor design, and process design. The direct hydrogenation of CO_2 to methanol is actually less exothermic, therefore, requiring less heat to remove. On the other hand, it will require redesigning the entire process.

Novel catalytic formulations are also required. Although the direct CO_2 hydrogenation into methanol can be performed over the commercial $Cu/ZnO/Al_2O_3$, its performance is far worse than that achieved with syngas as a feed, providing relatively low selectivities to CH_3OH production (less than 50%) and CO_2 conversions below 15%, which is too low for industrial applications. Catalyst deactivation is also an issue. There is a constant search for new catalytic formulations. One direction is to promote the existing Cu/ZnO catalyst by modifying or changing the support (e.g., ZrO_2, SiO_2, TiO_2 are considered). Another direction is to identify a new active phase materials such as transition metal carbides, e.g., Mo_2C [11, 18]. With respect to reactor design, the conventional design with some modification could provide a viable solution, which will only require some re-design of the entire process rather than a conceptually new solution. Conventional methanol synthesis reactors are typically tubular fixed beds surrounded by heat exchanger jackets with steam used as a heat transfer fluid to remove the heat generated.

1.7 Reverse Water Gas Shift Reaction

The thermocatalytic reduction of CO_2 to CO via the RWGS reaction,

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad \Delta H^{\circ}_{298K} = +41.2 \text{ kJ/mol} \tag{1.2}$$

is among the most promising processes for utilization of CO_2. The produced CO can be mixed with H_2 to generate syngas, a valuable feedstock for the chemical industry. Competitive pathways are the Sabatier reaction and CO methanation:

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H^{\circ}_{298K} = -164.9 \text{ kJ/mol} \tag{1.3}$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \quad \Delta H^{\circ}_{298K} = -206.1 \text{ kJ/mol} \tag{1.7}$$

The RWGS reaction is reversible and endothermic, therefore high CO_2 conversions are favored at high temperatures. However, elevated temperatures can lead to (undesirable for this process) formation of CH_4, especially if a catalyst is not highly selective to the formation of CO. Therefore, catalyst development is crucial for the process development.

Fortunately, as RWGS is a reversible reaction, catalysts which are active in the water gas shift (WGS) reaction,

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad \Delta H^{\circ}_{298K} = -41.2 \text{ kJ/mol} \tag{1.6}$$

are also active in the reverse reaction (RWGS). Therefore, Cu-based catalysts, which are also commercial WGS catalysts, are being investigated for RWGS. The catalytic mechanisms of the RWGS reaction are still being debated. There are several possible pathways that can occur or not occur depending on the type of the active phase and support, e.g., Fig. 1.14 [19].

Catalysts based on Cu are generally reveal almost complete selectivity to CO formation. However, such catalysts can only be operated at relatively low temperature, while temperatures above 900 K are required to achieve CO_2 conversions above 50%. Under these conditions Cu-based catalyst undergo rapid deactivation

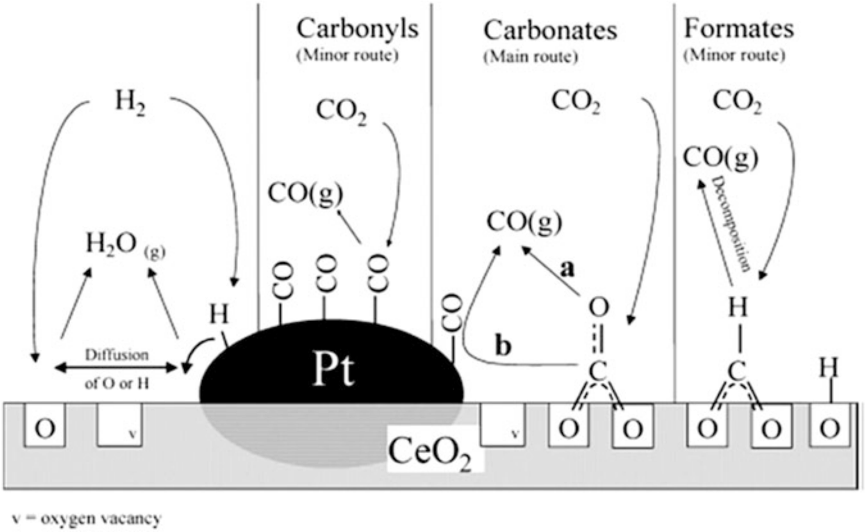


Fig. 1.14 Proposed mechanism of the RWGS reaction occurring on the Pt/CeO_2 surface [19]

by sintering of Cu nanoparticles. As with other heterogeneously catalyzed systems, approaches for improvement catalytic performance include addition of other metals to the active phase, including platinum group metals (e.g., Pt, Ru, and Rh), modification of support with promoters, and searching for new active phases (e.g., transition metal carbides).

The RWGS reaction has a large potential for large-scale utilization of CO_2, provided that a renewable technology for H_2 production is available. As compared to the MDR reaction discussed in Sect. 1.5, RWGS requires lower temperatures, as this reaction is only mildly endothermic. Probably the most difficult challenge is to identify a catalytic formulation that is highly selective to CO formation, but also can withstand high temperatures being stable with respect to sintering and coking. Catalyst activity is another important requirement, as highly active catalysts will allow for high production rates.

1.8 Sabatier Reaction, Power-to-Gas and Renewable Natural Gas

The increasing levels of global CO_2 emissions has prompted research in utilizing CO_2 as a feedstock for generating synthetic fuels and chemical. The current industrial usage of CO_2 is limited to processes such as synthesis of urea, salicylic acid and polycarbonates. Conversion of CO_2 into synthetic CH_4 via methanation, also called the Sabatier reaction, has recently gained increasing interest as a technologically advantageous route for CO_2 utilization. Historically, methanation systems were designed for conversion of synthesis gas (mixture of CO and H_2), but, recently, CO_2 was also considered as a feedstock for methanation. The highly exothermic Sabatier reaction, Eq. (1.3), is accompanied by the mildly endothermic reverse water gas shift, Eq. (1.2), and the strongly exothermic CO methanation, Eq. (1.7):

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad \Delta H^{\circ}_{298K} = +41.2 \text{ kJ/mol} \tag{1.2}$$

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H^{\circ}_{298K} = -164.9 \text{ kJ/mol} \tag{1.3}$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \quad \Delta H^{\circ}_{298K} = -206.1 \text{ kJ/mol} \tag{1.7}$$

The overall process is highly exothermic that requires efficient heat removal, in order to facilitate CH_4 production. In addition to this thermodynamic constrain, reactor overheating can also lead to fast catalyst deactivation by sintering and coking. From both thermodynamic and catalyst deactivation considerations operating temperatures should be kept below 800 K. Therefore, heat removal becomes a major problem. Two conventional configurations of methanation reactors are fixed bed and fluidized bed. Microchannel reactors, monolith reactors, and three-phase slurry reactors were also suggested as design solutions for carrying out methanation reactions. Reactor design considerations were discussed in Sect. 1.4. A comprehensive overview of the abovementioned concepts is available in the literature [3].

Briefly, for the adiabatic fixed bed reactor design, the primary approach is to use cascades of adiabatic reactors with intermediate cooling and gas recirculation. Though such systems can efficiently control the process temperature, the use of multiple reactors, recycle compressors, heat exchangers etc. results in system complexity and high capital cost investment. An alternative approach is to use an actively cooled packed-bed reactor that allows for performing methanation as a single-stage process. Structured, microchannel, and monolith reactors could be potentially used to overcome the overheating problem. However, while improved heat transfer characteristics and, ideally, nearly-isothermal operation significantly simplify process control, the reactor itself becomes more expensive. Fluidized-bed reactors are widely suggested as ideal isothermal reactors due to the excellent transport characteristics, allowing for the use of a single reactor and simplifying process control. However, catalyst attrition remains a major obstacle toward implementation of fluidized beds. Another disadvantage is that fluidized-bed reactors can only be operated in a narrow range of operating conditions dictated by the fluidization velocity, restricting reactor throughputs. Three-phase methanation reactors provide excellent heat transfer characteristics, allowing isothermal operation, but are restricted to a narrow operating window dictated by solvent/heat transfer fluid properties. Other major drawbacks are the gas-to-liquid mass transfer resistance and the fluid decomposition and evaporation.

The actively-cooled packed bed reactor design can potentially provide a low-cost solution for a single-pass methanation process. However, heat removal optimization is required. Nearly isothermal operation is only achievable when the heat transfer fluid flow rate is very high. On the other hand, process optimization will require minimizing the coolant flow rate, maximizing at the same time the reactor performance. One solution could be to use molten salts as a heat transfer fluid in order to optimize the removal of heat. Molten salts are advantageous over conventional heat carriers, such as steam and mineral oils, due to higher operating temperatures, low working pressure, high density and heat capacity, and non-flammability. A conceptual representation of the renewable natural gas (RNG) generation system comprising such a reactor is shown in Fig. 1.15. A CO_2-rich waste stream (e.g., biogas, landfill gas, or combustion flue gases) is first processed to remove poisonous impurities such as H_2S. Hydrogen, which is required for the Sabatier reaction, can be generated using renewable electricity via water electrolysis. The heat removed from the reactor by the molten salt can be used to preheat the feed, and can be utilized as well for electricity generation and residential heating.

One potential feedstock for the Sabatier process is landfill gas, or biogas, a product of the decomposition of an organic material in an anaerobic digester. As organic waste naturally undergoes anaerobic digestion which releases CH_4 (a greenhouse gas much more damaging than CO_2) into the environment, it is useful to collect organic waste and to process it in a controlled manner for future energy consumption. Raw landfill gas and biogas contain large fractions of CO_2 (25–50%).

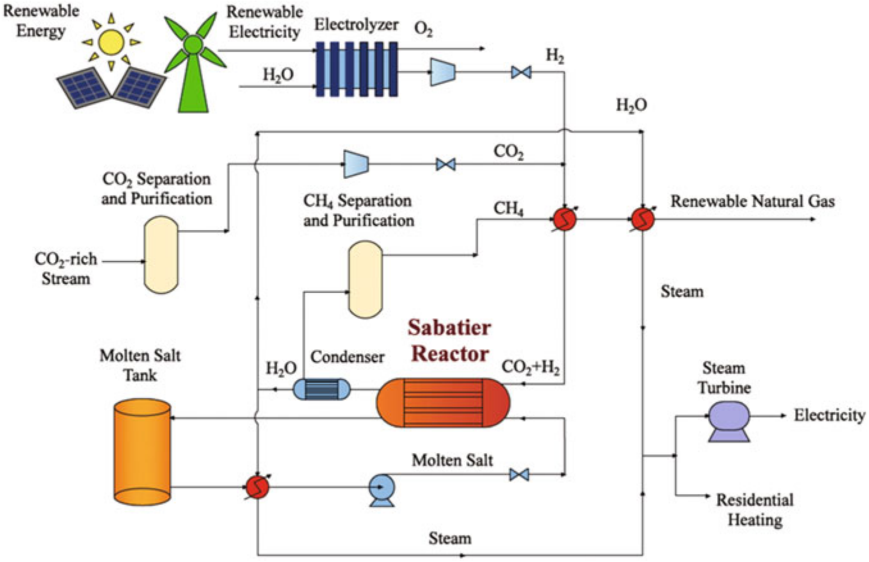


Fig. 1.15 Conceptual process flow diagram of the renewable natural gas generation system. The Sabatier reactor converts a mixture of CO_2 and H_2 into CH_4 and water. The reaction heat is removed from the reactor by the molten salt recirculation system

One approach is to process raw gases by separating CO_2 through pressure swing adsorption or amine scrubbing, producing renewable natural gas which is interchangeable with pipeline natural gas. The main disadvantage of this approach is high capital and operating costs required for CO_2 separation.

Another alternative is to use the raw landfill gas or biogas directly to generate electricity. An example of such process is illustrated in Fig. 1.16, showing a conceptual flow diagram summarizing the farm operation including the anaerobic digestion process and electricity generation. Anaerobic digesters are operated to treat the cattle waste and to produce biogas which is used to generate electricity on-site. The digesters could be operated continuously, allowing the solid waste to be broken down while producing biogas (typically 60 mol% CH_4 and 40 mol% CO_2). The solid co-product leftover from the digestion could be used as fertilizer. Pre-treatment processes will be required to remove H_2S and H_2O (e.g., scrubbing and condensation) prior to being fed into the combustion engine. The electricity generation efficiency in such a system will be ~35–40%, which are typical values for internal combustion engines such as diesel generators. Because of the relatively low efficiency, most of the energy content of the biogas will be converted to heat. This heat can be partially recovered from the cooling jacket, and be used for on-site heating. However, most of the heat will be lost to the surrounding. Heat recovery from the engine exhaust is problematic because in such low-quality heat is not of value on the site.

An alternative approach is to convert the CO_2 present in the raw biogas into CH_4 via the Sabatier reaction. Hydrogen can be generated by water electrolysis using carbon emission-free renewable energy sources such as wind, solar, and hydro-electricity. The use of clean energy sources for biogas upgrading reduces the overall carbon emission. Although the resulted synthetic natural gas is eventually used for power generation or residential heating emitting CO_2, a substantial fraction of its energy content is in fact renewable. In any case, the source of this emitted carbon is not fossil, as raw biogas itself is a renewable, non-fossil source.

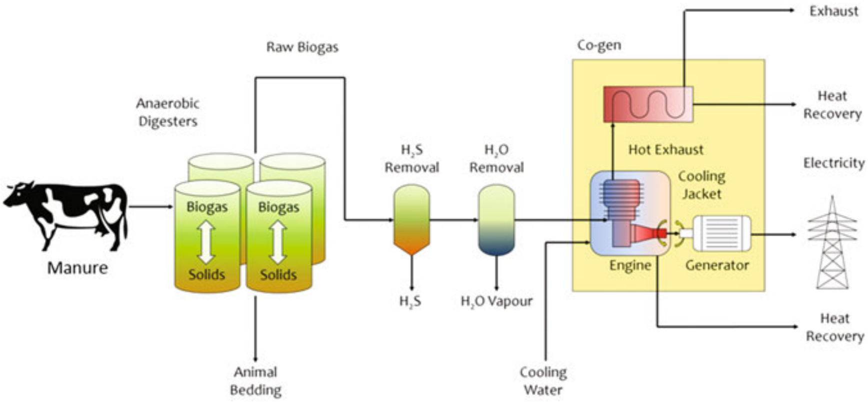


Fig. 1.16 Schematic representation of the renewable electricity generation system at a dairy farm: biogas is produced from organic waste and burned to produce electricity

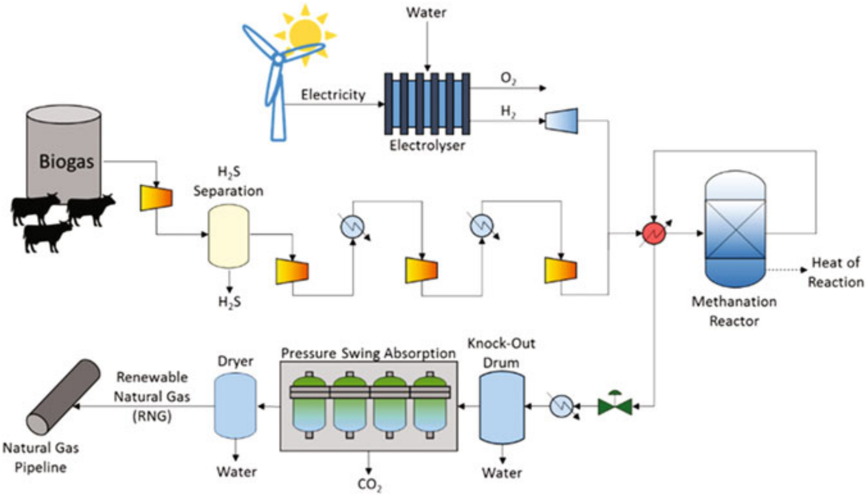


Fig. 1.17 Conceptual representation of the renewable natural gas generation system at a dairy farm: biogas is produced from organic waste and upgraded to renewable natural gas injected into the pipeline

Potentially, the renewable natural gas (RNG) stream can bolster the existing natural gas supply systems, while consuming captured feedstocks rich in greenhouse gases, and can be utilized as part of a power-to-gas infrastructure for surplus energy storage and redistribution. A conceptual flowsheet of the RNG generation system is shown in Fig. 1.17 (compare to Fig. 1.16).

Renewable natural gas (RNG) can potentially provide an effective solution to meet the future energy demand, while providing sustainability and reduction in greenhouse gas emissions at the same time. The fossil natural gas will clearly remain a part of the energy mix during the transition to more sustainable energy sources. During the transition period, RNG can be used to increase the renewable content of the natural gas in the overall distribution system. The generated RNG can be simply injected into the existing natural gas infrastructure, providing storage and transportation capacities. In the future, renewable natural gas can become an integrated part of the energy system and of the power-to-gas infrastructure, storing excess electricity in the form of chemical energy of CH_4, while utilizing CO_2 as a feedstock to generate that renewable synthetic fuel.

1.9 Future Perspectives

Despite significant research efforts driven by the need to reduce CO_2 emissions, technologies for chemical fixation of CO_2 are still under development. With respect to the thermo-catalytic hydrogenation of CO_2, major challenges of thermal management and catalyst performance remain to be resolved in order to make this technology truly commercially viable. One possible direction is the use of multi-functional reactors that combine exothermic and endothermic reactions and integrate reaction and separation steps in a single, highly-efficient catalytic unit. Design of such reactors is challenging but the potential is large, as such units can provide compact, economically feasible solutions for making synthetic fuels from CO_2.

To address the technological challenges related to the thermocatalytic CO_2, further research should rely on innovative approaches, including the use of emerging materials for catalysis, nano-structuring to create highly-active and stable catalyst morphologies (e.g., sub-nanoclusters and core-shell nanoparticles), and integrated reactor design. Materials with superior catalytic performance could potentially be identified among materials which are not conventionally used for thermocatalytic processes (such as transition metal carbides). Novel catalytic materials could be created (e.g., supported multi-metallic alloys or mixed carbides). The search for materials with superior catalytic properties could be guided by the density functional theory (DFT) [7–12].

In the conventional approach, catalyst development is often decoupled from the understanding interatomic interactions at the catalytic surface and from the large-scale reactor design. Conventional methodology relies on (1) selecting catalyst formulations (often based on largely empirical data), (2) scanning over the range of selected catalysts by testing a small amount of catalyst under controlled conditions, and (3) testing the identified best catalysts in a pilot plant reactor under more realistic conditions. Such approach does not provide fundamental understanding of the catalytic reaction mechanisms and does not explicitly account for the coupling of reaction and transport phenomena in a catalytic reactor. As a result, a catalyst which could be active and stable while using a small quantity under the specific conditions of the evaluation experiment may have poor performance under different conditions. Also, the catalyst may be found to be unsuitable when tested in a catalytic reactor, since reaction and transport limitations at a scale of the entire reactor were not accounted for in the catalyst design.

A multi-scale, integrative approach could be applied to develop novel catalytic systems for the thermocatalytic conversion of CO_2 into synthetic fuels. Such multi-scale approach could rely on understanding the catalytic properties of a new candidate material at the atomic scale (to derive reaction kinetics), coupling the reaction kinetics to the micro-scale level reaction-transport phenomena, validating and correcting the proposed reaction kinetics via experiments, and incorporating the obtained knowledge into the macro-scale reactor design. The current state-of-the-art in the field of thermo-catalytic hydrogenation of CO_2 could be further advanced by developing novel catalysts based on emerging materials and nano-structuring, designing highly-efficient reactors with optimized thermal management, and acquiring fundamental knowledge on the CO_2 activation on catalytic surfaces.

Advances in thermocatalytic chemical fixation of CO_2 are of great importance to the fields of heterogeneous catalysis and reaction engineering. There are also important practical aspects. For example, the process of generating synthetic natural gas from waste CO_2-reach streams and renewable H_2 could be a basis for power-to-gas technology that will allow for more efficient renewable energy storage and grid load balancing. The electrical grid was historically designed in such a way that it is not well-suited to transient renewable energy sources such as wind and solar. The introduction of renewable natural gas (RNG) into the energy distribution infrastructure could help to resolve this drawback.

Renewable energy is abundant but its efficient utilization is challenging due to its transient nature resulting in the supply-demand mismatch. Fluctuations in power supply can be compensated by storing off-peak electricity in the form of chemical energy of a renewable synthetic fuel. Although H_2 generation is required for the thermocatalytic CO_2 hydrogenation, H_2 could be produced via water electrolysis utilizing renewable energy sources. As a fuel, H_2 is not a good choice due to the difficulties related to it storage and transportation, especially if H_2 is generated in a distributed manner, which is the case of renewable energy sources. Therefore, converting H_2 and CO_2 into renewable synthetic fuels more suitable for storage and transportation, such as renewable synthetic methane and methanol, could be an attractive avenue. Yet, the cost of H_2 generation is expected to be among most significant contributions to the production cost of a renewable synthetic fuel. Therefore, reducing the production cost of renewable H_2 could lead to a breakthrough towards the widespread introduction of renewable synthetic fuels produced from CO_2 into the markets.

Producing synthetic renewable fuels from CO_2 and their introduction into the existing energy distribution infrastructure and chemical industry will reduce greenhouse gases emissions and will allow for establishment of a waste-to-fuel chain. Also, technologies that can fixate CO_2 could in principle eliminate the need for energy intensive CO_2 removal and storage. There are many sources of CO_2, including flue gases from fossil power plants, CO_2 contained in associated petroleum gas, fermentation off gas, landfill gas, and biogas. Currently, most of this CO_2 is emitted to the atmosphere. Successful implementation of CO_2 fixation technologies will also lead to creation of new jobs and a new, potentially large, source of revenue for the economy.

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Chapter 2
Electrocatalytic Reduction of CO_2

Renewable sources, such as solar and wind electricity, are attractive alternatives to fossil energy, because they are CO_2 neutral and, therefore, do not contribute to the greenhouse effect. However, these types of renewable energy are not available on demand due to their transient character. Therefore, there is a need in energy storage. Electrical grids can definitely absorb certain supplies of renewable electricity but there is a limit. The grid has to have a certain baseline that assures reliability of power supply. This baseline supply is typically realized through the use of large-scale fossil fuel, nuclear, and hydroelectric power plants, which cannot be easily switched off and on but have to be operated continuously. As more and more renewable sources are being connected to the electrical grid, the problem of electricity oversupply will eventually become the reality.

One option is to store this surplus electricity as a liquid fuel that has high volumetric energy density and can be easily transported, for example methanol. This power-to-fuel chain can be achieved indirectly, using electrolysis and thermocatalytic conversion, or directly by electrochemical reduction. In the first approach, renewable electricity is used to electrolyze water into hydrogen (H_2) and oxygen (O_2) as a valuable by-product. The generated hydrogen is then reacted with CO_2, e.g., via the water gas shift reaction to generated syngas (a mixture of CO and H_2), which can be in turn converted in a variety of value-added products. This pathway was discussed in Chap. 1.

An alternative pathway combines water electrolysis with CO_2 hydrogenation in an electrochemical cell fed with H_2O and CO_2 to produce liquid compounds such as formic acid and methanol. Such conversion technology, if implemented on a large scale, would recycle the otherwise emitted CO_2 into usable fuels, positively affecting the global carbon balance. It is also possible to reduce CO_2 into CO in an electrochemical reactor, therefore producing syngas. However, this approach is less attractive since the thermocatalytic reduction of CO_2 in CO is much more efficient in terms of conversion, throughput, and compactness.

D.S.A. Simakov, *Renewable Synthetic Fuels and Chemicals from Carbon Dioxide*,
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It should be emphasized at this point that dramatic improvements have been recently made in the design of photovoltaic devices leading to improved efficiency and significantly lower production costs. As a result, photovoltaic cells, alongside with wind turbines, are now commercially available and economically viable for small-to-medium scale power generation applications. On the other hand, efficiencies of electrochemical cells for CO_2 reduction to methanol and other liquid chemicals, such as formic acid, remain relatively poor. Improvements could be made through the development of highly efficient catalysts and advanced technological solutions for the electrochemical cell design to achieve high current density operation.

First demonstrations of electrochemical reduction of CO_2 date back to the 19th century and this topic has received a lot of renewed attention since the 80s of the 20th century due to the rapidly rising prices of fossil fuels. Since then, there is a continuous interest in this technology that represents a strategic pathway for conversion of CO_2 into fuels and chemicals including important feedstocks for chemical industry such as formic acid (HCOOH) and methanol (CH_3OH).

Research efforts on the electrochemical reduction of CO_2 have grown rapidly in the last few decades and the potential is enormous. However, the challenges are great. First of all, CO_2 is an extremely stable molecule, very difficult to activate. Activating the CO_2 molecule into its useful state by reduction requires not just a significant energy input but also highly active catalysts. Second, CO_2 solubility in aqueous environments required for electrochemistry is relatively low. These limitations pose fundamental challenges related to chemical catalysis, electrochemistry, and electrochemical cell engineering.

Below, the basic concept of the electrochemical reduction of CO_2 is explained first and the most fundamental challenges are addressed. The discussion focuses then on the CO_2 reduction catalysis and electrochemical cell design. Methanol synthesis is reviewed in more detail, as one of the most promising applications. Syngas production using solid oxide fuel cells is also addressed. In closing remarks, the feasibility of the electrochemical reduction of CO_2 for industrial applications is critically discussed.

2.1 Basics of Electrochemical Reduction of CO_2

In this section, basic principles of the electrochemical reduction of CO_2 in aqueous environments are briefly discussed. For more detailed information, the reader is referred to a number of excellent reviews [1–6]. In the electrochemical reduction of CO_2, electricity is supplied to an electrochemical cell containing an aqueous solution containing dissolved CO_2. The reduction of CO_2 occurs on the cathode and it is balanced by the electrolytic dissociation of water on the anode supplying the protons needed to hydrogenate CO_2 through a proton exchange membrane, as it is schematically depicted in Fig. 2.1, for the case of the CO_2 reduction to CO [7].

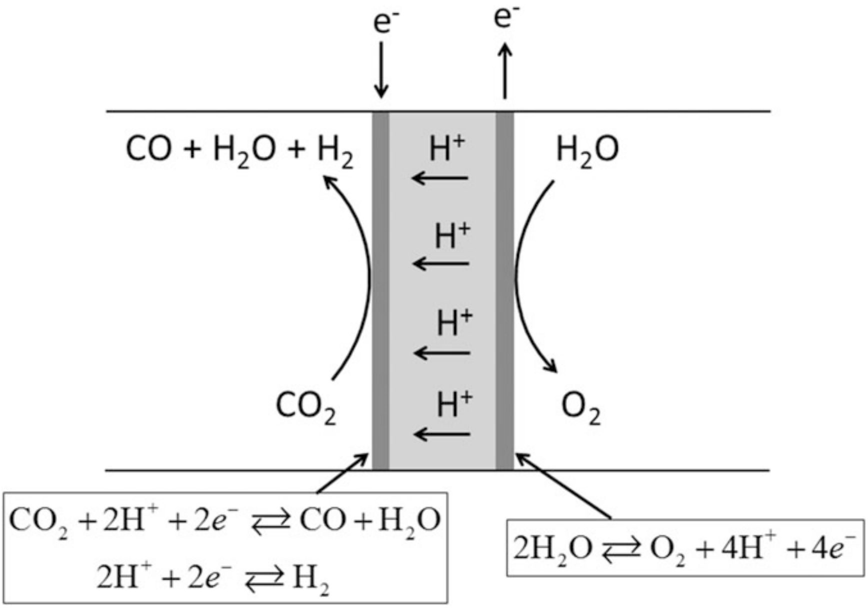

Fig. 2.1 Electrochemical cell with a cation-exchange membrane CEM as electrolyte. The design is similar to a proton-exchange membrane fuel cell

Looking at another example, of CO_2 conversion to methanol (CH_3OH), we find that the reduction and oxidation occurring on the cathode and anode, respectively, are described by the following reactions, showing the overall reaction as well (potentials are shown vs. saturated calomel electrode) [6]:

$$\begin{array}{lll} \text{Cathode:} & CO_2(aq) + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O & E^0 = -0.22\ \text{V} \\ \text{Anode:} & 3H_2O \rightarrow 1.5O_2 + 6H^+ + 6e^- & E^0 = +0.99\ \text{V} \\ \text{Overall:} & CO_2(aq) + 2H_2O \rightarrow CH_3OH + 1.5O_2 & E^0 = +1.21\ \text{V} \end{array} \quad (2.1)$$

To accelerate the reaction rates, a catalyst is typically deposited on the electrode surface. Catalysis for the electrochemical reduction of CO_2 and the electrochemical cell design are discussed in Sects. 2.3 and 2.4, respectively.

Hereafter, we focus on the cathode side, which is the limiting factor in the electrochemical cell performance. To supply CO_2 continuously to the electrochemical cell, it can be simply bubbled through the solution. However, the limited solubility of CO_2 poses a significant challenge, which will be addresses and discussed in detail in next section. Typically, the electrochemical reduction of CO_2 is carried out in neutral or slightly alkaline solutions because such environment facilitates the formation of the formate ion (HCO_2^-), which is a reaction intermediate in the CO_2 hydrogenation pathway. In more alkaline solutions, above pH = 9, the formation of the bicarbonate and carbonate ion will be facilitated, limiting the participation of CO_2 in the reduction reaction pathways. Lowering the pH of the electrolyte allows for dissolving more CO_2/H_2CO_3. However, acidic electrolytes facilitate the H_2 evolution reaction, while hindering the formation of the formate ion. There is still debate between researchers regarding the optimal pH of the electrolyte for the electrochemical reduction of CO_2.

While the electrochemical reduction of CO_2 is feasible thermodynamically, the reduction potential of CO_2 is only slightly different from that for water reduction. As a result, there is a competition between the CO_2 reduction and the more thermodynamically favored H_2 generation (potentials are shown versus standard hydrogen electrode, at 25 °C and pH = 14):

$$\begin{array}{ll} CO_2(aq) + H_2O + 2e^- \rightarrow HCO_2^- + OH^- & E^0 = -1.02\ \text{V} \\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- & E^0 = -0.83\ \text{V} \end{array} \tag{2.2}$$

Therefore, the electrical energy supplied to an electrochemical cell will be consumed by two competing reduction mechanisms: H_2 generation via water electrolysis and CO_2 reduction into a product of interest, e.g., methanol or formic acid. High selectivities to the desired product (typically defined as the Faradaic efficiency) and, therefore, high production rates of that desired product can only be achieved if the electrode material suppresses H_2 generation so that most of the supplied electricity is consumed in the CO_2 reduction reaction.

Certain cathode materials, such as Indium (In), Tin (Sn), and Lead (Pb), are known to kinetically suppress H_2 formation. The mechanism of this suppression is the existence of the high water reduction overpotential that results in low exchange current densities. On the other hand, these materials are known to have a relatively good exchange density for the reduction of CO_2. Therefore, even though H_2 formation is more favorable thermodynamically than the electrochemical reduction of CO_2, the formate ion can be produced quite efficiently given a suitable cathode material that limits the water reduction kinetically, while not suppressing the CO_2 reduction to same extent.

In addition to the water reduction, there are a number of other competing reactions occurring during the electrochemical reduction of CO_2. Possible reaction pathways, including the methanol, formic acid and formaldehyde formation, are listed below alongside with corresponding reduction potentials (shown versus normal hydrogen electrode, at 25 °C and pH = 7):

$$\begin{array}{ll} CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O & E^0 = -0.24\ \text{V} \\ CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O & E^0 = -0.38\ \text{V} \\ CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O & E^0 = -0.48\ \text{V} \\ CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O & E^0 = -0.53\ \text{V} \\ CO_2 + 2H^+ + 2e^- \rightarrow CHOOH & E^0 = -0.61\ \text{V} \\ CO_2 + e^- \rightarrow CO_2^{\cdot -} & E^0 = -1.90\ \text{V} \end{array} \tag{2.3}$$

Depending on the product of interest, some of the reactions listed above are called “parasitic reactions”. These undesirable reactions consume the electrical current supplied to the electrochemical cell, reducing the amount of the current consumed in the desired reaction pathway. Note that the single electron reduction of CO_2 is less favorable than the proton-coupled multi-electron pathways, which is in fact beneficial for the CO_2 reduction into liquid fuels and chemicals. The pathways shown in Eq. (2.3) are overall reactions. Each of them has several elementary steps and various probable reaction mechanisms. For example, in the electrochemical conversion of CO_2 into methanol there are at least two possible reactions pathways. One mechanism involves dioxymethylene ion ($HOCO^-$) and carbon monoxide (CO) as reaction intermediates, Eq. (2.4). Another mechanism proceeds through the formation of formate ($HCOO^-$) and formic acid (HCOOH), Eq. (2.5). Both mechanisms involve the formation of HCO species and formaldehyde (CH_2O) [6]:

$$\begin{array}{l} CO_2(aq) + e^- + H^+ \rightarrow HOCO^- \\ HOCO^- + e^- + H^+ \rightarrow H_2O + CO \\ CO + e^- + H^+ \rightarrow HCO \\ HCO + e^- + H^+ \rightarrow CH_2O \\ CH_2O + 2e^- + 2H^+ \rightarrow CH_3OH \end{array} \tag{2.4}$$

$$\begin{array}{l} CO_2(aq) + e^- + H^+ \rightarrow HCOO^- \\ HCOO^- + e^- + H^+ \rightarrow HCOOH \\ HCOOH + e^- + H^+ \rightarrow HCO + H_2O \\ HCO + e^- + H^+ \rightarrow CH_2O \\ CH_2O + 2e^- + 2H^+ \rightarrow CH_3OH \end{array} \tag{2.5}$$

2.2 Fundamental Challenges

In addition to the thermodynamic considerations discussed above, there are also kinetic limitations. Generally speaking, it is much more challenging to convert CO_2 into highly desirable organic compounds such as formic acid and methanol than into small molecules such as CO. Formation of more complex molecules requires multiple proton-coupled electron transfers, which results in significant kinetic barriers and, therefore, low conversion efficiency. Finding a suitable catalyst that can promote formation of all intermediates simultaneously, while not catalyzing undesirable parasitic reaction is a great challenge. Such a catalyst would have to have low kinetic barriers (activation energies) for each desirable reaction step. One option could be performing different reduction steps using different catalysts, but it is much more desirable from the practical point of view to convert CO_2 into a liquid compound directly, in a single electrochemical device.

One of the fundamental challenges in the electrochemical CO_2 reduction is the high cathode overpotential (the difference between the applied electrode potential and the thermodynamic potential). The overpotential consists of three components, namely ohmic overpotential, activation overpotential and concentration overpotential. The ohmic losses are due to electrode and electrolyte resistances. The activation overpotential reflects the kinetic barrier, i.e., the energy required to maintain the electrode reaction at a significant extent. The electrode surface can be deactivated by poisoning caused by adsorption of reaction intermediates. Therefore, selection of a proper electrode material is crucial. The concentration overpotential develops due to the mass transfer limitation caused by the diffusion of reactants and products towards/from the electrode surface. Since the electrochemical reduction of CO_2 is carried out in an aqueous medium at relatively low temperatures, the diffusion is relatively slow. If the diffusion rate of CO_2 to the electrode is significantly slower than the maximum rate of its consumption at the electrode surface, a limiting current is reached. Thus, the electrode morphology becomes a very important factor in the electrochemical cell performance. For any practical implementation, the issue of the limited mass transfer of CO_2 to the cathode surface has to be addressed.

Another intrinsic limitation is the low solubility of CO_2 in water. The CO_2 solubility in water exposed to pure CO_2 is about 30 mmol/L (at 101 kPa and 293 K). However, in aqueous electrolytes used in electrochemical reduction the CO_2 solubility is lower, due to the high ionic strength (up to 10 M). Providing a pure CO_2 stream will require pre-concentration of CO_2 containing feedstocks. This can be done by pressure swing adsorption or membrane separation, but capital and operation costs are high, which will result in a significant increase of the overall production cost. Using diluted CO_2 streams directly, without any upstream pre-concentration, is preferable. However, low CO_2 content (e.g., 10–15 mol% CO_2 in fossil fuel combustion flue gases) will result in lower concentration of the dissolved CO_2. The eventual negative outcome from the low CO_2 solubility in water and, thus, low concentration of aqueous CO_2 is the limiting current density that can be easily estimated using the following equation [2]:

$$i_L = nFk_mC_b \tag{2.6}$$

In this equation, n is the electron stoichiometry coefficient ($n = 2$), F is the Faraday constant (96485 kC/kmol), k_m is the mass transfer coefficient (10^{-5} m/s), and C_b is the bulk concentration of CO_2 (0.03 kmol/m^3 for pure CO_2 at 101 kPa and 293 K). Simple computation shows that the limiting current density is $i_L = 0.06$ kA/m^2. For diluted CO_2 containing streams, this limiting current will be further declined. Such geometric current densities, below 0.1 kA/m^2, are considered as insufficient for typical industrial applications involving electrochemical processes. The economics dictate that geometric current densities above 1 kA/m^2 with current efficiencies of at least 50% are usually required to make the technology profitable [2]. The reason is that the rate of an electrochemical reaction per electrode area (r, mol/(m^2 s) is directly proportional to the current density via Faraday's law (FE is faradaic efficiency, also called current efficiency):

$$r = \frac{R}{A} = i\frac{FE}{nF} \tag{2.7}$$

Solving this equation for A (total electrode area) gives the dependence of the required electrode area on the production rate (R, mol/s) and current density (i):

$$A = \frac{RnF}{i \times FE} \tag{2.8}$$

The above equation simply dictates that the required electrode area is inversely proportional to the current density. Therefore, for low current densities, large electrode surfaces will be required, resulting in a large size of the electrochemical device and, therefore, high capital investments and operating costs. In industrial applications, typical capital costs for electrochemical reactors are on the order of magnitude of \$10,000 m^{-2} of anode or cathode area. To afford such high capital investment, electrochemical processes are typically operated with current densities of 1 kA/m^2 and higher, with faradaic efficiencies above 50%. On the other hand, industrial space velocities for gaseous feed have to be at least higher than 100 h^{-1}, preferably on the order of magnitude of 1000 h^{-1} (contact times of seconds). These limitations set a challenging set of requirements for the design of an economically viable electrochemical device for the CO_2 conversion into liquid fuels and chemicals.

2.3 Catalysis for Electrochemical Reduction of CO_2

For the deployment of practical applications for the electrochemical reduction of CO_2 to liquid fuels and chemicals, highly efficient electrocatalysts have to be developed. An electrocatalyst participates in the electron transfer reaction on the electrode and facilitates the electrochemical reaction that takes place on the electrode surface, Fig. 2.2. For efficient electrocatalysis, both processes must be accelerated simultaneously. Thermodynamically, it has to be a good match between the redox potential for the electron transfer reaction and the catalyzed electrochemical reaction (reduction of CO_2). Ideally, an optimal electrocatalyst should

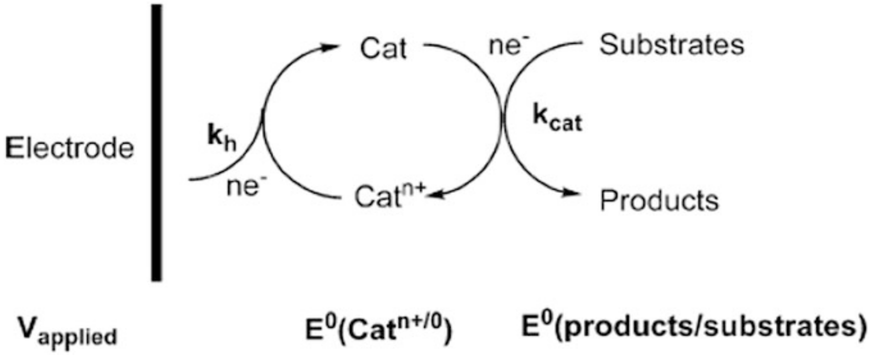

Fig. 2.2 Schematic representation of electrocatalysis in the proximity of the electrode surface with electron source [5]

operate near the thermodynamic potential of the occurring electrochemical reaction. In the search for an optimal electrocatalyst, various catalytic materials are typically screened for their redox potentials, as well as for the electron transfer rate, chemical kinetics, and current efficiencies. To identify highly efficient catalysts, all these characteristics have to be considered. Electrochemical phenomenon is quite complicated, as it involves both chemical kinetics and electrical processes.

As it was already mentioned in the previous section, direct electrochemical reduction of CO_2 on the electrode surface requires large overpotentials (the difference between the applied voltage and redox potentials of reactants and products). Large overpotentials result in low conversion efficiencies. Both thermodynamic and kinetic considerations have to be considered in order to overcome this limitation, at least to certain extant. In order to minimize the overpotential, the catalyst formal potential has to be well-matched with redox potentials of species participating in the electrochemical reaction. In addition, the reaction rate constant (k_{cat} in Fig. 2.2) and the rate constant for the electrocatalyst reduction (k_h in Fig. 2.2) must be high at the applied voltage. Common approaches for evaluation of rate constants for a given catalyst are cyclic voltammetry and rotating disk voltammetry [5].

Herein, it is useful to differentiate between *redox catalysts* and *chemical catalysts*. In redox catalysis, the catalyst is an electron transfer agent shuttling electrons between the electrode and the reactant. The chemical reaction acceleration is due to more efficient electron supply, which can be also achieved by improving the electrode morphology to make it porous as opposed to a classical flat electrode surface. In chemical catalysis, a catalyst undergoes more intimate interaction with chemical species undergoing chemical transformations. An ideal catalyst/electrode assembly would facilitate both mechanisms, significantly lowering the overpotential and the activation energy of the electrochemical reaction.

It is also necessary to distinguish between *homogeneous* and *heterogeneous catalysis*. While the electrochemical CO_2 reduction can be catalyzed either homogenously or heterogeneously, the two approaches have different reaction mechanisms and require different electrochemical cell designs. In homogeneous catalysis, the catalyst molecules, which are dispersed in the electrolyte solution containing the substrate, diffuse to or from the electrode surface. Homogenous catalysts for the electrochemical reduction of CO_2 are typically reduced states of transition metal complexes with macrocyclic, bipyridine or phosphine ligands [5]. In heterogeneous catalysis, the electrode material itself can act as electrocatalyst, or another catalytic material can be dispersed or immobilized on the porous electrode surface [8]. In early studies, bulk metals (e.g., Cu, Ni, Fe, Ti) were used as catalysts, employing single-element metallic electrodes in polycrystalline form. More recently, new types of heterogeneous electrocatalyst morphologies were developed, including transition metal nanoparticles, nanotubes, nanowires, core-shell structures, and nano-porous films. Homogeneous catalysts are generally less prone to deactivation since the bulk electrolyte provides a constant source of catalytic molecules replacing those that have been deactivated during each catalytic cycle. However, heterogeneous systems with the catalyst deposited or immobilized within the highly porous electrode surface have a very important advantage of compactness.

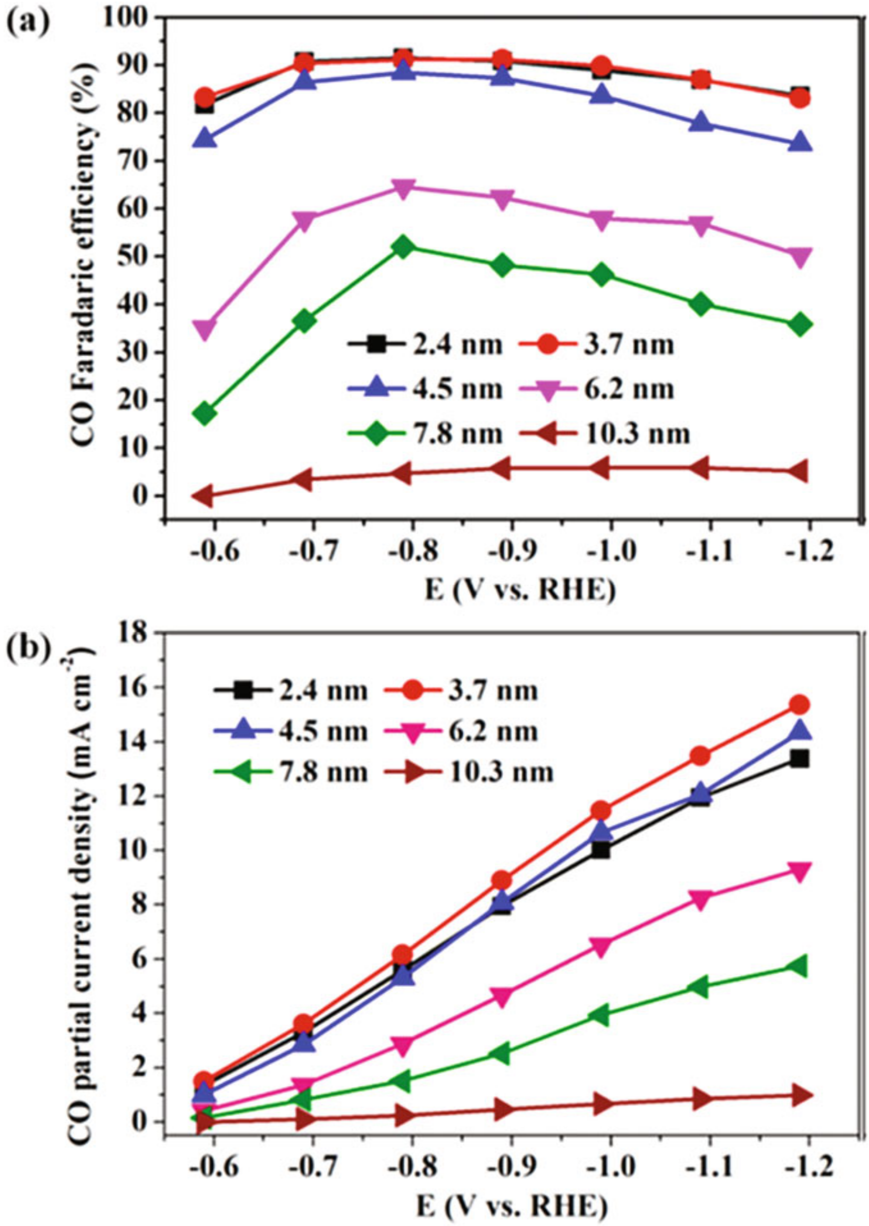

Fig. 2.3 Applied potential dependence of Faradaic efficiencies (**a**) and current densities for CO production over Pd nanoparticles with different sizes [9]

Among homogeneous catalysts, metal complexes such phthalocyanine and tetraazomacrocyclic complexes of cobalt and nickel were demonstrated for the electrocatalytic reduction of CO_2 to CO, providing faradaic efficiencies of up to 98%. Rhenium and ruthenium bipyridine complexes and phosphine complexes of rhodium and palladium were also reported to be active in the electrochemical reduction of CO_2. One of the concerns regarding practical implementation of such catalysts is obviously the high cost of the catalyst that, in combination with low production density (rate of production per device volume), limits the economic viability of this approach. In heterogeneous catalysis, the use of transition metal nanoparticles as electrocatalysts is a promising avenue. The size of nanoparticles is of crucial importance because, similar to thermocatalysis, there is a strong size-activity relationship. For example, a prominent size-dependent activity and selectivity was identified in the electrocatalytic reduction of CO_2 to CO over Pd nanoparticles with sizes ranging from 2.4 to 10.3 nm [9]. Faradaic efficiencies varied from 5.8% over 10.3 nm nanoparticles to 91.2% over 3.7 nm nanoparticles, along with an 18-fold increase in current density, Fig. 2.3.

2.4 Electrochemical Cell Design

The majority of the work reported on the CO_2 electroreduction is on electrocatalysis, mainly focusing on catalytic characteristics of the electrode reactions. For such investigations, laboratory experiments are typically performed in small batch electrochemical cells under ideal conditions that do not reflect practical applications. These studies are of course of crucial importance for identification of optimal catalytic systems and understanding cathodic mass transfer limitations. However, for practical implementation, the next step has to be the design of a scaled-up, continuous flow device. So far, there is only a limited number of reports that refer to industrially feasible applications [2].

In terms of the electrochemical cell configuration, there are several conceptual options [7], Fig. 2.4. Some configurations are less suitable for the electrochemical CO_2 reduction. For example, the fuel cell-like configuration, Fig. 2.4a, could be unfavorable for CO_2 reduction due to the competing H_2 evolution reaction. To prevent the excessive flux of protons towards the cathode, a pH-buffer could be introduced, Fig. 2.4b. However, in this case the cell resistance could be too high if the buffer layer is thick. Another option is to use an anion-exchange membrane, Fig. 2.4c, simplifying the buffer-layer-based system. Yet another configuration is based on the use of a Nafion membrane in its K^+ form, which allows the oxygen evolution reaction to be carried out in alkaline conditions and CO_2 reduction on the cathode, Fig. 2.4d. An important breakthrough was the successful implementation of gas diffusion electrodes (which are used in fuel cells) in the electrochemical cell for CO_2 electro-reduction [10], Fig. 2.5. The use of the gas diffusion electrode is a promising approach as it can improve mass transfer characteristics. However, it is

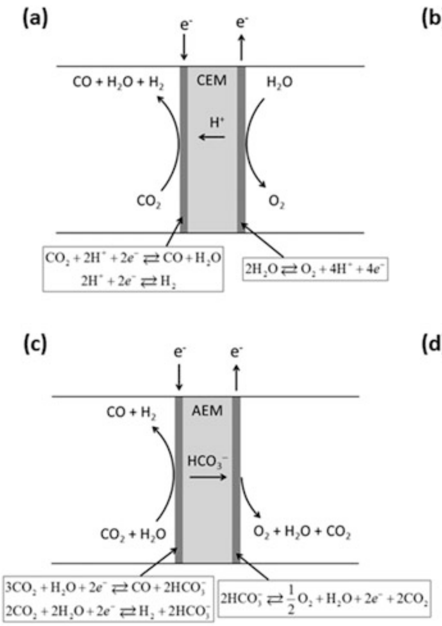

Fig. 2.4 Various designs of electrochemical cells: electrochemical cell with a cation-exchange membrane (CEM) as electrolyte (**a**), modified cell with a pH-buffer layer of aqueous $KHCO_3$ (**b**), electrochemical cell with an anion exchange membrane (AEM) as electrolyte (**c**), and electrochemical cell based on a cation-exchange membrane in the K^+-form (**d**)

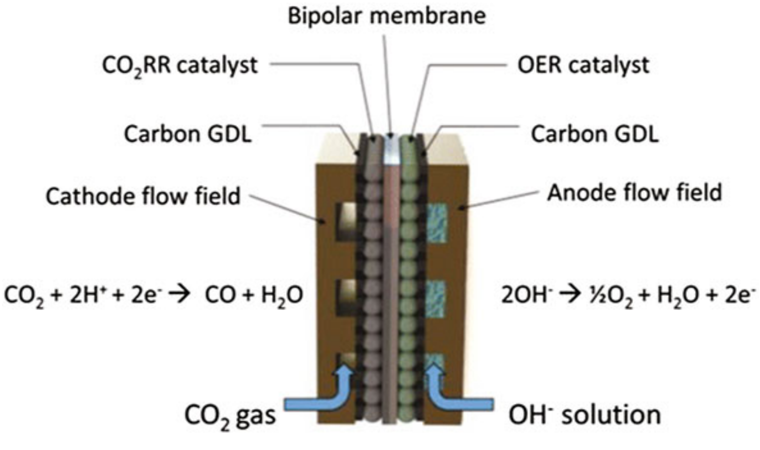

Fig. 2.5 Schematic drawing of the electrochemical device for CO_2 reduction with serpentine flow fields and gas diffusion layer (GDL) made of porous carbon paper [10]

associated with the drawback of the accumulation of liquid phase products in the gas diffusion electrode pores leading to blockage.

2.5 Methanol Synthesis

Among various approaches for CO_2 utilization, the electrochemical reduction of CO_2 appears to be an attractive alternative, since in this technology electrical energy (including renewable electricity) is used to convert CO_2 into value-added chemicals under mild conditions. This approach provides a method to recycle the emitted CO_2 creating a carbon neutral cycle and, at the same time, to store the renewable (or excess) energy from intermittent sources in the chemical energy of a synthetic fuel. There is, therefore, a significant potential to reduce our dependence on fossil fuels. Among the products which can be generated via the electrochemical reduction of CO_2, methanol is of particular interest as an important platform chemical.

Methanol has quite high energy density, which is almost half of the energy density of the gasoline (15.6 MJ/L vs. 34.2 MJ/L). In addition, methanol is also an essential intermediate for many important chemicals including paints and plastics. For the use as an energy carrier, it is beneficial to convert H_2 into methanol, which has much higher volumetric energy density than H_2 and can be stored at atmospheric pressure in liquid form. Importantly, methanol can be also directly utilized in energy converting systems such as internal combustion engines and direct methanol fuel cells. Due to the abovementioned benefits, the CO_2 electroreduction into methanol has recently gained growing attention. Yet, although significant advances have been made in this direction, more work is still required in order to develop an economically viable technology which can be commercialized on an industrial scale. Currently, most of methanol worldwide is produced in large scale industrial plants via steam reforming of natural gas to produce syngas, which is then converted to methanol in high pressure (20–30 MPa) synthesis. In contrast, the electrochemical transformation of CO_2 is performed under ambient conditions and CO_2 emitted from fossil fuel power plants and other industries can be in principle utilized. If such “methanol economy” would be implemented on large scale, it could contribute significantly to solving the problem of climate change and to reduction of our dependence on fossil fuels, Fig. 2.6 [6].

A significant progress has been made in understanding the mechanisms of the electrochemical reduction of CO_2 into methanol. The formation of methanol is known to occur heterogeneously on several electrocatalysts. Applied cathodic materials include copper (Cu), as well as its oxides and alloys with other metals, such as Ni, Sn, Pb, Zn, Ag and Cd [6]. Other electrocatalytic materials such as molybdenum (Mo) and ruthenium (Ru) are also active in the CO_2 electroreduction to methanol providing faradaic efficiencies up to 60%. Other transitions metals (e.g., Fe, Ti) can be also used, as well as noble metals (Pt and Pd). Among all these materials, the oxidized Cu-based electrodes seem to be the most promising as they provide both high selectivities and current efficiencies [6].

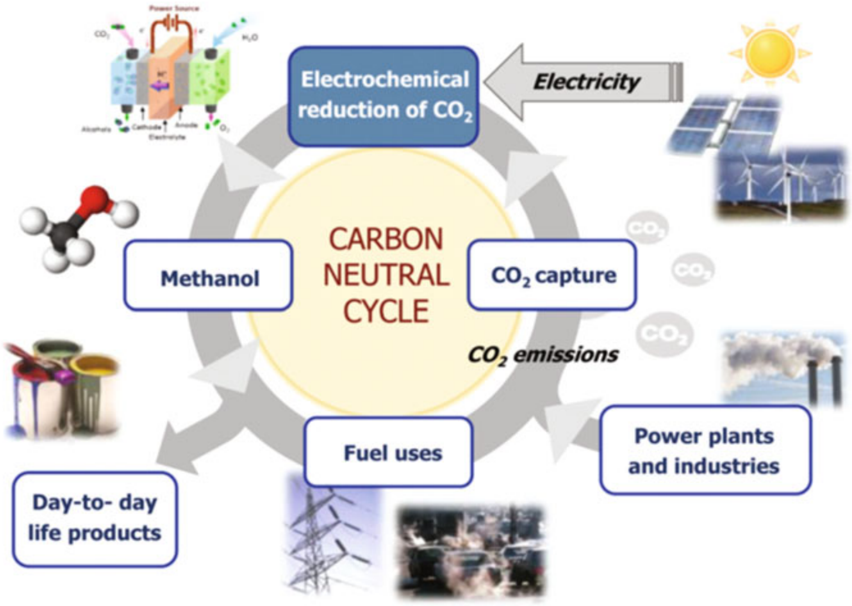

Fig. 2.6 The methanol-based economy cycle model [6]

Despite recent progress, the production of methanol via the electrochemical route is still far from its practical application. Several fundamental drawback have to be resolved in order to make this technology economically viable. First, the electrocatalyst stability at high current densities is still poor. The major problem is that reaction intermediates poison the active sites leading to fast catalyst deactivation. The development of highly stable catalysts is, therefore, among highest priorities, but these stable catalysts have to be highly active and selective to methanol production at high current densities at the same time. Second, activities and selectivities of the existing catalysts are still low. The research in this direction should focus on novel catalytic materials, still unexplored for electrochemical methanol synthesis. In addition to the catalytic material selection, the electrode morphology should be also optimized to maximize the catalytic surface per the geometric area of the electrode. This can be achieved by implementation of novel materials with high specific surface area, e.g., metal organic frameworks (MOFs). The ultimate goal is to create an optimized electrode morphology that can facilitate both electron transfer and mass transport, while having a highly active and selective catalyst that facilitates reaction rates. Finally, there is still a lot of work to be done with respect to the design of a compact and highly efficient electrochemical cell that can be scaled-up for industrial applications.

2.6 Syngas Production in Solid Oxide Fuel Cells

Fuel cells are electrochemical conversion devices that directly generate electricity by oxidizing a fuel. In a solid oxide fuel cell (SOFC), a solid oxide electrolyte is used, to differentiate from other types of fuel cells based on liquid or polymer electrolytes. There are several advantages associated with the use of SOFCs, including fuel flexibility (other than H_2 fuels can be directly used), high efficiency, long-term stability, and relatively low cost. However, due to the low electrolyte conductivity SOFCs have to be operated at high temperatures (typically 800–850 °C), which results in long start-up times and mechanical stability issues. As any other type of fuel cells, SOFCs can operate not just as a fuel cell but also as an electrolyzer [1, 11, 12]. In the fuel cell operation mode, the SOFC converts the chemical energy of a fuel into electricity through a chemical reaction. In the electrolysis mode of operation, the cell can reduce water and CO_2 into H_2 and CO, producing syngas. In this case, it is more appropriate to refer to the electrochemical cell as solid oxide electrolysis cell (SOEC), Fig. 2.7.

The advantage of the solid oxide electrolyte is that this type of electrolyte conducts oxide ions. Therefore, the SOEC can directly reduce both CO_2 and H_2O to CO and H_2. The mixture of CO and H_2 is syngas, an important chemical feedstock for the Fischer-Tropsch process and methanol synthesis. Other types of fuel cells are based on electrolytes that conduct protons (proton exchange membrane fuel cell, PEMFC), or hydroxide ions (alkaline fuel cells, AFC, or anion exchange membrane fuel cells, AEMFC). The high operation temperature of SOECs (above 800 °C) provides both thermodynamic benefit (high efficiency) and kinetic advantages (accelerating splitting of the reactants). As a result, SOECs operate with lower electricity consumption and the need for (often expensive) highly active catalysts is eliminated, as at such elevated temperatures kinetics is very fast.

In terms of practical implementation, the use of SOECs for CO_2 reduction seems as a very promising approach. In such a process, CO_2 and steam can be co-fed to an array of SOECs producing synthetic gas (syngas, a mixture of CO and H_2), Fig. 2.7. The high operating temperature allows for heat integration with other processes, such as downstream conversion of syngas into synthetic fuels and

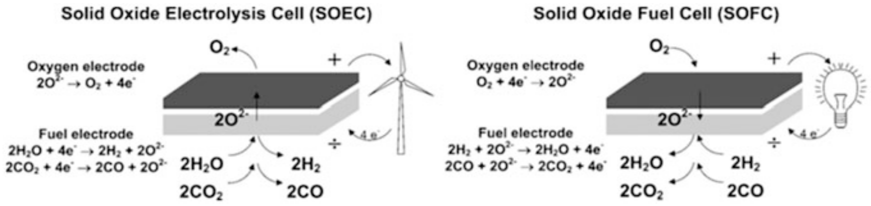

Fig. 2.7 Schematic presentation of the operational principle of a solid oxide electrolysis cell (SOEC) and a solid oxide fuel cell (SOFC) [11]

chemicals, increasing the overall efficiency. For example, the heat generated in the downstream fuel synthesis can be utilized for generation of steam fed to the SOEC. Therefore, arrays of SOECs have a potential to be implemented for high throughput production of synthetic fuels from steam and captured CO_2, at a high efficiency, relatively low capital investment (SOECs are based on ceramic materials). The main drawback is related to mechanical instabilities of the cell materials subject to high temperatures and repeated start-up/shut-down cycles.

2.7 Concluding Remarks

The electrochemical reduction of CO_2 is an attractive avenue for converting captured CO_2 into value-added synthetic fuels and chemicals. Various sources of CO_2 can be potentially utilized, including combustion off-gases, biogas from farming, and landfill gas. Conceptually speaking, probably the most important advantage of this technology is that electricity can be directly converted into chemical energy of a synthetic compound in an electrochemical device. This energy conversion pathway allows for storing intermittent renewable or surplus electricity in the form of an easily transportable chemical feedstock, such as methanol or formic acid. In principle, it is possible to generate negative carbon footprint fuels and chemicals using solar, wind, and hydro energy, water and captured CO_2. Among possible products of the CO_2 electroreduction, the most practical are probably methanol (used in the polymer and paint industries, can be used as a fuel), formic acid (used in the textile industry and as a preservative), and syngas (can be converted to methanol or synthetic crude via the Fischer-Tropsch process).

The potential is enormous but the challenges are difficult to overcome. First of all, there are some fundamental, intrinsic drawbacks related to the low CO_2 solubility in aqueous environments and similar redox potentials of competing reactions. These limitations can be referred to as thermodynamic in their nature, as they cannot be overcome in a classical electrochemical cell. Other issues stem from kinetic and mass transfer constrains leading to large electrode overpotentials and limiting current. Further advances are required in the CO_2 reduction electrocatalysis and electrode morphology design. However, the development of a highly active, selective, and stable catalyst and an optimized electrode morphology will not immediately lead to large-scale industrial implementation. The optimized electrode has to be incorporated in a highly efficient electrochemical cell, which has to be scalable. In addition to the mass transfer limitations near the electrode surface, there will be mass transport constrains at the level of the entire electrochemical device as well. Only once a scalable electrochemical device for the CO_2 electroreduction has been designed, the question of the economic feasibility of this technological pathway can be properly addressed.

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Chapter 3
Photocatalytic Reduction of CO_2

As compared to other methods for CO_2 reduction, the photocatalytic conversion of CO_2 has a unique advantage of direct utilization of solar energy. In this sense, this pathway is similar to the biological photosynthesis. About 105 TW of solar energy is delivered to the Earth's surface (the Earth receives 174,000 TW of incoming solar radiation at the upper atmosphere, but approximately 30% is reflected back to space). The global energy consumption for a whole year is equivalent to less than 2 h of sunlight. In most populated areas, insolation levels range from 0.15 to 0.3 kW/m^2. Since solar energy is abundant and its use has zero carbon footprint, the use of the photocatalytic reduction of CO_2 for production of synthetic fuels and chemicals has a great potential to cut CO_2 emissions and to reduce our dependence on fossil fuels. Similar to thermocatalytic and electrocatalytic conversion pathways, the photocatalytic CO_2 reduction into synthetic fuels offers an alternative to the CO_2 storage approach that has disadvantages related to the high capital investment and environmental concerns, such as the possibility of leakage.

Due to the growing concerns of climate change caused by accelerated CO_2 emissions, there was a substantial increase in research activities in the field of the artificial photocatalytic conversion of CO_2 into valuable chemicals and synthetic renewable fuels during past few decades. However, challenges are great and there still are many drawbacks to overcome. The process of converting sunlight into the chemical energy of a synthetic fuel has its own thermodynamic constrains, as well as kinetic and transport limitations. Fortunately, recent developments in nanotechnology and photocatalysis resulted in significant advances in the catalytic CO_2 photoreduction leading to substantially improved efficiencies. Still, more efforts are required to further improve the efficiency of the CO_2 photoreduction reaction.

One of the most important directions is the development of novel photocatalysts based on emerging materials and nanostructuring. As for any catalytic system, the most important properties are activity, selectivity to CO_2 reduction, and stability. Ideally, all these characteristics should be maximized, but there is a place for compromise and trade-off. For example, if a catalyst has very high selectivity to the desirable product and its long-term stability is good, such catalyst could be

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considered as a good choice even if its activity is not that high. Despites decades of quite intensive research, mechanisms of the catalytic photoreduction of CO_2 are still not well-understood, which limits our ability to select novel catalytic systems. The design of an efficient photocatalytic reactor is still challenging. To sum up, although the potential of the CO_2 photoreduction is large, challenges are still great and this technology is not yet economically viable.

In the following discussion, basic principles of the photocatalytic reduction of CO_2 are first explained. Afterwards, main disadvantages and challenges of this technology are addressed. Next, recent advances in photocatalysis are outlined and the photocatalytic reactor design is subsequently discussed. Operational constrains and the feasibility of industrial applications are critically discussed at the end of this chapter.

3.1 Basic Principles

In the photocatalytic reduction of CO_2, a semiconductor promotes CO_2 splitting in the presence of light irradiation. The process involves photophysical and photochemical phenomena and proceeds in three main steps: generation of an electron-hole pair upon absorption of a photon, charge carrier separation and transfer, and a chemical reaction between a surface specie and a charge carrier, as it is schematically depicted in Fig. 3.1 [1].

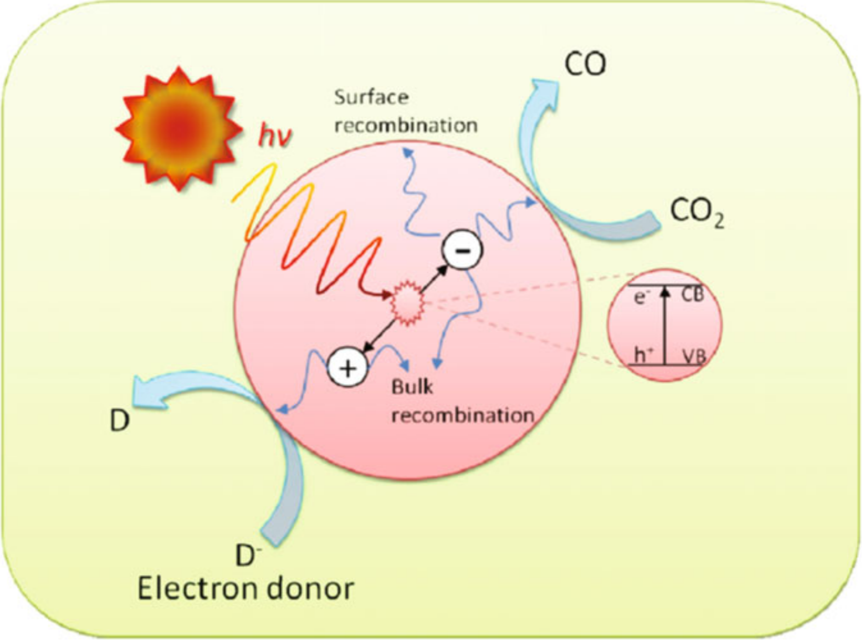

Fig. 3.1 Schematic diagram of photoexcitation and electron transfer process [1]

The photoexcitation occurs when the photon energy is equal to or greater than the band gap of a semiconductor photocatalyst, leading to the electron excitation from the valence band (VB) to the conduction band (CB). Not all charge carriers (electron and holes) participate in the desirable surface reactions. Some of the generated electron and holes combine at the trap sites through the radiative or non-radiative recombination pathways. It is highly desirable to slow down the bulk electron-hole recombination process to ensure that most of the generated electrons and holes participate in the surface reactions. The electrons travel to the semiconductor surface, which is in contact with the aqueous solution, and react with the CO_2 species adsorbed on the surface; the holes oxidize the water molecules.

There are a number of excellent reviews in the literature explaining the details of the CO_2 photoreduction mechanisms [1–4]. The two most essential reactions are shown below in Eq. 3.1, where standard Nernst potentials are shown vs. the normal hydrogen electrode (NHE) at pH = 7, 25 °C, and 1 atm gas pressure. The photogenerated holes react at the semiconductor surface abstracting electrons from an electron donor (water molecules), Fig. 3.1, which are oxidized to form molecular oxygen and protons. The photogenerated electrons reduce the CO_2 species adsorbed on the semiconductor surface.

$$\begin{aligned} 2H_2O + 4h^+ &\rightarrow O_2 + 4H^+ \quad E^0_{ox} = +0.82\ \mathrm{V} \\ CO_2 + e^- &\rightarrow CO_2^{\cdot -} \quad E^0_{red} = -1.90\ \mathrm{V} \end{aligned} \tag{3.1}$$

However, the single electron CO_2 reduction is less probable as it requires a very negative potential, because no protons are involved in stabilizing the CO_2 anion radical. Other, less energy intensive reduction pathways involve both photogenerated electrons and protons, which are the product of H2O oxidation. Possible products of these multi-electron and multi-proton reactions include carbon monoxide (CO), methane (CH_4), formic acid (HCO_2H), formaldehyde (HCHO), and methanol (CH_3OH), Eq. 3.2. Some of protons can combine into H_2 molecules (last reaction in Eq. 3.2), which is the undesirable pathway competing with CO_2 reduction. In the reactions below, standard potentials are shown versus NHE at pH = 7 in aqueous solution, 25 °C, 1 atm gas pressure, and 1 M for solutes.

$$\begin{aligned} CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad & E^0 = -0.24\ \mathrm{V} \\ CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad & E^0 = -0.38\ \mathrm{V} \\ CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \quad & E^0 = -0.48\ \mathrm{V} \\ CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad & E^0 = -0.53\ \mathrm{V} \\ CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \quad & E^0 = -0.61\ \mathrm{V} \\ 2H^+ + 2e^- \rightarrow H_2 \quad & E^0 = -0.41\ \mathrm{V} \end{aligned} \tag{3.2}$$

Among the possible products, CO and formic acid are most easily generated because the formation of these compounds only involves two electrons. Methanol formation is highly desirable due to the potential large market for the photocatalytically-produced methanol in chemical industry and as a fuel. The photocatalytic generation of renewable synthetic methane is also an attractive pathway. However, the CO_2 photoreduction to these compounds involves transfer of multiple electrons, making these reactions mechanistically complex and, therefore, relatively slow. Advanced photocatalysis is required in order to direct the selectivity of the CO_2 photoreduction to desired products. This topic is discussed below, in Sect. 3.3.

3.2 Main Drawbacks

Converting CO_2 and water into synthetic chemical fuels using sunlight mimics biological photosynthesis and, as such, provides an attractive pathway for the reduction of our dependences on fossil fuels by replacing them with synthetic "solar" fuels. The basic idea is known for decades, but the technology for "artificial photosynthesis" of synthetic fuels is still far away from its practical, economically viable implementation. The most fundamental scientific challenge still to be resolved is to perform the multi-electron transfer reactions of photocatalytic H_2O oxidation and CO_2 reduction in a highly efficient way. Current conversion efficiencies are still very low. The most important limiting factors are (1) the mismatch between the solar spectrum and the absorption band of a semiconductor, (2) the poor separation efficiencies of charge carriers, (3) the low CO_2 solubility in aqueous environments, and (4) the competitive hydrogen evolution reaction.

Performing H_2O oxidation and CO_2 reduction simultaneously on a single photoelectrode can be only achieved if the semiconductor band gap is wide enough. Accounting for the electrode overpotential, a practical band gap energy of approximately 3 eV is required for a single photosystem. Unfortunately, this band gap corresponds to a photon energy of the UV range of the solar spectrum. Only 7% of the total energy emitted from the sun lies in the UV part of the spectrum. Much larger part of the spectrum ($\sim$43%) is in the visible range. The remaining fraction is mostly in the near-infrared range (49%) ($\sim$1% is emitted as x-rays, gamma waves, and radio waves). Since sunlight contains only a small fraction of UV irradiation, the use of semiconducting materials with the band gap of $\sim$3 eV leads to a maximum theoretical solar energy conversion of only a few percent.

In order to provide a driving force for charge carrier transport, an overpotential is necessary. As a result, the energy required for CO_2 conversion is greater than the theoretical thermodynamic of the CO_2 photoreduction reaction. This restriction further limits the process efficiency, which is the major bottleneck of practical implementation of the CO_2 photoreduction systems. There are also transport limitations, mostly related to the low CO_2 solubility in water (33.6 mmol/L at 100 kPa of pure CO_2 at 25 °C). Another drawback is a competing H_2O reduction by photogenerated electrons, Eq. (3.2), since the photocatalytic CO_2 reduction is performed in aqueous environments.

Thermodynamically and kinetically, water reduction is more favorable than most of the CO_2 reduction pathways. The reduction potential of water is more positive than the reduction potentials of CO_2 conversion to CO, formic acid, and formaldehyde, Eq. (3.2). From the kinetic viewpoint, the H_2O reduction, which is a two-electron process, is more favorable than the CO_2 reduction pathways that involve multi-electron steps. Unlike the CO_2 reduction, the H_2O reduction is not limited by solubility. To address the problem of the competitive water reduction, the photocatalyst morphology can be modified to change the exposed surface in such a way that this reaction is less favorable kinetically.

Achieving the desired selectivity in the CO_2 photoreduction is very challenging. From the thermodynamic viewpoint, formation of methane (CH_4) and methanol (CH_3OH) is more favorable, because of lower reduction potentials, Eq. (3.2). However, since these reactions involve multiple electron and proton transfers, CH_4 and CH_3OH generation is less favorable kinetically, as compared to the CO_2 reduction to carbon monoxide (CO), formaldehyde (HCHO) and formic acid (HCO_2H). Generally speaking, it is extremely difficult to induce a CO_2 conversion pathway that involves 2–8 electrons and protons reactions to obtain the desired product. Instead of the multi-electron, multi-proton process, the interaction between the photocatalyst surface and absorbed species can undergo a series of single electron processes leading to formation of undesirable products. Therefore, one of the most essential requirements to photocatalytic materials is the ability to generate large amount of electron-hole pairs, while separating charges efficiently at the same time, and providing large amount of active catalytic sites at the interface between the photocatalyst surface and the liquid phase.

In addition to the thermodynamic and kinetic limitations discussed above, there are also numerous challenges related to the design of a photocatalytic cell. The photocatalytic CO_2 reduction cell comprises of several components, which have to be carefully designed in order to optimize the cell performance. The ultimate goal is to maximize the sunlight-to-fuel conversion given the thermodynamic and kinetic constrains related to the photocatalytic CO_2 reduction. The three most essential processes in the photocatalytic CO_2 reduction cell are light absorption, photocatalysis, and the ion transport between the two chambers of the photocatalytic cell.

3.3 Photocatalysis for CO_2 Conversion

The process of the photochemical reduction of CO_2 can be catalyzed homogeneously or heterogeneously. In the homogeneous CO_2 photoreduction, a molecular catalyst is dispersed in a liquid phase. In the heterogeneous photocatalytic reduction of CO_2, a p-type semiconductor surface acts as a photocathode. The catalytic performance of the photocathode can be improved by catalytic nanoparticles dispersed on its surface. The catalytic CO_2 photoreduction could be performed homogeneously (by a dissolved molecular catalyst) or heterogeneously, either by a molecular catalyst attached to the semiconductor photocathode surface, directly by a semiconductor photocathode, or by metal nanoparticles dispersed on a semiconductor photocathode [4].

The main role of a photocatalyst is to provide favorable electron transfer kinetics. It is important to note that not all the electrons reaching the surface participate in CO_2 reduction. Carbon dioxide is a thermodynamically stable, inert compound. Activation of CO_2 molecules require photoelectrons with high reduction potential that can offer driving force for the desired conversion pathway. The reduction potential is a measure of the capability of a chemical specie to gain electrons. Low reduction potential species gain electrons (being reduced), while species with higher (more negative) reduction potentials donate electrons (being oxidized). The reduction of CO_2 require photoelectrons with more negative chemical potential. For the competitive reaction of water oxidation, photogenerated holes with more positive potential level are required.

The heterogeneous photocatalytic reduction of CO_2 using a Pt/TiO_2 photocatalyst is schematically depicted in Fig. 3.2 [5]. The process is initiated by absorption of protons with the energy greater than the semiconductor band gap (Eg). The photon absorption results in the generation of excited photoelectrons in the semiconductor conduction band (CB) and holes in the semiconductor valence band (VB). Once a photo-excited electron-hole pair was created in the bulk of the semiconducting material, it can undergo two alternative processes. The first, desirable pathway is charge separation and migration of the electron and hole to the surface of the TiO_2 particle. The competitive, undesirable pathway is bulk recombination that consumes the electron-hole pair. The photoelectrons that reach the surface participate in the reduction of the CO_2 molecules absorbed at the solid-liquid interface. This process can be greatly accelerated by the presence of catalytic metallic nanoparticles on the semiconductor surface, Fig. 3.2. Water molecules are oxidized by the photo-induced holes that reached the semiconductor surface to produce oxygen and protons; the generated protons participate in CO_2 conversion, Eq. (3.2).

Metal oxides are preferable photocatalysts for CO_2 photoreduction, most notably TiO_2. Several other types of metal oxides have been reported, including ZrO_2, Ga_2O_3, Ta_2O_5, $SrTiO_3$, $CaFe_2O_4$, $NaNbO_3$, $ZnGa_2O_4$, Zn_2GeO_4 and $BaLa_4TiO_{15}$ [1]. These materials have wide band gaps and, therefore, UV active. Metal oxide-based photocatalytic materials are safe to handle, have relatively low cost and provide considerably good stable. The photocatalyst morphology is a very important factor. Recently, advanced nanomaterials such as nanorods and nanotubes have attracted a lot attention due to their large surface area, reduced grain boundaries, and facilitated charge transport paths.

Depositing a co-catalyst on the metal oxide surface, as in the example above (Fig. 3.2), is a common strategy to enhance the CO_2 conversion efficiency and the selectivity to the desired product. Noble metals nanoparticles are known to improve the CO_2 reduction reaction [1]. Metal oxide nanoparticles, on the other hand, are found to accelerate the water oxidation reaction. The role of the co-catalyst is crucial as it provides additional catalytically active sites. Moreover, these catalytic sites typically provide selectivities different from those of the metal oxide semiconductor surface. An additional function of the co-catalyst is to extract the photogenerated electrons from the semiconductor bulk, thus prolonging their lifetime.

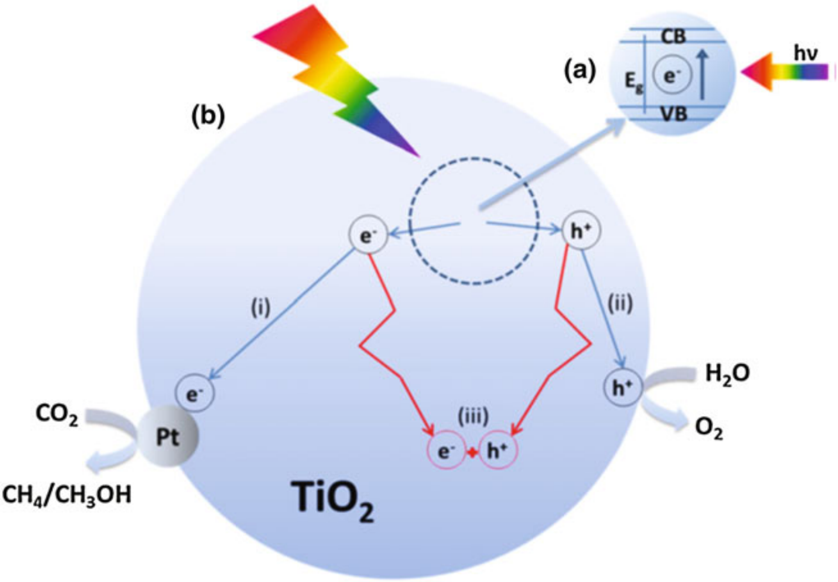

Fig. 3.2 Photoreduction of CO_2 by water using Pt-TiO_2 photocatalyst; photo-excitation in the electronic band structure of the photocatalyst (**a**), and migration of generated electron-hole pairs to the photocatalyst surface, driving redox reactions (**b**) [5]

Electron accumulation on the metal nanoparticle co-catalyst is favorable for the highly desirable multi-electron CO_2 conversion pathways. Metal oxide co-catalyst do not provide catalytic reduction sites, but can improve the performance by extracting the photogenerated holes providing better charge separation and extending, therefore, the lifetime of the photoelectrons. Although it is well known that noble metal co-catalysts can improve the photocatalytic activity significantly, the associated capital cost can prohibit practical applications. Therefore, low-cost co-catalysts, which are not based on noble metals, are preferable. To date, several types of non-noble metal co-catalysts were reported to be active in photocatalytic reactions, including NiO, MoS_2, and WS_2 [1].

Competition with the process of water reduction by the photogenerated electrons (Sect. 3.2) is a great challenge as the photocatalytic CO_2 reduction is carried out in aqueous environment with water molecules serving as electron donors. This drawback can be addressed by controlling the photocatalyst morphology via modifying the exposed facets and introducing new reaction sides. The idea is that some particular atom arrangements on the photocatalyst surface can be more favorable to absorption of CO_2 molecules than to absorption of H_2O molecules.

Reducing the photocatalyst particle size or, more generally, increasing the specific surface area of the photoelectrode can improve the efficiency of the CO_2 photoreduction simply by providing more active sites for adsorption of the CO_2 molecules. Smaller particle size is also beneficial because it provides shorter distances for transferring charge carriers (electron and holes) to the photocatalyst surface. In this sense, novel nanomaterials such as nanotubes and nanorods provide a great promise to improve the efficiency due to their large specific surface area and unique charge transfer pathways.

3.4 Photochemical Reactor Design

In order to perform the photocatalytic CO_2 reduction on a practical scale, a photocatalyst has to be incorporated in a photocatalytic device, a photoreactor. The photoreactor is a multifunctional device that serves several functions including mass transfer, radiation transfer, charge separation, electron and proton transfer, and product collection. Optimal photoreactor design is crucial to improve the CO_2 photoreduction efficiency. In the most basic configuration, the semiconductor photocatalyst micro- or nanoparticles are suspended in water. In this arrangement, each semiconductor particle acts as a reaction center. In a typical laboratory installation, a suspension containing the photocatalyst particles is continuously mixed using a magnetic stirrer. Light irradiation is supplied using a UV lamp immersed into the suspension and CO_2 is continuously bubbled through the suspension, Fig. 3.3 [6].

Photobioreactor scale-up requires more efficient light distribution, which can be done using multiple optical fibers, Fig. 3.4 [6]. In the example shown, the photocatalyst (TiO_2) was coated on the outer walls of the optical fibers and the fluid was directed to form a plug-flow velocity distribution. The optical fibers delivered light uniformly within the Photobioreactor, directly to the surface of the photocatalyst. When light travels inside the fiber, part of the light is reflected and transmitted along the fiber and the rest of the light penetrates and excites the photocatalyst layer. Such

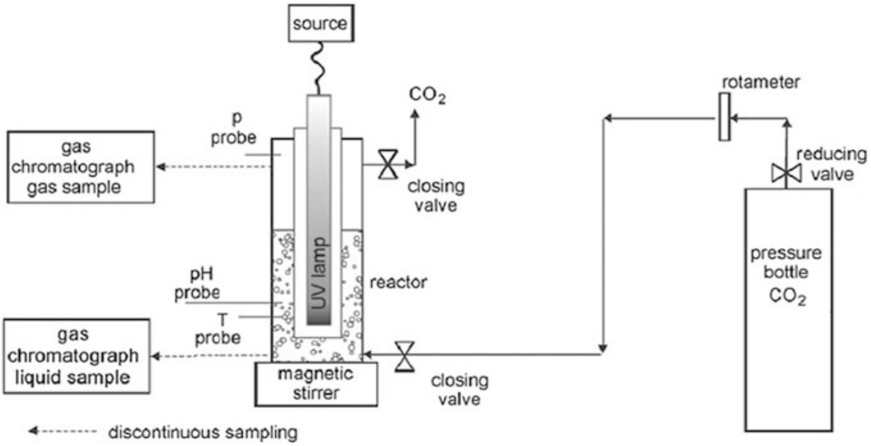

Fig. 3.3 Batch-type photocatalytic reactor with suspended catalyst [6]

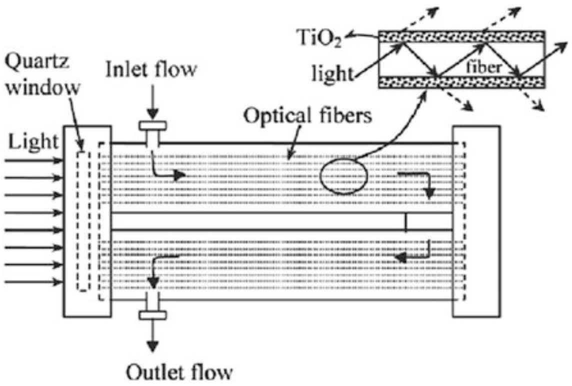

Fig. 3.4 Monolith optical-fiber photocatalytic reactor [6]

configuration provides advantages in terms of the simultaneous control of radiative transfer and mass transport by minimizing the transfer distance. The small distance between the optical fibers lowers the mass transfer resistance by reducing the diffusion length of reactants. The use of multiple optical fibers allows for improved light distribution within the reaction medium. These improvements can dramatically increase the photoreactor power density, thus significantly lowering the capital investment and operational costs.

In the two configurations described above, the photocatalyst (as either a particle or a layer) acts as a reaction center where both the CO_2 reduction and H_2O oxidation are carried out on the same surface. Another option is to separate these two processes using a proton exchange membrane, Fig. 3.5 [3]. In this design, the photoreactor has a configuration of a photoelectrochemical cell (PEC) divided into

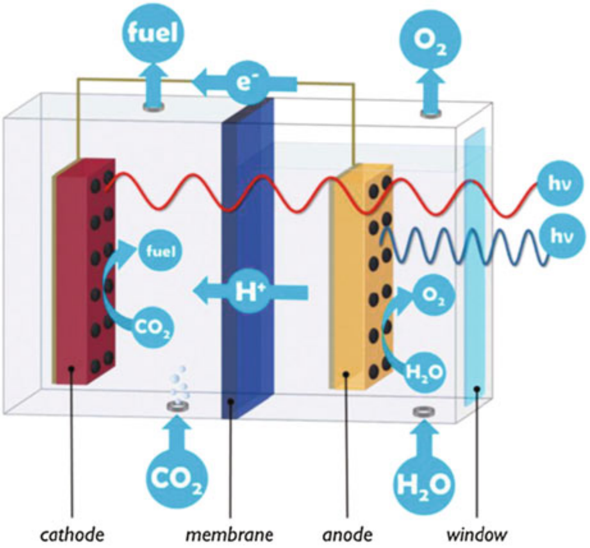

Fig. 3.5 Conceptual drawing of a liquid-phase, two-compartment PEC cell with photoanode, photocathode and proton exchange membrane. The pathways of light, reagents, protons, electrons and reaction products are indicated [3]

two compartments by a proton exchange membrane (PEM), e.g., Nafion, the same type of membrane which is used in PEM fuel cells (PEMFC). Both electrodes are photoactive, but for different reactions. The important advantage of this configuration is that the membrane directs protons towards the CO_2 reduction photocathode, reducing the chance of the back reaction between protons and oxygen.

Electron transport is achieved through an external wire, Fig. 3.5. When the electrodes are connected externally, current-collecting contacts are required, as well as good electronic connection between the semiconductor electrode and the catalytic sites responsible for reduction and oxidation reactions. Unfortunately, photocatalytically active materials are typically not good electrical conductors. To improve the conductivity, the semiconductor morphology has to be carefully designed at nano-scale to insure high quality of the electrode material. Ionic transport also imposes limitations on the overall cell performance. Although proton exchange membranes (PEM) are in use for a long time for fuel cells and their proton conducting properties were optimized, there is an inherent limitation of proton transport through a membrane, which is typically orders of magnitude slower than the transport of electrons through a metallic wire. In the configuration shown in Fig. 3.5, protons have to diffuse through the electrolyte before they reach the membrane surface, imposing additional transport limitation. In a liquid electrolyte, operation at low pH is an obvious approach to increase the proton conductivity. However, changing the acidity of the liquid electrolyte, which serves as a reaction medium as well, affects the redox properties of the catalytic centers on the surface of the semiconductor electrode.

The proton transfer distance is a crucial, limiting factor in the photoelectrochemical cell performance. To eliminate the proton transport through the liquid electrolyte, the photocatalyst can be deposited directly on the membrane, similar to the membrane-electrode assembly (MEA) used in PEM fuel cells. Moreover, it is possible to eliminate the need in wiring by the use of a dual-function electrode [4]. Fabrication of such electrode assembly is a challenging task. On the other hand, the simple structure of the cell could be beneficial for practical applications. The major challenge for this type of photoreactor is identifying a photocatalyst that has low overpotentials for both CO_2 reduction and H_2O oxidation. It is preferable that such catalyst would be based on earth-abundant materials rather than on noble metals. The stability of a proton-exchange membrane in such configuration is also a concern.

Any type of photochemical reactor will require the input of light irradiation. Therefore, the cell casing should be transparent or contain a window to allow solar illumination. For that purpose, window materials and anti-reflection coatings, which were already developed for photovoltaic panels, can be used. There is an additional requirement for these materials for the use in the CO_2 photoreduction: they have to be chemically stable while in contact with the electrolyte. To maximize the irradiation efficiency, any material located on the pathway between the light source and the semiconductor photocatalyst should be maximally transparent. This requirement restricts the choice of materials for a photochemical reactor. For the configuration shown in Fig. 3.5, when both photoelectrodes contain semiconductors, the photoanode should be transparent to longer wavelengths that can be absorbed by the photocathode. This requirement implies that the photoanode has to have the wider band gap. Alternatively, the cell can be illuminated from both sides, but this approach complicate the design. One possible solution is the use of optical fibers, as in the configuration shown in Fig. 3.4. Another option is nanostructuring that can provide novel materials for an optimal absorption of the incident light in a certain wavelength range. Still, there are always drawbacks such as bubble formation on the surface of the semiconductor photoelectrode and parasitic light absorption by co-catalysts based on metal nanoparticles.

3.5 Operational Constraints and Feasibility of Practical Operations

Sunlight is an abundant renewable energy source. However, the diffuse and transient nature of solar energy necessitates its conversion into other forms of energy for storage and transportation. Currently, the most established method for solar energy conversion is photovoltaics. Commercial photovoltaics cells based on silicon single junction are typically operated at 12–20% efficiencies of the solar energy conversion into electricity; the theoretical limit exceeds 40%. Considering that the solar irradiation is freely available, photovoltaics technology has a great potential. However, using electricity as an energy carrier requires extensive, high capital cost infrastructure for transportation and storage. Storing sunlight in chemical bonds of synthetic chemicals and fuels is an attractive alternative, in particular if CO_2 is utilized as a source of carbon. However, making the photocatalytic reduction of CO_2 a practical, economically viable technology is very challenging.

There are several fundamental limitations in the process of the CO_2 photoreduction. Altogether, these restrictions result in very low sunlight conversion efficiencies. Several directions are currently being explored. First, the development of novel heterostructured photocatalysts is of most essential, paramount importance. Highly efficient photocatalysts have to be active, selective to CO_2 reduction, and stable at the same time. Among the ways to improve the photocatalyst performance, the addition of a co-catalyst has been proved to be an effective approach. However, the mechanisms of the co-catalyst action should be better understood in order to guide further developments in this direction. The design of a highly efficient photochemical reactor is not less important and vital for practical applications. To sum up, once can conclude that the technology of the photocatalytic reduction of CO_2 is rather challenging to implement on a practical scale, at least in its current state. Further efforts in the photocatalyst development, photochemical reactor design, and system integration are required.

Even if the performance of a lab-scale photochemical reactor could be significantly improved, the widespread commercialization of the CO_2 photoreduction would be still very challenging. The reason is that providing CO_2 in efficient way is a challenging task. The use of atmospheric CO_2 is probably not an option due to the low CO_2 concentration in the atmosphere ($\sim$400 ppm), though this approach could be considered for localized, small scale applications. It is much more practical to utilize industrial and agricultural waste streams containing CO_2, such as combustion flue gases, biogas and landfill gas. However, such feedstocks are not pure CO_2 streams and it is not clear how other compounds and impurities will affect the photochemical cell performance. Also, using diluted streams will require larger photochemical reactors, therefore higher capital and operational costs. There is always an option of pre-concentration and purification, to increase the CO_2 content and to remove the impurities that can poison the photocatalyst, but it will add additional costs to the process. Even if a pure CO_2 stream can be provided, the cell performance will be still largely limited by the low solubility of CO_2 in water ($\sim$34 mmol/L under pure CO_2 at standard temperature and pressure).

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Chapter 4
Biological Conversion of CO_2

Utilizing CO_2, as a concept of converting a greenhouse gas into a value-added feedstock, has gained considerable attention in recent years. In a search for sustainable and economically viable routes, scientists and engineers mainly focused on chemical conversion methods, either thermocatalytic, electrocatalytic, or photocatalytic. However, photosynthetic organisms have been converting CO_2 and water into organic matter over more than two billions of years. Over this vast period of time, the sophisticated and, at the same time, robust mechanisms of CO_2 fixation into complex biological molecules have evolved. Among various valuable chemicals that can be produced through the biological CO_2 conversion, probably the most notable ones are bio-alcohols and bio-diesel. As compared to the CO_2 streams currently utilized in the chemical industry (mostly synthesis of urea and methanol and production of pigments and carbonates) totaling more than 100 Mt per year worldwide, terrestrial and marine photosynthetic organisms convert more than 100 Gt per year of CO_2 into biomass. This huge resource could potentially become a disruptive technology for CO_2 conversion into renewable fuels and chemicals.

However, growing and harvesting biomass is energy intensive. Converting biomass into useful products also requires high capital investment and operating costs. Biological photosynthesis is a low efficiency process. While artificial devices (photovoltaic cells) can convert solar energy directly into electrical power with efficiencies ranging from 10 to 40%, the photosynthesis efficiency is usually less than 1%! Such low efficiency of sunlight conversion into biomass implies very large areas required to collect solar irradiation. On the other hand, biological organisms evolved over billions of year and already have robust biochemical machinery for converting CO_2 into very specific products. Moreover, gen engineering, metabolic engineering, and synthetic biology provide tools for improvement of the photosynthesis efficiency.

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A classical approach for biofuels production is to cultivate and harvest biomass (e.g., corn, sugarcane, or lignocellulose) and then to extract a compound of interest through downstream processing and separation. For example, bioethanol is separated by distillation from a mixture of mainly water and ethanol, which is a product of fermentation. Unfortunately, harvesting, transportation, and processing of cultivated biomass require significant investments in terms of both infrastructure and operating costs, making biofuels relatively expensive. Still, such technologies are well developed and became an integrated part of transportation fuels infrastructure in many countries around the world.

An alternative pathway is to bypass the biomass processing and fermentation using CO_2-fixing microorganism that produce the desired biofuel directly, in a controllable manner within a confined environment, i.e., a bioreactor. In this approach, biological CO_2 fixation does not necessary depend on sunlight. Light irradiation can be provided using an artificial source. Moreover, the light reactions that transform the energy of photons into molecular energy carriers (ATP and NADPH) can be separated from the dark reactions that reduce CO_2 to carbohydrates. Such approach is different from the natural photosynthesis in which both light and dark reactions occur in the same cell of a biological organism, either unicellular or multicellular. For sustainability, the energy needed to drive the artificially-controlled biological CO_2 reduction has to originate from the solar irradiation. For practical applications, the process of the CO_2 fixation using microorganisms should be performed in a controllable manner within a bioreactor, or a photobioreactor.

This chapter focuses on recent advances in biological fuels and chemical production via active utilization of concentrated CO_2 streams using microorganisms. It is important to differentiate this approach from the conventional biofuel production in which plants (or algae grown in open ponds) extract CO_2 from the air. Photosynthetic processes using algae and cyanobacteria are outlined, as well as non-photosynthetic processes using lithoautotrophic organisms that derive energy from reduced compounds of mineral origin, such as *Ralstonia eutropha*. Challenges and opportunities are discussed.

4.1 Biological Fixation of CO_2 Using Microorganisms

A variety of compounds can be directly generated by autotrophic microorganisms, including ethanol, butanol, alkanes and lipids. Autotrophs produce complex organic compounds using sunlight (photosynthesis) or chemical reactions (chemosynthesis). Metabolic pathways are summarized in Fig. 4.1 [1]. Among the most attractive microorganisms are microalgae that are capable of accumulating enormous amounts of lipids, making them a perfect candidate for direct biodiesel production. It has been proposed that algal-based biofuels has a potential to partially replace petroleum but their production costs are still too high for widespread commercialization.

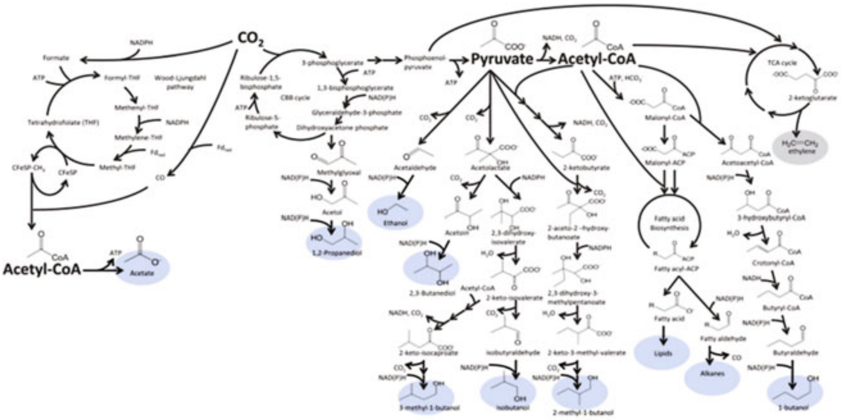


Fig. 4.1 Metabolic pathways for biofuels and biochemicals synthesis using autotrophic microorganisms. CBB cycle stands for Calvin–Benson–Bassham cycle, TCA cycle denotes tricarboxylic acid cycle, and ACP stands for acyl carrier protein [1]

Research in this direction has mainly focused on isolating and selecting microalgae species with highest lipid accumulation levels, fast growth rate, and high efficiencies of light utilization. Recent developments in genome sequencing and molecular biology might make possible metabolic engineering in the near future. However, metabolic engineering of eukaryotic organisms is very challenging.

Because cyanobacteria are prokaryotic microorganisms, their genetic engineering is less difficult. Moreover, fuel and chemicals can be produced by these photosynthetic organisms directly, without going through the lipid synthesis pathway. Recently, synthetic pathways were introduced into the cyanobacteria metabolism generating a variety of chemicals including ethanol and butanol. Cyanobacteria also produce a variety of alkanes, Fig. 4.1; the corresponding genes have been recently identified [1]. Although the metabolic engineering of cyanobacteria is simpler than that for microalgae, it is still challenging as compared to other, already utilized on industrial scale, prokaryotes (bacteria).

Organisms capable of CO_2 assimilation are not restricted to photosynthetic organisms (plants, algae, and cyanobacteria). In Fig. 4.2, the most extensively studied CO_2-utilizing microorganisms that could potentially be implemented in industrial-scale bioprocesses are summarized [2], including proteobacteria, clostridia, and archaea. These microorganisms have different CO_2 fixation pathways and their own inherent advantages and disadvantages with respect to their implementation for CO_2 utilization. Concerns include growth characteristics, thermal stability, and tolerance to inhibitors. Also, most of these microorganisms have to be optimized first for production of desired chemical. Tools include genetic and metabolic engineering and synthetic biology.

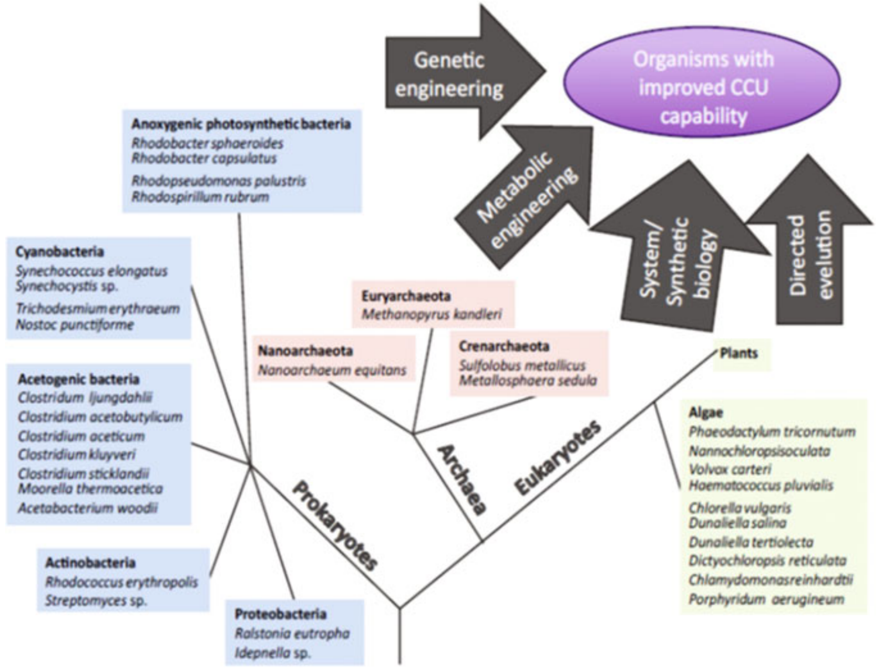


Fig. 4.2 A summary of organisms capable of CO_2 fixation [2]

4.2 Synthetic Biology

Synthetic biology is an interdisciplinary field of research that combines numerous disciplines including biotechnology, systems biology, molecular biology, genetic engineering, metabolic engineering, as well as biophysics and computer engineering. Synthetic biology integrates the abovementioned disciplines to build artificially-modified microorganisms, with the ultimate goal to build a fully synthetic biological system that is to create life! With this ultimate future goal in mind, researches look for ways to program biological organisms in such a way that they fulfill the desirable functions, e.g., produce a synthetic chemical.

Microorganisms have many constrains that often restrict their direct application for production of synthetic fuels. These limitations include slow growth rate, demanding cultivation conditions, low product yield etc. With the help of synthetic biology, it could be possible to engineer microorganisms by alteration of their biochemical mechanisms, or introduction of new metabolic pathways to maximize the production of the desired compound. With the recent advances in protein, genetic and metabolic engineering and in system biology, synthetic biology could become a powerful tool for enhancing desirable biological processes to ultimately make them economically viable. In recent years, synthetic biology has become a relevant engineering tool for biological conversion of CO_2 into synthetic renewable fuels.

Some notable examples include *Escherichia coli* and *Saccharomyces cerevisiae* [2]. The Gram-negative, heterotrophic bacterium *Escherichia coli* remains one of the most studied microorganisms for biological conversion of CO_2, due to simple cultivation conditions, high growth rate, and, particularly, an extensive library of available genetic engineering tools. By expressing certain enzymes in *Escherichia coli*, it is now possible to biologically fix CO_2. Due to genetic engineering, it is now also possible to convert photosynthetically accumulated biomass into valuable chemicals, e.g., brown algae. One of the main problems with utilization of algae is that conventionally used microorganisms are not able to metabolize the polysaccharide alginate (one of the main components of the cell walls of brown algae). By encoding expression of the enzymes responsible for alginate metabolism in *Escherichia coli*, it is possible to produce ethanol from the brown algae biomass [2]. Among the most widely investigated eukaryotic model microorganisms is the species of yeast *Saccharomyces cerevisiae*, for which synthetic expression of the CO_2 fixing enzymes was recently reported [2].

4.3 Biological Electrofuels

An ideal process for renewable chemicals generation should directly use sunlight energy and carbon from CO_2 to synthesize renewable fuels and platform chemicals. Photosynthetic microorganisms already have this capability. In photosynthesis, light reactions that convert solar irradiation to biochemical energy are coupled to dark reactions that convert CO_2 into complex molecules using that energy, within a single biological cell. The idea of biological electrofuels is based on separation of the light and dark reactions in space by replacing the biological light reactions with artificial devices such as photovoltaic cells. Photons (light irradiation) are first converted into electrons (photovoltaic electricity) that drive the biological CO_2 conversion using metabolically engineering pathways.

One of the very important advantages of this approach is that the intermittent solar (or wind) energy converted to electricity is utilized to drive the dark reactions, as an alternative to electricity storage in batteries. The dark reactions can be then performed in a bulk, large-scale bioreactor, eliminating the need in photobioreactors that suffer from light transfer limitations and, therefore, limited to medium-to-small scale. Moreover, production of biological electrofuels could potentially improve the efficiency of conversion of solar energy into fuels and chemicals. The reason is that photosynthesis has very low efficiency converting only a small fraction of sunlight (3–6%) into biomass. On the other hand, artificial devices such as photovoltaic cells can convert solar irradiation into electricity with efficiencies ranging from 10 to 40%. Therefore, the land requirement could be dramatically reduced.

Another advantage of biological electrofuels is that biological fixation of CO_2 is not limited anymore to photosynthetic organisms. Lithoautotrophic microorganisms (microbes that derive their energy from reduced compounds of mineral origin) can be explored now. Lithoautotrophs have diverse physiological features and a variety of metabolic pathways, providing multiple avenues for production of renewable synthetic fuels and chemicals. While photosynthetic microalgae and cyanobacteria exclusive utilize the Calve–Benson–Bassham cycle for CO_2 fixation, lithoautotrophic microorganisms utilize a variety of CO_2 fixation pathways that also have higher efficiency, Fig. 4.2. For example, the Wood–Ljungdahl pathway is used by some bacteria and archaea to utilize hydrogen as an electron donor and CO_2 as an electron acceptor and as a building block for biosynthesis, reducing CO_2 to formic acid and formyl and methyl groups. An interesting fact is that some recent studies suggest that this pathway was used by the last universal common ancestor (LUCA) of all biological organisms.

Transfer of electrons to the microbes can occur either directly from an electrode or indirectly through an electron mediator, Fig. 4.3 [1]. Early investigations have shown that some microorganisms, e.g., *Geobacter metallireducens* and a methanogen *Methanobacterium palustre*, are able to accept electrons directly from electrodes, making it possible to grow an electron-accepting microbial biofilm on a cathode. More recent studies have identified a broad range of microorganisms, including some *Sporomusa* species, *Clostridium* species, and *Moorella thermoacetica*, as able of accepting electrons directly from the electrode with high current efficiencies and relatively low overpotentials, producing compounds such as acetate from CO_2 [1]. All these developments indicate the potential for the direct electron transfer approach for generating synthetic fuels from renewable electricity and CO_2.

Alternatively, electrons can be delivered to the microbes dispersed in an aqueous solution via electron carriers, Fig. 4.3. From a practical point of view, these carriers should be low-cost, environmentally benign molecules, such as hydrogen (H_2) and formic acid (HCOOH). Hydrogen could be in principal generated via the

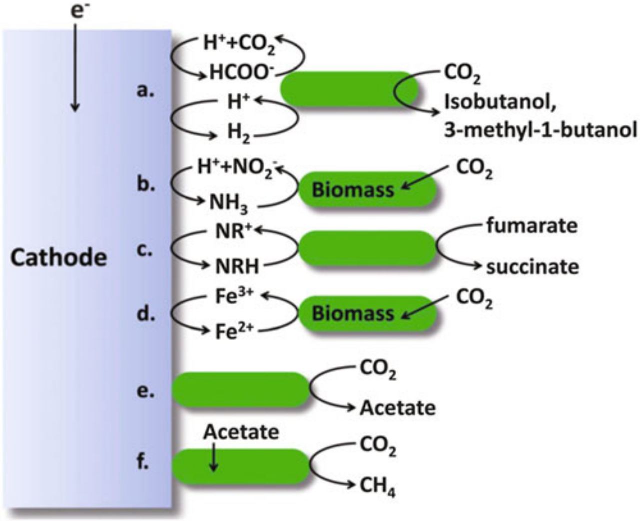
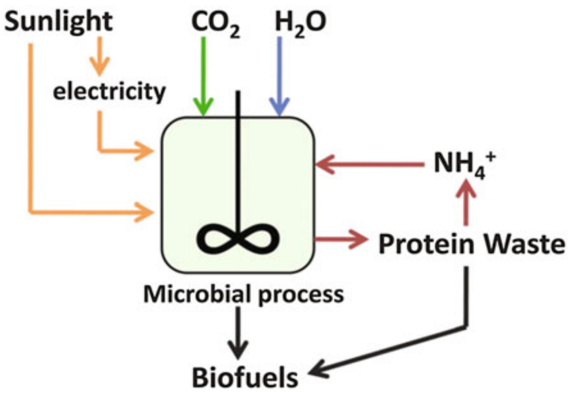


Fig. 4.3 Direct and indirect methods to transfer electrons to the microorganisms [1]

Fig. 4.4 Nitrogen recycling for a biofuel production system [1]



photocatalytic water splitting and even in situ, i.e., within the bioreactor containing the microbial culture. The economics look promising, as the cost of renewable H_2 (currently ~4–7 $/kg) is approaching that of the H_2 produced via natural gas reforming (~1–2 $/kg). However, hydrogen is probably not the best choice because of its low solubility in aqueous environments that causes quite significant mass transfer limitations. Formic acid is probably a better choice as this chemical is highly soluble in water and can be also easily handled as it is liquid under standard conditions. Also, the formate-based metabolic pathways are utilized by a large variety of microorganisms. Generally speaking, it is highly desirable to identify electron carriers that are low-cost, non-toxic, and easy to handle.

Although biological electrofuels, if implemented on large scale, can potentially create a semi-artificial carbon cycle significantly reducing CO_2 emissions, closing the nitrogen cycle remains a challenge. Among many nutrients required to support microbes, ammonium (the reduced form of nitrogen) is the one required at largest amounts, as it is a necessary ingredient for the synthesis of amino acids (building blocks of proteins) and nucleotides (building blocks of RNA and DNA). Some microbes, e.g., cyanobacteria, have the ability to fix N_2 from the air. However, most of microorganisms relevant to biological electrofuels applications cannot fix N_2. In the agriculture, ammonium generated in large scale industrial plants (via the Haber–Bosch process) is supplied through fertilizers. To close the nitrogen cycle in the biological electrofuel generation process, the residual biomass can be used as a source of nitrogen, Fig. 4.4. This approach allows for the use of renewable sources such as algae biomass.

4.4 Biological Hydrogenation of CO_2

A general scheme for the production of biological renewable synthetic fuels from H_2 and CO_2 is shown in Fig. 4.5. Hydrogen is activated by the enzyme hydrogenase that catalyzes the reversible oxidation of molecular hydrogen into protons in the presence of suitable electron acceptors (A) and donors (D):

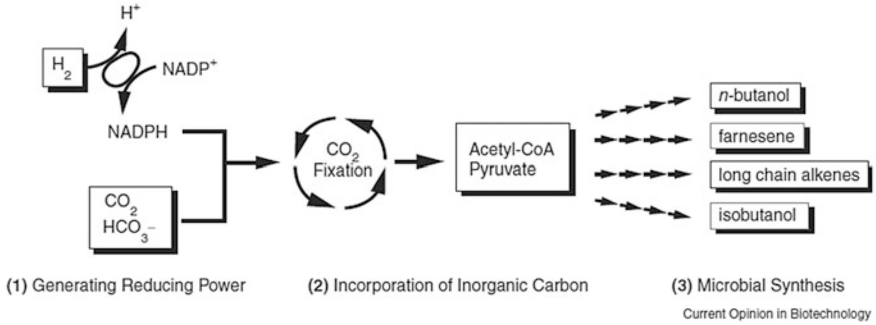


Fig. 4.5 Schematic drawing of the primary biochemical modules involved in electrofuel formation. Intracellular reducing power is generated from hydrogen gas via hydrogenase enzymes. Carbon fixation cycle incorporates inorganic carbon into central metabolism via key intermediates. Microbial synthesis of the target fuel molecule proceeds via endogenous and/or engineered metabolic pathways [3]

$$\begin{aligned} H_2 + A_{ox} &\rightarrow 2H^+ + A_{red} \\ 2H^+ + D_{red} &\rightarrow H_2 + D_{ox} \end{aligned} \tag{4.1}$$

Hydrogen oxidation is coupled to the reduction of electron acceptors such as oxygen, nitrate, sulfate, fumarate, and, importantly, CO_2. The proton reduction reaction is coupled to the oxidation of electron donors such as ferredoxin, disposing excess electrons in cells, a process essential in pyruvate fermentation, Fig. 4.5. Hydrogenases can be categorized by the metal atoms in their active sites into [NiFe]-hydrogenases, [FeFe]-hydrogenases, and [Fe]-hydrogenases [3]. The types of the hydrogenase and the electron carrier is very important, since the CO_2 fixation pathway needs to coordinate acquisition of reductant with carbon flux.

One of the promising directions is the use of methanogens, the microbes that produce methane (CH_4) as a metabolic byproduct in anaerobic conditions. These microorganisms (uniquely belonging to the domain of *archaea*) are common in wetlands, marine sediments, and the digestive tracts of animals. Methanogens are known to have the capability to utilize CO_2 as an electron acceptor and some of these microorganisms can produce CH_4 from a mixture of H_2 and CO_2 without any source of organic carbon, utilizing H_2 as an electron donor [4], Fig. 4.6. The overall reaction of the biological conversion of CO_2 can be summarized as follows:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{4.2}$$

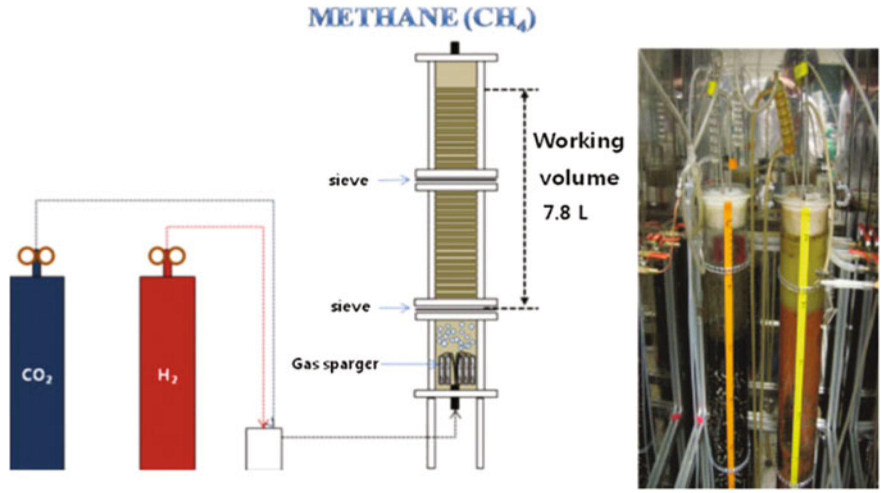


Fig. 4.6 Experimental set-up for biological conversion of CO_2 to CH_4 in a fixed bed bioreactor [4]

4.5 Challenges and Opportunities

The availability of a vast array of CO_2-utilizing microorganisms and our ability to modify these microorganisms via tools such as genetic engineering, metabolic engineering, and synthetic biology provide the opportunity for generation of a large variety of bio-based products while utilizing waste streams containing CO_2. This pathway is a sustainable alternative to the current fossil fuel-based chemical industry. However, many challenges have to be overcome first in order to make the biological routes of CO_2 fixation economically viable and ready for widespread commercialization. To achieve this goal, scientists, engineers, and governments have to collaborate. Engineering is required in order to scale-up the laboratory proof-of-concept to the industrial scale. Governmental involvement is crucial to provide the infrastructure and policies that will allow practical realization.

Currently, probably the most economically viable option for the biological fixation of concentrated CO_2 streams is production of biofuels from microalgae. A significant progress has been already achieved in engineering large-scale cultivation of microalgae. However, most of efforts focused on algae growth in open ponds, thus using atmospheric CO_2 as a source of carbon. While that approach is definitely of high relevance for the sustainable future, this book focuses on utilization of concentrated CO_2 streams, not atmospheric CO_2. For same reason, the discussion of bioethanol production from crops such as corn and sugarcane is omitted herein. Before continuing the discussion on the implementation of

CO_2-fixing microorganisms in confided devices (bioreactors), it is worth to mention that the inherent disadvantage of the use of open ponds for microalgae growth and of agricultural cultivation of crops is large land requirement. The reasons are the low concentration of CO_2 in the atmosphere, the slow rate of plants growth, and the low biomass concentrations in open ponds.

Another, more relevant to the discussion herein, option for microalgae growth is the use of photobioreactors. While open ponds are simple to design and construct, they require large surface area, have low biomass productivity, and suffer from contamination. Microalgae cultivation in a confined environment using photobioreactors resolve these problems but capital investment and operating costs are high, affecting the production cost of the biofuel. Still, photobioreactors allows for utilization of concentrated CO_2 streams such as industrial flue gases. One of the major challenges in the design of photobioreactors is the efficiency of light transfer. Oxygen poisoning and insufficient heat removal are also concerns. Insufficient irradiation results in poor growth, while excessive light intensity induces photoinhibition. Cyanobacteria can be also cultivated in photobioreactors. Readers interested in more details on the design of photobioreactors are referred to some excellent reviews on this subject [5–7].

Much less progress has been achieved in process engineering of the biological CO_2-fixation routes based on lithoautotrophic microorganisms. So far, the majority of research work done was on a lab-scale proof-of-concept, not considering the practical aspects of large-scale implementation. Theoretically, it should be possible to grow the lithoautotrophic microbes in bulk bioreactors if H_2 and CO_2 could be directly utilized. Gases could be simply bubbled through a dispersed culture or a fixed bed with immobilized microbes. However, a lot of work needs to be done in order to optimize cultivation conditions and maximize the yield of the desired product. Any new identified biological route for conversion of CO_2 into a fuel or chemical should be assessed for its feasibility of practical implementation. The eventual translation into a viable, large-scale process is not straightforward, neither necessary successful.

Regardless the type of the biological CO_2 conversion, some common design considerations have to be accounted for successful implementation. First of all, the appropriate strain selection is crucial, just as catalyst selection is crucial for thermo-, electro-, and photo-catalytic non-biological routes. Parameters such as cell density, growth characteristics, CO_2 fixation rate, product type and yield etc. have to be carefully considered. Second, a proper choice of bioreactor has to be made. Similar to non-biological pathways, options include batch bioreactors and continuous operation using continuous stirred tanks, fixed bed bioreactors, and photobioreactors. For biological electrofuels, a bioreactor should be also designed in such a way that electrons are efficiently supplied to CO_2-fixing microorganisms. In addition to technological aspects, there also critical factors related to research funding, governmental policies, and incentives for CO_2 utilization.

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Closing Remarks

Since the beginning of the Industrial Revolution, the rate of the human-made changes of the environment has increased tremendously. At some point, hopefully not too late, the humanity will have to address this issue on a large, world-wide scale. Among other contributions to the rapidly changing environment, the extensive use of fossil fuels is one of the most significant ones. The accelerating emission of CO_2 to the atmosphere is becoming an important factor affecting the climate of the planet Earth, most profoundly through the contribution to the Global Warming. But this is not the only concern. Although the humanity is not yet running out of fossil fuels, they are limited in supply and will be eventually depleted, probably in quite near future. Fossil energy accumulated throughout tens and hundreds millions years is being burnt out in just moments on a geological time scale.

Among possible solutions for the reduction of CO_2 emissions is the CO_2 conversion into Synthetic Renewable Fuels, which will also reduce our dependence on fossil fuels. This book outlined four major directions in the utilization of CO_2 as a feedstock for the chemical industry. The three among these pathways are purely synthetic: thermocatalytic, electrocatalytic, and photocatalytic. All of them rely on the use of catalysis to accelerate reaction rates. The fourth pathway is semi-artificial as it relies on microorganisms. All four pathways can be based on renewable energy sources to provide the energy required for the CO_2 molecule activation, either directly or indirectly. Opportunities are large but so are the challenges. The eventual solution will probably rely on combination of various conversion pathways, creating a diversity of the renewable energy storage and distribution routes.

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