Catalysis Today 148 (2009) 191–205

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Opportunities and prospects in the chemical recycling of carbon dioxide to fuels[☆]

Gabriele Centi [a,b,*], Siglinda Perathoner [a,b]

[a] *Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, Università di Messina, Salita Sperone 31, 98166 Messina, Italy*
[b] *CASPE (INSTM Laboratory of Catalysis for Sustainable Production and Energy), Salita Sperone 31, 98166 Messina, Italy*

ARTICLE INFO

Article history:
Available online 8 August 2009

Keywords:
Carbon dioxide
Methanol
Syngas
Hydrogenation
Reaction with hydrocarbon
Photo and photoelectrochemical conversion

ABSTRACT

This review analyses the opportunities and prospects in the chemical recycling of carbon dioxide to fuels, as a complementary technology to carbon sequestration and storage (CSS). It is remarked that the requisites for this objective are (i) minimize as much as possible the consumption of hydrogen (or hydrogen sources), (ii) produce fuels that can be easily stored and transported, and (iii) use renewable energy sources. From this perspective, the preferable option is to produce alcohols (preferably $\geq$C2) using solar energy to produce the protons and electrons necessary for the reaction of CO_2 reduction. It is evidenced, however, that this is still a long-term objective, even if already some good advances in this direction exist. The different topics discussed in the review include CO_2 (i) reverse water–gas shift and (ii) hydrogenation to hydrocarbons, alcohols, dimethyl ether and formic acid, (iii) reaction with hydrocarbons to syngas, (iv) photo- and electrochemical/catalytic conversion, and (v) thermochemical conversion. Other relevant options, such as the use of micro-algae or other bio-catalysis based processes, or the use of microwave and plasma processes are instead not addressed. Therefore, the area of carbon dioxide conversion to fuels and chemicals is a very active R&D sector, and it is anticipated that it represents a challenging possibility for companies to develop complementary strategies to CSS to reduce greenhouse gas emissions.

1. Introduction

Carbon dioxide is turning image recently and there are increasing attempts to consider it a resource and a business opportunity rather than a waste with a cost of disposal [1–3]. Increasing amounts of low-cost and relatively pure CO_2 will be soon available from current and planned plants for carbon sequestration and storage (CSS). Therefore, CO_2 will be a feedstock of nearly zero (or even negative) cost for conversion to fuels and chemicals, in addition to the many benefits in terms of positive image for companies, which will adopt politics of reduction of CO_2 emissions. The other factor stimulating the interest in CO_2 chemical recycling is the presence of many emissions for which the CSS option is unsuitable: distance from safe sequestration sites, diluted concentration of CO_2 in the emitting gas, small-medium size sources, and uncertain on the impact on environment. It can be roughly estimated that about 5–10% of the total CO_2 emissions (about 30 Gt worldwide in 2008 [4]) could be suited for production of fuels and chemicals [1], e.g. about one order of magnitude higher than actual use of CO_2 in industry.

The use of CO_2 as a building block in organic syntheses to obtain valuable chemicals and materials has been discussed in many reports and review articles [5–13]. Currently, the utilization of CO_2 as chemical feedstock is limited to a few processes: synthesis of urea (for nitrogen fertilizers and plastics), salicylic acid (a pharmaceutical ingredient), and polycarbonates (for plastics). However, the actual use corresponds to a few percentage of the potential CO_2 suitable to be converted to chemicals. Therefore, a chemical recycling of CO_2 may significantly contribute to a reduction of its emissions only when the target products are components for the fuel pool, which worldwide consumption is two order of magnitude higher than that of chemicals. The main products of CO_2 conversion must be fuels to reduce CO_2 emissions significantly and to create great economic value, although some of them (methanol, ethanol, etc.) could be considered in the double role of fuel and chemical. In addition, valorisation of carbon dioxide emissions could be one important part of the general strategy for reducing CO_2 emissions and push chemical and energy companies towards a more sustainable use of the resources [14,15].

There are different options to convert CO_2. Hydrogenation of CO_2 to form oxygenates and/or hydrocarbons are the most intensively investigated area of CO_2 conversion. Methanol synthesis from CO_2 and H_2 has been investigated at the pilot plant stage

---

[☆] Plenary lecture at ICCDU-X (10th International Conference on Carbon Dioxide Utilization, May 17th–23rd, 2009 in Tianjin (China)).

[*] Corresponding author at: Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, University Messina, Salita Sperone 31, 98166 Messina, Italy.
Tel.: +39 090 6765609; fax: +39 090 391518.
E-mail addresses: centi@unime.it (G. Centi), perathon@unime.it (S. Perathoner).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.07.075

with promising results. The alternative possibility is the production of DME, a clean-burning fuel that is a potential diesel substitute. Ethanol formation, either directly or via methanol homologation, or the conversion of CO_2 to formic acid are also potentially interesting routes. Methanol, ethanol, and formic acid may be used as feedstocks in fuel cells, providing a route to store energy from CO_2 and then produce electricity.

Hydrogenation of carbon dioxide to hydrocarbons consumes much more hydrogen (per unit of product) than formation of oxygenates. Therefore, this route is valuable in principle only when hydrogen is made mainly from renewable or non-fossil resources, but other thermodynamic aspects have to be also considered. Dry reforming of methane with CO_2 is a known technology that is available on a nearly industrial scale, although the positive impact on CO_2 emissions is questionable, i.e. whether CO_2 emissions due to energy consumption are larger than the amount of CO_2 consumed in the reaction. An improvement in the positive direction is the tri-reforming, which operates autothermically and does not require a pure CO_2 feed stream, but large-scale demonstration is necessary.

This review will introduce these different options and then focus the discussion on the processes that are at an early stage, but with relevant potential in the future. In the long term, the thermal, photocatalytic, and photoelectrocatalytic reduction of CO_2 under solar irradiation could greatly increase carbon recycling and reduce fossil fuel consumption. Biological conversion of CO_2, and in particular the use of micro-algae for producing chemicals or fuels [16], is another attractive route, but it still needs much development to become economically feasible.

In a recent report, the US Department of Energy (DoE) [17] has identified the challenges in catalysis for sustainable energy and priority areas in this field. In particular, one of the three priority research directions for advanced catalysis science for energy applications is the development of advanced catalysts for the photo- and electro-driven conversion of carbon dioxide and water.

The conversion of CO_2 at r.t. and atmospheric pressure using solar light represents a highly challenging approach to close the CO_2 cycle and develop photosynthesis mimic approaches. An interesting solution to realize this objective is a novel photoelectrochemical (PEC) reactor operating in the gas phase and using nanoconfined electrodes [18–21], differently from the conventional PEC systems. On one side of the proposed device, water is converted to O_2, electron and protons on a nanostructured TiO_2 thin film. This photocatalyst is growth over a porous titanium layer, which acts as electron collector and is in contact with the proton membrane to transport the protons on the other side of the cell. A wire connects the Ti substrate with the electrocatalyst on the other side of the cell. On the other side of the cell, an electrocatalyst based on metal nanoparticles deposited on conductive nanostructured carbon (carbon nanotubes or other similar C-based materials) and assembled to form a GDM (gas diffusion membrane) layer is present. On this electrocatalyst, CO_2 reacts with the electrons and protons (generated on the other side of the cell) to form hydrocarbons and alcohols.

These results evidence the possibility to develop “artificial trees” [21] able to capture the CO_2 and convert it to liquid fuels (hydrocarbons, alcohols). Therefore, the implementation of this concept will allow to reduce the levels of CO_2 in the atmosphere and at the same time capture a renewable source of energy (solar radiation) transforming it in a form (liquid fuels) which can be stored, used and transformed, preserving thus the large investments made on fossil fuels. The liquid hydrocarbons and alcohols can be alternatively used also as chemical feedstocks.

In summary, carbon dioxide conversion to fuels and chemicals is a very active R&D area that presents great challenges and opportunities for industry, along with great benefits to society. Further advances in catalysts, reactors, separations, processes, unconventional energy sources, and combinations of processes will be needed. Some of these aspects will be discussed here, with specific focus on catalysis, although it is not possible an exhaustive review of the topic. Further details can be found in Ref. [1]. To be mentioned also the recent reviews on the electrocatalytic and homogeneous reduction of carbon dioxide to liquid fuels [22] and on the advances in CO_2 capture, storage, fixation, and utilization [23]. The latter, in addition to carbon capture and storage, overviews some aspects of the chemical fixation of CO_2, in particular of the conversion to fuels (methanol, formic acid, di-Me carbonate, Me formate, higher hydrocarbons, photoreduction of CO_2. The problem of solar photocatalysis for hydrogen production and CO_2 conversion has been reviewed by Minero et al. [24], while the conversion of carbon dioxide to methanol and dimethyl ether by Olah et al. [25].

2. Industrial opportunities for using CO_2 as a feedstock

In addition to the aspects discussed in the introduction, it is worthy to briefly summarize some of the opportunities for companies developing R&D activities for conversion of carbon dioxide to fuel and chemicals, or use of CO_2 in chemical processes:

(i) Improvement of the public image for their contribution in converting a greenhouse gas onto valuable chemicals or fuels.
(ii) Decrease in costs for CO_2 disposal or emission reduction credits.
(iii) Development of innovative processes and products using a feedstock of low or even negative value, and possible gain market share.
(iv) Production of liquid fuels from CO_2 which integrate within the existing infrastructure and having a higher energy density and easier transport/storage than competing solutions (hydrogen, in particular).
(v) Possible CO_2 chemical recycling using renewable resources (solar energy).
(vi) Development of safer chemicals, for example, replacing phosgene with dimethyl carbonate (DMC).
(vii) Use of a nontoxic, noncorrosive, and nonflammable reactant, which can be easily stored in liquid form under mild pressure, e.g. safety and environmental benefits in process development.

3. Conversion processes

3.1. Background

An important preliminary distinction in discussing the possible options in the conversion processes of CO_2 regards the need of a pure CO_2 feedstock. There are some cases such as the CO_2 tri-reforming process, which do not require pure CO_2 streams, e.g. a preliminary process of separation of CO_2 from the flue gas is not needed. However, at least in a short-medium term, the majority of the CO_2 conversion technologies will be either a side process of CSS technology, e.g. concentred pure CO_2 will be anyway available, or will use CO_2 streams for which the processes using direct carbon dioxide use will be not applicable. Therefore, the direct use of CO_2 without separation does not appear a determining factor for the selection, even if this aspect should be analyzed in the specific and cannot be a generalized statement.

Typically, recover of CO_2 is made by absorption in suitable solvents (mainly alkanolamines), but the alternative use of membranes or solid adsorbents is increasing in relevance. New selective sorbents has been developed recently [26]. Further aspects will be also discussed in other contributions of this issue.

CO_2 has low reactivity, but there are many pathways for its activation, in particular using homogeneous or heterogeneous catalysts [8,27,28]. CO_2 oxygen atoms show a weak Lewis basicity, while the carbon atom is electrophilic. Therefore, the reactions of CO_2 are dominated by nucleophilic attach at carbon atom and reaction with electron-donating reagents. Carbonic and carbamic acids can be easy obtained by reaction with water, alkoxides, and amines. CO_2 can also be activated from nucleophilic centers on the surface of solids or in organometallic complexes. Therefore, there are various possibilities to activate and convert CO_2, but it is necessary to overcome a thermodynamic barrier. For this reason, providing the energy for the reaction is the critical aspect in evaluating the alternative routes for CO_2 conversion.

For the conversion of CO_2 to chemicals, the main classes of reactions of interest are the reduction, the addition or coupling, and acid–base reactions. A variety of organic chemicals or intermediates for the chemical industry could be produced [6]. The most relevant include esters, carbamic esters, salicylic acid, and cyclic carbonates [6–11,29,30]. Of interest is the incorporation of carbon dioxide into polymers, an active area of research and one that is very promising for future applications [31–33]. Examples are the synthesis of polycarbonates, polypyrones, lactone intermediates, and polyurethanes.

Less options exist for the conversion to fuels. A main route of conversion is the hydrogenation to produce methanol, for example [34,35], which may be eventually made using electrons and protons [36,37]. A modification is the use of other hydrocarbons, particularly methane, as the source of hydrogen (CO_2 reforming) [10,26,38]. The syngas (CO/H_2) which is produced could be then converted to chemicals or clean fuels [39]. The alternative is to produce CO by breaking the C–O bond in carbon dioxide. This requires high reaction temperatures (>2000 °C) using concentred solar furnaces, or alternatively a different, milder approach such as in photocatalytic or photoelectrocatalytic systems [40]. Enzymatic conversion, particularly using micro-algae ([41–43], is another route very attractive, but which it is expected to be applied only in medium-long term.

In general, there are four main approaches to convert CO_2 [9]:

1. To use high-energy starting materials such as hydrogen, unsaturated compounds, small-membered ring compounds, and organometallics.
2. To choose oxidized low-energy synthetic targets such as organic carbonates.
3. To shift the equilibrium to the product side by removing a particular compound.
4. To supply physical energy such as light or electricity.

However, for a sustainable conversion of CO_2 to fuels, only the latter is suitable in a longer-term prospect. In this perspective, the conversion of CO_2 may be thus viewed as a way to store renewable (transportable) energy to use in a second time (may be in a different location), but the objective should be to form liquid fuels. In fact, the latter is the best way to store and transport energy. Therefore, the conversion of CO_2 to fuel should have the production of liquid transportable fuel has a main objective. This further restricts the number of possible options.

We will overview in the following sections the main possible options in the conversion of carbon dioxide to fuels, to concentrate the discussion later on the specific case of the conversion of CO_2 to liquid fuels using solar energy, which appear the preferable option in a long term, although research on this direction is still at an early stage. However, to focus discussion we will not discuss the biological routes to convert CO_2 to fuel, either direct or indirect (micro-algae, for example).

3.2. Reaction with H_2

Many products, from C1-type molecules (CH_4, CH_3OH) to higher molecular weight alkanes, alkenes and alcohols through C–C bond formation, could be produced by hydrogenation of CO_2 [44]. This class of reaction comprises large-volume chemicals such as methanol and dimethyl ether (DME), and other interesting products such as carboxylic acids (formic and acetic acids). It may be distinguished between processes, where the first step is the catalytic hydrogenation of carbon dioxide to water and carbon monoxide (reverse water–gas shift reaction) followed by consecutive steps in which CO/H_2 mixtures are converted to alcohols or hydrocarbons, and those where direct CO_2 hydrogenation to products occurs. The Sabatier reaction (CO_2 to methane) also belongs to this class, but this reaction involves the largest use of hydrogen per molecule and is thus is of limited interest. The general issue is the availability of hydrogen or of hydrogen sources for hydrogenation. The latter includes water and the energy source, preferably renewable, necessary to produce H_2.

Homogeneous and heterogeneous catalysts have been used to hydrogenate CO_2 [5,11,13]. The latter is preferable in terms of stability, separation, handling and reuse of the catalyst, and reactor design, which reflect in lower costs for large-scale productions. However, the challenge is the combination of the possibility of better tuning of the properties of homogeneous catalysts to the technical advantages of heterogeneous catalysts. Significant progresses have been made in this direction. The use of new solvents such as ionic liquids, possibly in combination with supercritical CO_2, offers additional possibilities to achieve this goal [45,46].

3.2.1. Reverse water–gas shift (RWGS)

The reverse water–gas shift reaction is a key reaction in the catalytic hydrogenation of carbon dioxide. It is a mildly endothermic reaction with enthalpy and free energy changes of $\Delta H_{298\ K} = 41.2$ kJ/mol and $\Delta G_{298\ K} = 28.6$ kJ/mol:

$$CO_2 + H_2 \leftrightharpoons CO + H_2O \tag{1}$$

The reaction is known from over two century, but there is still the need to develop improved catalysts, since for example iron-chromium catalysts are active at temperatures of 400 °C or greater, but at this temperature the equilibrium constant is low and there is a significant problem in driving the RWGS reaction to completion. The equilibrium can be shifted to the right by (i) increasing the CO_2 concentration to force the complete consumption of H_2 (recycling then the excess CO_2), (ii) operating at high H_2 concentration to force the complete consumption of the CO_2 (recycling then the excess H_2) and (iii) removing water vapor from the reactor, thereby driving the reaction to the right. The latter system could be realized with either a desiccant bed, or a membrane permeoselective to water. Various studies have been reported recently on membrane application in Fischer–Tropsch (FT) synthesis reactors [47,48], where silico-alumina or zeolitic membranes are used for the selective removal of the by-product H_2O which deactivates FT catalysts and inhibits the reaction rate. The same concept could be applied for shifting the equilibrium in RWGS reaction.

The RWGS reaction is the first step in producing fuels by carbon dioxide hydrogenation. In Japan, RITE, in collaboration with NIMC, ONRI and NIRE, has proposed a process concept for CO_2 recycle composed of four key technologies [49,50]: CO_2 separation and liquefaction process, methanol synthesis process, water electrolysis for hydrogen production and supply process and transportation process. The key technologies are those for membrane separation of CO_2 emitted from stationary sources, for H_2 production by water electrolysis using electric power derived from non-fossil energy and for methanol synthesis by the catalytic hydrogenation of CO_2. A similar project is also running in U.K. [51] to produce liquid fuels from CO_2 and marine energy. H_2 is produced by water electrolysis using the electrical energy produced using wind and waves. Different options as liquid fuels are evaluated, in particular in terms of energy efficiency: methanol, mixed alcohols and gasoline (via methanol).

Being RWGS a reversible reaction (Eq. (1)), catalysts active in the direct gas shift reaction are also active in the reverse reaction. Different classes of catalysts have been studied for WGS reaction [52]: (i) copper-based catalysts, particularly CuO/ZnO oxides modified by alumina, zirconia, titania and/or silica [53]. Cu–ZnO based catalysts suffer from the drawback of being pyrophoric and highly susceptible to poisons. (ii) Iron-based catalysts, essentially modifications of commercial high temperature Fe-Cr catalyst. Iron-based catalysts require reaction temperature above 400 °C and are not suited for RWGS reaction. (iii) Cerium-based catalysts.

Although ceria or ceria-promoted formulations are mainly reported in conjunction with precious metals (PGM), non-PGM–ceria WGS catalysts have also been developed [54]. NexTech Materials has developed a non-pyrophoric Pt/CeO_2 catalyst for medium-high temperature applications (300–400 °C) [55], but Johnson Matthey reported that this catalyst, despite the high initial activity in the medium–high temperature range (325–400 °C), loses activity under synthetic and real reformate [52].

Still debate exists about the reaction mechanism in RWGS reaction. Two main reaction mechanisms have been proposed [56]: (i) In the "redox" mechanism, CO is adsorbed on reduced metal sites and reacts with an oxygen atom coming from the support to CO_2. In the following, the reduced support is subsequently reoxidized by water, releasing hydrogen [57]. (ii) In the associative "formate" mechanism, the main reaction intermediate is a bi-dentate formate, produced by the reaction of CO with terminal hydroxyl groups on the oxide support, which decomposes to form H_2 and a mono-dentate carbonate [58]. Using operando transient reactivity and spectroscopic studies, Meunier et al. [59] concluded recently that on a 2 wt.% Pt/CeO_2 catalyst the formates are essentially spectator species at 433 K, while probably a main reaction intermediates at 493 K.

3.2.2. Production of methanol or dimethyl ether

CO, produced by RWGS reaction, could be further hydrogenated to methanol. Total global methanol consumption reached 40.3 million m.t. in 2007 and is projected to grow to reach 58.6 million m.t. by 2012. In fact, methanol find application both to produce fuel additives components (methyl tertiary-butyl ether – MTBE, transesterification of vegetable oils) and as chemical. Methanol could be synthesized from a feed of CO_2 and H_2 under commercially feasible conditions, in a single or two steps approaches, e.g. with integrated or separated stage for RWGS. Retrofit of existing plants to pure CO_2 feed is possible [60], but experience is limited, while the use of CO/CO_2 mixtures could be better adapted. Nobel Laureate Olah [61] published a book recently dedicated to the "Methanol Economy" emphasizing the production of methanol (or dimethyl ether) by chemical recycling of CO_2.

Although from a technical point of view methanol from CO_2 is already at a nearly commercial stage, the availability and cost of hydrogen, particularly if the requirement is a production using renewable energy, is the issue. From this perspective, the production of methanol by catalytic hydrogenation of CO_2 should be focused at small-size delocalized productions alternative to the large-scale methanol synthesis by methane (or other hydrocarbons) steam reforming. This would require also the development of suitable small-scale efficient technologies based on process intensification [15]. There are several studies on methanol reforming in microreactor [62,63] and thus exist the bases also for implementing the reverse reaction of synthesis of methanol from CO_2 and H_2.

Although several evidence indicate that CO_2, rather than CO, is the direct precursor to methanol on the catalyst surface, e.g. through the formation of surface carbonates and formates, and it is known that for a syngas feed containing a small fraction of CO_2, the reaction proceeds faster, the critical issue in methanol synthesis from CO_2 is water formation:

$$CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O \tag{2}$$

The RWGS reaction results in an initial rapid conversion of H_2 and CO_2 to CO and H_2O. However, water acts as an inhibitor on the catalyst, slowing down the consecutive step of methanol synthesis. The critical issue to develop a process using a carbon dioxide–hydrogen feed is thus to improve current syngas-methanol catalysts both in terms of low temperature activity and of water tolerance. Improved catalysts have been reported recently for CO_2 hydrogenation to methanol [64,65]. They are based on Cu-Zn oxides containing various additives in addition to alumina (ZrO_2, Ga_2O_3, and SiO_2). These additives improve the specific activity, active surface area (dispersion), thermal stability, and long-term stability (sintering of support and active phases), but it is generally not considered water tolerance. Per pass yields reported for the advanced catalysts are low (10%). Liu et al. [66] reviewed the advances in catalysts for methanol synthesis via hydrogenation of CO and CO_2, but the issue of water tolerance was not considered in depth.

Multicomponent systems ($Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$) show the better performances with a stable productivity under realistic reaction conditions, but the productivity is typically 3–10 times lower using pure CO_2 feed with respect to a CO/CO_2 feed. Therefore, catalyst performances have to be still improved to match the performances using syngas type feedstock. In addition, the competitive cost advantage in using CO_2 instead of CO is partially compensated from the higher consumption of H_2 starting from carbon dioxide. Other aspects are relevant in comparing methanol production starting from CO_2 with respect to CO. Water accelerates the crystallization of Cu, ZnO in the catalysts, leading to a faster sintering and deactivation using CO_2 instead of CO [67]. CO_2 has a higher oxidation power than CO, and this has a negative effect on the catalyst. The purity of crude methanol produced with a CO_2/H_2 feed is different from that obtained using a syngas type feed. All these factors contribute in making still not economically advantageous the use of CO_2 instead of syngas for the production of methanol, but the process economy depends on the cost advantage in using carbon dioxide and the availability of H_2. The technical feasibility of the production of methanol from CO_2 has been already demonstrated in pilot plants using a two-step approach (RWGS separate from methanol synthesis) or a single step approach (the two stages integrated in a single reactor). The first approach seems preferable in terms of higher catalyst productivity, lower gas recycle and reactor size [1] (Table 1).

An alternative to methanol synthesis is the formation of dimethyl ether, a clean-burning substitute for diesel. The traditional route to DME is the dehydration of methanol over an acid catalyst.

$$2CH_3OH \leftrightharpoons CH_3OCH_3 + H_2O \tag{3}$$

If acidic functionality is added to a methanol synthesis/WGS catalyst, the complete synthesis can be performed in a single reactor starting from syngas. The favorable thermodynamics of the dehydration reaction can be used to drive to the methanol synthesis reaction, thereby increasing reactor productivity. In addition, DME production is possible according to two reactions:

$$2CO + 4H_2 \leftrightharpoons CH_3OCH_3 + H_2O \tag{4}$$

Table 1
One and two steps processes for CO_2 conversion to methanol. Source: adapted from CDRS (Carbon Dioxide Reduction and Sequestration) R&D Center, Korea (2007).

Process	One step (1)	Two steps (2)
Catalyst	$CuO/ZnO/ZrO_2/Ga_2O_3/Al_2O_3$	1st step: $ZnAl_2O_4$, $ZnCr_2O_4$ 2nd step: $CuO/ZnO/ZrO_2/Ga_2O_3$
Amount of gas recycle (for 100 kg_{CH_3OH}/day)	67.1 kmol	31.2 kmol
Catalyst productivity	600 g_{CH_3OH}/kg_{cat} h (250 °C, 50 bar)	760 g_{CH_3OH}/kg_{cat} h (240 °C, 27 bar)
Reactor size (for 100 kg_{CH_3OH}/day)	6 L	2 L

Data from bench-scale (50 – 100kg_{CH_3OH}/day) tests: (1) NIRE/RITE and (2) KIST(CAMERE) processes.

$$3CO + 3H_2 \leftrightharpoons CH_3OCH_3 + CO_2 \quad (5)$$

Due to the greater thermodynamic stability of CO_2 as compared to H_2O, the equilibrium yields of DME, particularly at the higher temperature, exceed those for methanol, in particular for a 1:1 $CO:H_2$ ratio (Eq. (5)). DME synthesis from syngas is thus thermodynamically favored with respect to methanol synthesis. However, when the same thermodynamic evaluations are made for CO_2/H_2 feed [68], the gains achievable over methanol synthesis are marginal, being roughly 5% net increase for a given temperature at 100 bar (for a 1:3 feed). In other words, thermodynamic analysis indicated that DME synthesis is a valuable alternative using syngas, while it is a less worthy alternative starting from CO_2/H_2 mixtures.

3.2.3. Production of hydrocarbons

Carbon dioxide can be also hydrogenated to hydrocarbons either by direct or indirect routes, e.g. via syngas and/or methanol intermediate formation. The indirect route can be either a multi-stage approach, e.g. with different reactors, or a single-stage approach, using hybrid catalysts to perform simultaneously the multi-step transformation ($CO_2 \rightarrow CO \rightarrow CH_3OH \rightarrow$ light olefins, for example). Direct reaction is similar to Fischer–Tropsch synthesis, but using a CO_2/H_2 feed. CO_2 hydrogenation to methane (Sabatier reaction) is also well known, but the larger consumption of H_2, lower energy per volume and more difficult storage with respect to oxygenated (methanol, DME), do not indicate this route as suitable for the conversion of carbon dioxide to fuels using H_2. In general, the production of hydrocarbons with respect to oxygenated from CO_2 requires a more intensive use of the resources (energy, H_2, more reaction steps, etc.) and is thus in principle is a less favorable route for the production of fuels. However, other motivations/incentives may justify this route. For example, market needs, better integration with the infrastructure, etc. Therefore, an integrated techno-economic and life-cycle assessment is necessary to evaluate the different options, but limited data on these aspects are available on literature.

The production of light alkanes from carbon dioxide is essentially a modification of the Fischer–Tropsch synthesis, where CO_2 is used instead of CO, and in which the catalyst composition is tailored to maximize the production of light alkanes. These products could be used as LPG or petrochemical feedstocks. A one or two-stage approach is possible. The latter can be either RWGS followed by FT, or a stage of CO_2-to-methanol followed by methanol to olefin in the presence of a hydrogenation component to convert consecutively the alkenes. A third possibility is to combine a methanation catalyst to a methane homologation catalyst. Co/SiO_2catalysts are active in methane homologation [69], but this do not appear a suitable route. A forth pathway is reduction or dissociation of CO_2 to CO at high temperature (for example, using a thermochemical solar approach) followed by standard FT of CO/H_2.

The direct FT route is preferable, although the methanol route using hybrid catalysts to convert in situ the methanol formed is also possible. In FT route, the relative competition between CO and CO_2 is an important aspect to consider. The conversion of CO/H_2, CO_2/H_2 and $(CO + CO_2)/H_2$ mixture using cobalt catalysts under typical FT conditions has been investigated by Zhang et al. [70,71]. They showed that in the presence of CO, the hydrogenation of CO_2 is slow. Similar catalytic activities, but different selectivities, were obtained by feeding only CO or CO_2. In CO hydrogenation, normal FT synthesis product distributions were observed with a α factor of about 0.80. Differently, the CO_2 hydrogenation products contained about 70% or more of methane. Therefore, CO_2 and CO hydrogenation follow different reaction pathways. There are also differences in terms of catalyst stability. The catalyst deactivates faster feeding CO instead of CO_2 even though the H_2O/H_2 ratio is at least two times larger for the conversion of CO_2.

However, on a Fe-Al_2O_3-Cu-K catalyst the same hydrocarbon products were obtained in CO_2 or CO hydrogenation [72]. The different behavior in Fe- and Co-based FT catalysts was explained by a different inhibition of methane formation and product desorption as a prerequisite for chain growth [72]. In the case of iron, there is irreversible carbiding and alkali surface coverage, while in the case of cobalt there is a strong reversible CO adsorption. Alumina was observed to be the best support for CO_2 hydrogenation and potassium was an excellent promoter [72]. It should be also considered that for iron catalysts the active phase forms in situ (formation of iron carbide – Fe_5C_2) [73]. It was observed that the lattice parameters of iron and cobalt carbides change as a function of the feed composition [74]. The lattice parameters are constant in CO/H_2 but decrease in CO_2/H_2. Furthermore, the CO/H_2 reaction occurs without a preliminary reduction unlike under CO_2/H_2, in which it is necessary.

Therefore, the effective catalysts for CO/H_2 or CO_2/H_2 FT reactions are different, even starting from the same catalyst. In terms of performances, Co-based catalysts form high amounts of methane, while Fe-based catalysts give better results, comparable with those feeding syngas.

Combining the iron-based FT catalyst with zeolites it is possible to maximize the formation of isoalkanes. Bai et al. [75] observed the synthesis of isoalkanes from carbon dioxide hydrogenation over Fe-Zn-Zr/HY composite catalysts. Ni et al. [76] also investigated similar catalysts suggesting that iso-butane is formed from propylene and methanol through MTG (methanol to gasoline) reaction and iso-pentane obtained from the reaction of C2 and C3 through the additive dimerization.

A further possibility to improve the performances is to couple CO_2-FT synthesis with a membrane permeoselective to water [47,48]. The conversion of CO_2 to long-chain hydrocarbons via CO_2 shift and FT reaction can be enhanced by in situ H_2O removal through an integrated silica membrane. Though the membrane exhibits low permeoselectivities regarding H_2O under FT conditions, the deficiencies in permeoselectivity can be overcome by the choice of H_2 and H_2/CO_2 as the sweep-gas. Novel membrane reactor for FT synthesis was developed by CeraMem Corporation (US, http://www.ceramem.com) as part of a US DoE SBIR project. The feasibility of the membrane reactor was demonstrated.

3.2.4. Synthesis of ethanol and formic acid

Ethanol is preferable to methanol as product of CO_2 hydrogenation, in terms of safer handling and transport, and better compatibility to gasoline. Ethanol can be produced directly from syngas, but typically is produced indirectly via methanol homologation. The latter route do not appear economical with respect to the production of ethanol from biomass [14], but the direct

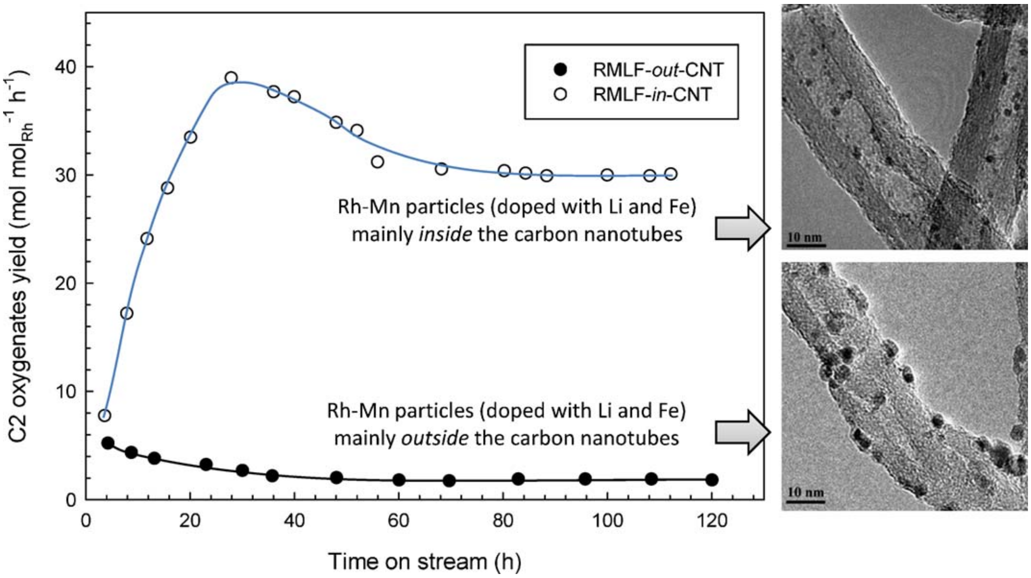

Fig. 1. C2 oxygenate formation activities as a function of time on stream for RhMn nanoparticles deposited inside or outside of the walls of carbon nanotubes (CNT). Reaction temperature: 320 °C. The transmission electron microscopy images of the respective fresh samples are also reported. Source: adapted from Ref. [78].

synthesis of ethanol from CO_2 (e.g. not through methanol formation) could have a better interest. Note that the H_2:CO_2 ratio for the synthesis of ethanol is the same for methanol.

$$2CO_2 + 6H_2 \leftrightharpoons C_2H_5OH + 3H_2O \tag{6}$$

The reaction can be regarded as the combination of the direct formation of ethanol from syngas and the RWGS reaction. A catalyst that is active for both these reactions under the same conditions would be expected to be active for the net overall reaction. Catalysts for the synthesis of ethanol are analogous to those for methanol, but need of centers promoting the C–C bond formation. Potassium promotes the formation of C_{2+}-alcohols in Fe-based FT catalysts. Therefore, combining a K/Fe catalyst for syngas to a Cu/ZnO catalyst for RWGS and methanol formation leads to promote the formation of ethanol. Arakawa [77] reported that combining K_2CO_3 with a Cu/Fe/ZnO catalyst there is an increase in selectivity to ethanol at 300 °C from about 6 to 20%. However, the most abundant products were C_{2+} hydrocarbons. Furthermore, deactivation rate was relatively high.

An alternative route to improve the synthesis of ethanol from CO_2 was based on the observation that Rh/SiO_2 catalysts form ethanol in syngas conversion. By doping this catalyst, it was possible to promote the formation of ethanol also starting from CO_2/H_2 feed. On a 5 wt.% Rh-Fe-Li(1:1:1)/SiO_2 catalyst a 14% CO_2 conversion and an ethanol selectivity of 34% were observed at 260 °C [77]. An extension and improvement of this concept has been reported recently by Bao and co-workers [78,79]. They have shown the enhancement of the catalytic activity of Rh-based particles confined inside nanotubes for the conversion of CO and H_2 to ethanol. Rh and Mn nanoparticles with Li and Fe as the additives (composition 1:1:0.075:0.05 by weight; indicated with the acronym RMLF), deposited on the inner or outer surface of carbon nanotubes (CNT with 4–8 nm inner diameter and 250–500 nm length; 1.2 wt.% Rh loading) show quite different behavior in C2 oxygenates formation (Fig. 1). The C2 oxygenates yield (containing up to 76% ethanol) of RMLF-*in*-CNTs is about one order of magnitude higher than that of the analogous RMLF-*out*-CNT sample, and also large than that of similar catalysts prepared using silica as the support [78].

More recently, the same authors [79] studied the effects of different carbon materials (CB, CMK-3 and AC) as supports for Rh-based catalysts promoted by multi-component additives (Mn, Li and Fe) for catalyzing syngas conversion to C2 oxygenates. There are strong additional promoting effects of Li and Fe compared to the bimetallic RhMn catalyst, which might outbalance that of CNTs. Even so, RMLF/CNTs still exhibit a highest activity among the four catalysts. Although Rh is very well dispersed on the high surface area AC, this catalyst exhibits a lowest overall activity and a lowest yield of C2 oxygenates. The results suggest that combination of the nanochannels and graphitic structure may play an important role in promoting this reaction in addition to the metal dispersion, particle size and presence of dopants.

Although these authors have not reported the behavior using CO_2/H_2 feed, these results appear a promising direction for the direct synthesis of ethanol from carbon dioxide feedstock. It should be mentioned that an efficient synthesis of ethanol from CO_2/H_2 was reported by Kurakata et al. [80] using an $Rh_{10}Se$ catalyst supported on TiO_2. The procedure of preparation and activation leads to form a cluster with the Se in the inner core. Selectivity to ethanol up to 83% could be reached, although problems of deactivation of the catalyst exist. This indicates, however, that the tuning of the properties of Rh nanoclusters, combined probably with the effect of nanoconfinement in carbon nanotube supports, is a promising direction to explore. The mechanism proposed for ethanol synthesis on [$Rh_{10}Se$]/TiO_2 is represented in Fig. 2 [81]. The CH_x(ads) species on rhodium, produced from CO_2 direct hydrogenation not involving the first step of dissociation to form CO (a

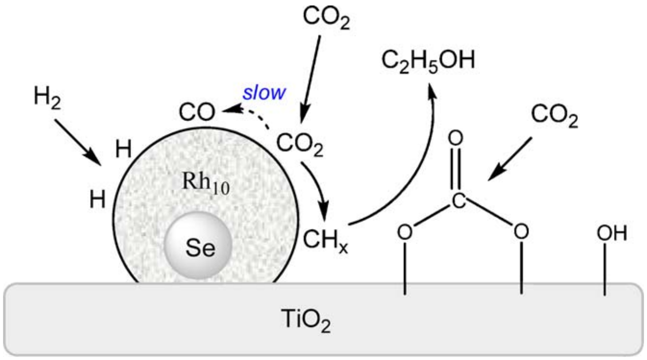

Fig. 2. Proposed mechanism for the ethanol synthesis from $CO_2 + H_2$ on [$Rh_{10}Se$]TiO_2 catalyst. Source: adapted from Ref. [81].

slow reaction), react with CO_2(ads) in the presence of chemisorbed hydrogen to give ethanol. The "rhodium selenide"-like electronic state inhibited methane formation, but tuned the reaction path to ethanol by promoting the C–C bond formation of CH, with the carbonyl derivative. Although there are many unclear aspects in this proposed mechanism, the key feature is a reaction pathway that does not involves the intermediate formation of carbon monoxide and the reaction between surface adsorbed CO_2 species and CH_x species in the presence of chemisorbed hydrogen species. A better understanding and proof of this mechanism is a necessary step to develop improved systems for direct synthesis of ethanol and probably higher alcohols from CO_2. This is a promising route for the conversion of carbon dioxide to fuels.

Formic acid synthesis is an alternative possibility to convert CO_2 to liquid products that may be used as both fuels and chemicals. The interest on formic acid, especially in UK, is related to what was called "The Formic Acid Economy". A consortium was formed within EPSRC activities in UK to investigate formic acid synthesis (from CO_2), and its use including as feedstock for fuel cells. A renewed interest on this reaction is also present in Japan after a significant improvement in the understanding of the active form of the catalyst and rate determining step to convert CO_2 into formic acid using water as a green solvent [82,83]. Formic acid interest in relation to CO_2 conversion derives from the fact that is the liquid product of CO_2 hydrogenation requiring the lower consumption of H_2

$$CO_2 + H_2 \leftrightharpoons HCOOH \tag{7}$$

On the other hand, formic acid is a toxic chemical (the US OSHA Permissible Exposure Level of formic acid vapor in the work environment is 5 ppm) and some animal experiments have demonstrated it to be a mutagen. It is thus unlikely that it may be proposed on a large scale as a suitable chemical to be produced from carbon dioxide. Nevertheless, there is an active research on the synthesis of formic acid particularly using homogeneous catalysts [11,13]. New opportunities have been also offered from ionic liquids. Zhang et al. [84] reported recently that the combination of a basic ionic liquid (IL) and a silica-supported ruthenium complex catalyzes the hydrogenation of CO_2 with satisfactory activity and selectivity. The resulting formic acid is easily collected. The IL and catalyst can be reused directly after an easy separation step.

3.3. Reaction of CO_2 with hydrocarbons

The most relevant reaction in this class is the reforming of methane with carbon dioxide to produce syngas. This process is indicated as "dry" reforming, in contrast to "wet" reforming by steam.

$$CH_4 + CO_2 \leftrightharpoons 2CO + 2H_2 \qquad \Delta H_{298\,K} = 247\,\mathrm{kJ/mol} \tag{8}$$

$$CH_4 + H_2O \leftrightharpoons CO + 3H_2 \qquad \Delta H_{298\,K} = 206\,\mathrm{kJ/mol} \tag{9}$$

The CO/H_2 ratio produced in the dry reforming is 1, but the RWGS reaction occurs simultaneously, making the effective ratio <1 and the CO_2 conversion greater than that of methane. The CO/H_2 ratio is appropriated for FT synthesis of alkanes (which requires a ratio between 0.5 and 1). A 7 barrel per day pilot plant operates on this concept from 2005 at Japan Oil, Gas and Metals National Corporation (JAPAN – GTL process; Ref. [85]). As the pilot plant tests at Yufutsu (Hokkaido, Japan) was successful achieving the targets, 500 barrels per day demonstration test project commenced in 2006 (http://www.nippon-gtl.or.jp/pdf/nippongtl.pdf). Noble metals (Rh and/or Ru) on MgO carriers were used as the catalyst [85b]. Stability of the operations with a H_2/CO ratio of 2.0 for approximately 7000 h has been demonstrated [85b].

Often in natural gas deposits, CO_2 is present together with methane. Therefore, the use dry reforming at or near well-head coupled to FT would produce liquid hydrocarbons easy to transport from remote areas (stranded gas). The additional potential advantage is that the process converts two of the principal gases responsible for greenhouse effect. It should be remarked, however, that CO_2 is typically reintroduced in the well to increase the deposit exploitation. Biogas upgrading is another target application for dry reforming.

The dry reforming is a strong endothermic reaction and requires temperatures above 700 °C to have reasonable conversions. A key problem is how to supply the energy needed to sustain the reaction, which under industrial conditions is limited from the rate of heat transfer. A typical reactor configuration is to use packed-bed tubes directly put inside the furnace. Advances in this area regard mainly the reactor design to improve efficiency of this heat transfer.

Catalysts active for steam reforming also work for dry reforming, but the issue of carbon formation is more critical due to the lower steam-to-carbon ratio in dry reforming than for steam reforming. Various supported catalysts, typically of the VIII group, have been investigated for reforming of CH_4 with CO_2. Bradford and Vannice [86] have compiled a list of catalysts reported in literature and their kinetic parameters (TOF, activation energy, and order of reaction). Various authors have also reviewed recently this reaction [87–89]. An important factor for catalyst reactivity and stability lies in the catalyst's resistance to carbon deposits, which could lead to active site blocking. Apart from directly altering the metal's properties by additives, an important factor is to use a support suppressing carbon deposition. This can be achieved with so-called oxy-transporters, such as ZrO_2 or CeO_2, which are capable of oxidizing deposited carbon. Additionally, because of their redox properties, these supports can actively participate in the catalytic reaction by oxidizing or reducing reaction intermediates. For example, CeO_2 has an active role in the WGS reaction. In general, ceria-containing supports have attracted a lot of attention in recent catalyst research. Especially CeO_2-Al_2O_3, $Ce_xZr_{1-x}O_2$, and $CeZrO_x$-Al_2O_3 supports are extensively investigated. Part of the Ni (NiO) incorporates in the surface of the $Ce_xZr_{1-x}O_2$-support and the resulting strong interaction between NiO and the $Ce_xZr_{1-x}O_2$ matrix inhibits the reduction of NiO. Roh et al. [90] found that coprecipitated Ni-Ce-ZrO_2 catalysts are most active for CH_4-CO_2 reforming when they have cubic phase ($Ce_{0.8}Zr_{0.2}O_2$), instead of tetragonal phase ($Ce_{0.2}Zr_{0.8}O_2$) or mixed phase ($Ce_{0.5}Zr_{0.5}O_2$). The effect, however, is more complex than a simple electronic interaction with the support.

It has been observed that the size and morphology of Ni particles changes under strongly reducing conditions (dry reforming at 750 °C), becoming flattened by stabilization on the partially-reduced ceria surface [91]. Smaller size Ni particles also form less carbon in comparison with larger particles. Fig. 3 shows that there is a relationship between the coking threshold and coking rate during steam methane reforming and the Ni crystal size [92]. To explain this result it is useful to remember that the mechanism of formation and grown of carbon nanofiber on Ni crystals depends on the crystal size [93]. In fact, the mechanism for carbon nanofiber growth involves several steps. Methane is adsorbed on the surface, and is converted into adsorbed carbon through surface reaction. Then, segregation of surface carbon into the layers near the surface occurs. The carbon diffuses through the Ni and precipitates on the rear side of the Ni crystal. A small crystal size of Ni results in a large saturation concentration leading to a low driving force of carbon diffusion and hence a lower coking rate. The saturation concentration of carbon in the nickel crystals is the main contribution to the difference in the coking threshold and difficult nucleation of filamentous carbon on the smallest Ni

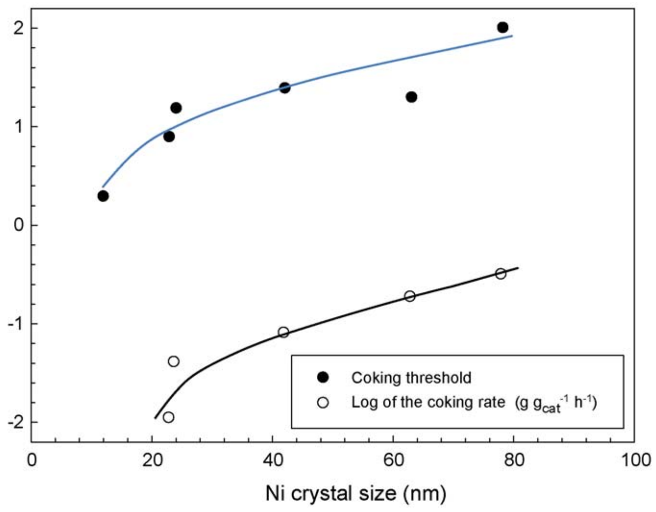

Fig. 3. Influence of the particle size on the coking rate (wt.%/h) at steam-to-carbon ratio of 0.5 and on carbon thresholds for steam methane reforming (*T* = 823 K and *P* = 20 bar). Source: adapted from Ref. [92].

crystals. On the other hand, the interaction with the support would influence this mechanism. It is known that basic supports such as MgO and CaO can favor coke gasification and hence decrease the carbon formation [94]. However, they will affect the electronic properties of the supported Ni particles, and hence their reactivity with carbon, thus influencing the rate of coking.

The interaction of the Ni particles with the support is another critical parameter influencing the rate of coking. Liu and co-workers [95] investigating Ni/Al_2O_3 catalyst treated by glow discharge plasma showed that they exhibit an excellent anti-coke property for CO_2 reforming of methane. The plasma treated catalyst contains high concentrations of close packed plane with improved Ni dispersion and enhanced Ni-alumina interaction, which lead to high catalytic activity and excellent resistance to formations of filamentous carbon and encapsulating carbon. The same authors [96] also showed that in silica-supported Ni catalysts, the plasma treatment enhances the interactions between the Ni particles and the SiO_2. This effect significantly improves the Ni dispersion and the coke resistance in the CO_2 reforming of methane.

In the mixed reforming, methane is reacted with carbon dioxide, steam and/or oxygen in various proportions. The potential advantages include preventing carbon deposition, increase the range of H_2:CO ratio, and a more autothermic operation than dry reforming. The mixed reforming has been studied by several research groups [97], but the more developed concept is the tri-reforming [26,98] can directly use CO_2 in the flue gases without the need of preliminary separation. The tri-reforming process is a synergetic combination of endothermic CO_2 reforming, steam reforming, and exothermic partial oxidation of CH_4 in a single reactor for producing syngas. The combination of dry reforming with steam reforming can produce syngas with desired H_2/CO ratios and mitigate the carbon formation, while incorporating oxygen in the reaction generates heat in situ that can be used to increase energy efficiency; oxygen also reduces or eliminates the carbon formation on the reforming catalyst. Tri-reforming together with other reactions of methane reforming has been discussed in detail in various reviews: Halmann and Steinfeld [99], Hu and Ruckenstein [38], Song [26] and more recently Moon [87].

3.4. Photo- and electrochemical/catalytic conversion of CO_2

The use of solar energy can be direct (photochemical/catalytic approach) or indirect, e.g. by generation of electrons which are then used for the reduction of carbon oxide. The latter can be a two-step approach, e.g. generation of electricity in photovoltaic cells, wind, etc. and then use of the electrons to reduce electrochemically/catalytically carbon dioxide in a physically separate cell. Alternatively, it is possible a one-step approach by coupling the two processes in a single unit, e.g. photoelectrochemical/catalytic approach. Notwithstanding the growing research interest, it is still not defined the preferable approach as well the better class of efficient catalysts for the conversion of carbon dioxide into fuels [17]. Most of known electrocatalysts or photocatalysts showing activity for carbon dioxide conversion to simple energy-storage products, such as carbon monoxide or formic acid, are inefficient and/or require use of sacrificial reducing agents. Some new routes, for example the direct conversion of CO_2 to liquid fuels such as isopropanol (see later), have been proven, but there is still long R&D necessary for their use.

To note that the terms chemical and catalytic are used to indicate the same process and thus the indication chemical/catalytic was used above. In fact, the photon- and electron-induced processes of CO_2 reduction are catalytic and not stoichiometric (chemical) reactions and need thus a catalyst. However, the indication "chemical" is still the most used in literature, even if not properly correct.

3.4.1. Electrochemical/catalytic conversion of CO_2

The electrochemical reduction of carbon dioxide has been reviewed by DuBois [100] and Gattrell et al. [101] and Hori [102]. There are two main approaches, depending whether the conversion of CO_2 is studied in aqueous or non-aqueous solutions. Formic acid is the main reaction product in electrolyses of aqueous solution of CO_2. The main issue in aqueous solution is carbon dioxide low solubility in water at standard temperature and pressure, e.g. at the surface of the electrode there are very small amounts of CO_2 available for the reaction to proceed. For aqueous solutions, in order to speed the reaction rate, the pressure must be increased. Numerous studies have been made on the electrochemical reduction of CO_2 under high pressure on various electrodes in an aqueous electrolyte. The main products observed are CO, H_2 and formic acid. Methane and C2 hydrocarbons are observed in traces. A fast deactivation is also often observed.

Solvents with high solubility for CO_2 are used in the non-aqueous electrochemical reduction of CO_2. CO_2 concentration in dimethyl-formamide is about 20 times higher than in aqueous solutions, and in propylene carbonate and methanol the CO_2 solubility is about eight and five times higher, respectively. However, high CO_2 solubility requires larger current density, but low electrolytic conductivity leads to high ohmic losses. For this reason, methanol is often used to balance these two aspects. Cu-based foils give the best results as electrodes. Another problem is that very high current densities at the copper cathode are necessary to maximize the formation of hydrocarbons, but a fast deactivation is present in these conditions [103].

Hori et al. [103] using immobilized CuCl on Cu-mesh electrode reported a Faradaic efficiency of about 70% to C_2H_4, although the electrode fast deactivate. In addition, corrosive media (high pressure, metal halides) are used, because metal halides are necessary to promote surface concentration of CO_2 at the electrode. To note also that Cu is the only metal, which gives appreciable amounts of C2 hydrocarbons. Several critical aspects determine the performances, such as (a) the gas evolution in the electrochemical cells, which reduce electrolyte conductivity and increase ohmic resistance, (b) the pH and reaction temperature, which opposite influence the solubility of CO_2 and selectivity to C2 products [104], and (c) the porosity of electrodes. Using TiO_2 nanotube composite electrodes for the electrochemical reduction of CO_2 to methanol [105], current efficiencies over 60% were reported (Table 2).

Table 2
Faradaic efficiencies of the electrochemical reduction of CO_2 on various electrodes (2 h of reaction). Source: adapted from Ref. [105].

Electrode	Faradaic efficiency for CH_3OH (%)
RuO_x	30.5
RuO_2/TiO_2 NPs composite	40.2
RuO_2/TiO_2 NTs composite	60.5

The reaction network in the CO_2 electrocatalytic reduction on Cu electrodes involves an initial stage of formation of the carbon dioxide anion radical ${}^{\bullet}CO_2^{-}$ which explains why metal halides are necessary to promote the reaction. The consecutive step lead to the formation of adsorbed carbon monoxide (CO) which can react with protons and electrons (in the presence hydroxide anions) to give water and chemisorbed methylene ($:CH_2$). The latter may be further hydrogenated to CH_4 or react with another methylene intermediate following a Fischer–Tropsch like chain growth mechanism. Two recent reviews [101,106] discussed in detail the reaction mechanism, as well as the performances of the different electrocatalysts and the dependence of the behavior from the reaction conditions.

Alkanes and alkenes up to C6 hydrocarbons were recently reported by Shibata et al. [107] using a Cu electrode not pre-treated by electropolishing. The product distribution follows the Schultz–Flory distribution and, depending on the applied potential, the chain growth probability (α) ranges from 0.23 to 0.31, values lower than those obtained in Fischer–Tropsch synthesis over heterogeneous Co- or Fe-based catalysts. When the same electrode material was pre-treated by electropolishing it behaved like a pure Cu electrode, giving mainly methane and ethene. It was suggested that the oxygen coverage of the electrodes is a function of the surface crystallinity, but the mechanism of this marked effect on the surface reactivity is unclear as well as difficult the reproducibility of the results.

On the other hand, the feasibility of CO_2 conversion to fuels depends on the possibility to form long-chain hydrocarbons and/or alcohols, which can be easily collected without the need to distillate from liquid solutions. These liquid fuels can be easily stored and transported. Therefore, from the application point of view, it is necessary to develop a process for solventless electrocatalytic reduction of CO_2 to longer chain alcohols. There are very few studies based on this approach, but it was demonstrated that using nanostructured carbon based electrodes it is possible to electrocatalytic reduce CO_2 in the gas phase using the protons flowing through a membrane. Long-chain hydrocarbons and alcohols up to C9–C10 are formed, with preferential formation of isopropanol using carbon nanotube based electrodes [19,21,108,109]. Productivities are still limited, but these results proof the concept of a new approach to recycle CO_2 back to fuels.

An example of the results is shown in Fig. 4 reporting the formation of the main products obtained at 20 °C and 60 °C during the electrocatalytic reduction of CO_2 using a carbon cloth/Pt on carbon black/Nafion assembled electrode (GDM – gas diffusion electrode), which features are the same of the electrodes used in PEM fuel cells [21,108]. The electrocatalyst is the Pt supported on carbon black, which is then deposited on a conductive carbon cloth to allow the electrical contact and the diffusion of gas phase CO_2 to the electrocatalyst. The Pt particles are at the contact of Nafion through which diffuse protons. On the Pt nanoparticles, the gas phase CO_2 reacts with the electrons and protons to be reduced to longer chain hydrocarbons and alcohols, which relative distributions depends on the reaction temperature. Acetone is the major product on this electrocatalyst.

Using a similar GDM configuration, but with carbon nanotube as the substrate for the electrocatalyst nanoparticles instead of carbon black, it is possible to form isopropanol as the main product of reaction (Fig. 5) [21]. This figure also evidences that using carbon nanotubes it is possible to use also iron nanoparticles instead of noble metal, although the latter shows a better stability. Fig. 5 also evidences that the use of N-doped carbon nanotubes (N/CNT) allows a further improvement in the productivity to isopropanol.

An important aspect is the use of nanocavities, which could favor the local increase of CO_2 concentration (nanoconfinement) and thus the consecutive conversion of intermediates with formation of C–C bonds. The reaction mechanism of formation of isopropanol as the main reaction intermediate is still unclear. The product distribution is quite different from a Schultz–Flory distribution, as in the mentioned results reported by Shibata et al. [107]. This suggests that the mechanism could be different from that present in FT synthesis, although it is not possible to have better conclusions. Note, however, that isopropanol and not n-propanol is formed, and that no methane was formed. It could be also observed that comparing the results of Fe10-CNT with those of Fe10-N/CNT (e.g. a similar electrocatalyst, but using N-doped

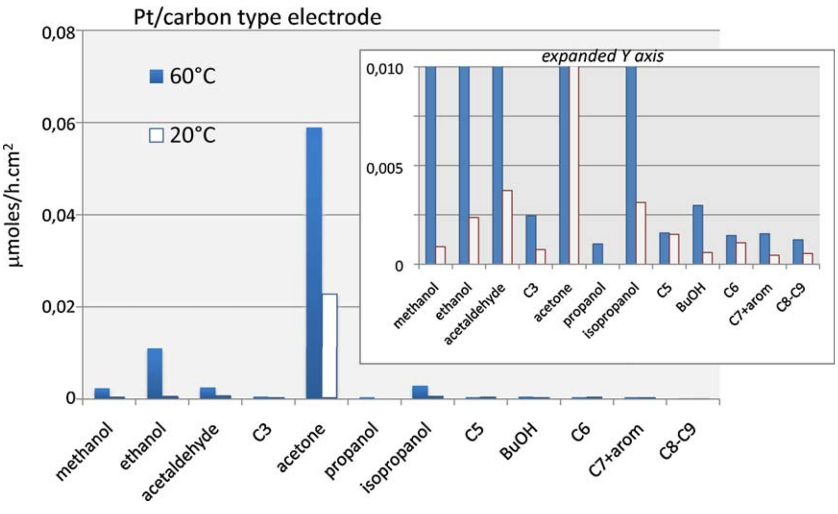

Fig. 4. Effect of the temperature on the products distribution in the electrocatalytic reduction of carbon dioxide in gas phase (20 °C and 60 °C) over Nafion 117/(Pt(10%)/carbon black)$_{20\%}$/carbon cloth GDM (gas diffusion membrane) electrode. Tests in a semi-batch cell, using a 0.5 M KCO_3 electrolyte on the anode side and operating the cathode in the gas phase with a continuous feed of 50% CO_2 in humidified nitrogen. Source: adapted from Refs. [21,108].

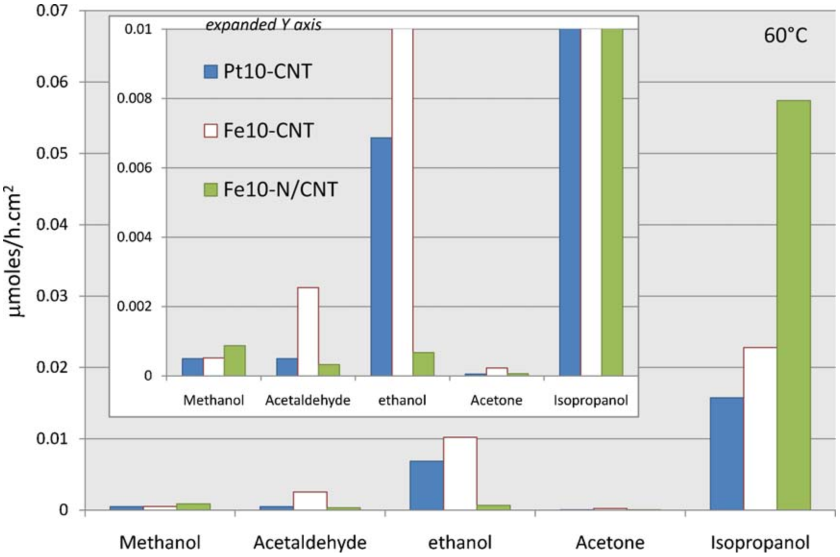

Fig. 5. Products distribution at 60 °C in the electrocatalytic reduction of carbon dioxide in gas phase over Nafion 117/(Pt or Fe(10%)/CNT)$_{20\%}$/carbon cloth GDM (gas diffusion membrane) electrode. Tests as those in Fig. 4. Source: adapted from Refs. [21,108].

carbon nanotube as substrate), the ethanol formation decreases and increases that of isopropanol.

3.4.2. Photo(electro)chemical/catalytic conversion of CO_2

This approach for the electrocatalytic reduction of CO_2 to fuel is sustainable only when the electrons and protons necessary for the reaction are supply using renewable resources, e.g. using solar energy by integrating a photoanode cell on which the photodissociation of water produces the electrons and protons necessary for the electrocatalytic reduction of CO_2 [19,21]. An effective device should thus integrate the photoanode (for water dissociation) to the electrocatalyst (for CO_2 reduction) in a photoelectrocatalytic (PEC) device. The latter shows strong analogies to PEM fuels cells (Fig. 5) and can take effective advantages of the large technological developments made on these systems in the recent years [19,21] (Fig. 6).

An alternative conceptual approach was proposed in the cited US DoE report “Catalysis for energy” [17], where a model of a multifunctional photocatalyst for the reduction of carbon dioxide to methanol using water as the electron donor was shown (Fig. 7). In this conceptual model, a semiconducting electrode is synthesized with channels that permit proton communication between cells containing half-reaction catalysts, but do not permit reactants or products through. Molecular catalysts for water oxidation and carbon dioxide reduction are anchored to opposite sides of the electrode. The electrode is designed to absorb solar radiation and facilitate diffusion of resulting point charges to the respective molecular catalysts responsible for the carbon dioxide reduction and water oxidation chemistry. Although this catalytic system is conceptually simple, there are significant scientific challenges hindering the achievement of high activity with molecular systems anchored to a porous semiconductor material that absorbs visible light and permits only proton communication through its pores.

An attempt to go in this direction was reported recently by Grimes and co-workers [110]. These authors investigated the use of N-doped TiO_2 nanotube array for the solar conversion of carbon dioxide and water vapor to methane and other hydrocarbons. The

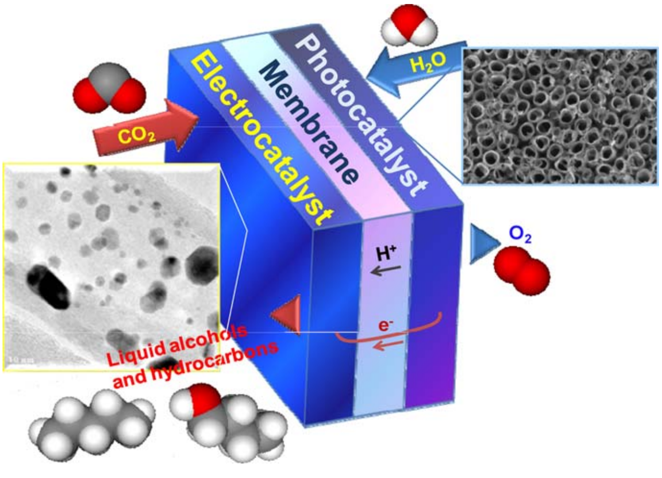

Fig. 6. Simplified scheme of a photoelectrocatalytic device for the CO_2 reduction to fuels using solar energy. Source: adapted from Refs. [19,21].

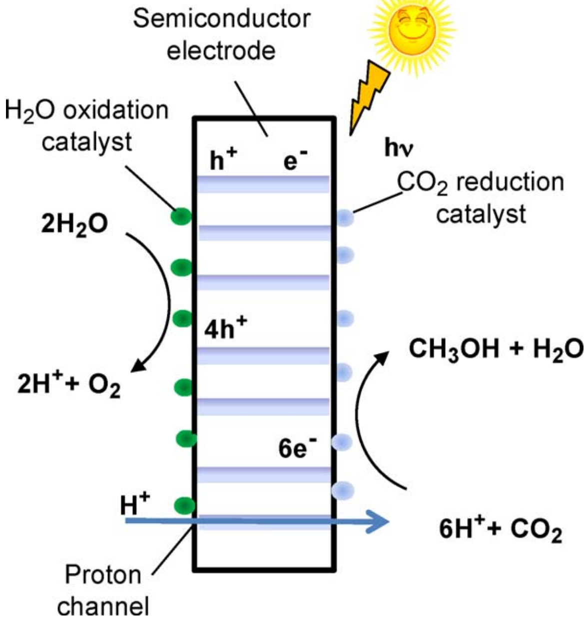

Fig. 7. Conceptual model of photocatalyst to reduce carbon dioxide to methanol. Source: adapted from Bell et al. [17].

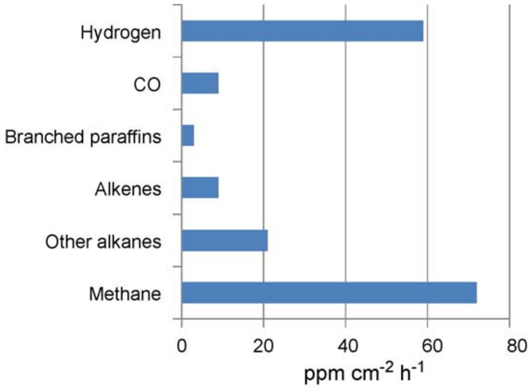

Fig. 8. Product yield from a nitrogen-doped nanotube array sample annealed at 600 °C (film thickness about 50 μm) and with Cu as cocatalyst (52% of the surface area decorated with Cu particles) in the conversion of CO_2 under sunlight illumination. Source: adapted from Grimes and co-workers [110].

thickness of the film was about 50–100 μm and was produced by anodic oxidation (0.3 M ammonium fluoride in 2 vol.% water containing ethylene glycol at 55 V). Pt or Cu were used as cocatalysts to enhance the performances. Although the tests were made in a batch-type photo reactor, the use of a flow-through photocatalytic membrane design as indicated in Fig. 7 was indicated as desirable. The best results were obtained for a N-doped titania nanotube array annealed at 600 °C and using Cu as cocatalysts (about half of the surface area covered by copper nanoparticles). Fig. 8 reports the productivities obtained in CO_2 conversion under sunlight illumination. Using 400 nm wavelength high-pass filter the productivities lower significatively (to about one fifth), but this filter do not cut completely the radiation below 400 nm. To note that only hydrocarbons and not alcohols were detected by Grimes and co-workers [110], while other authors investigating the CO_2 photoreduction on TiO_2-based catalysts observed mainly the formation of oxygenated products (Table 3). To note that this type of TiO_2 nanotube array used by Grimes and co-workers [110] is the same as that proposed as optimal configuration for the photoanode in the PEC device (Fig. 7).

In 1979, Inoue first reported the photocatalytic reduction of CO_2 in aqueous solution to produce formaldehyde (HCHO), formic acid (HCOOH), methyl alcohol (CH_3OH), and trace amounts of methane (CH_4) using various semiconductors, such as tungsten trioxide (WO_3), titanium dioxide (TiO_2), zinc oxide (ZnO), cadmium sulfide (CdS), gallium phosphide (GaP), and silicon carbide (SiC). These semiconductors were activated by both xenon- and mercury-lamp irradiation. In later years, many research groups have studied the mechanism and efficiency of CO_2 photocatalytic reduction using a variety of semiconductors. Two recent reviews discussed the development in this area (Usubharatana et al. [37], Kitano et al. [111]). Table 3 reports some selected examples of the behavior of heterogeneous photocatalysts in the reduction of CO_2 (Refs. [112–116]).

Table 4
Yields of CH_4 and CH_3OH in the photocatalytic reduction of CO_2 with H_2O at 323 K on the Ti-β(OH), TS-1, Ti-β(F) and TiO_2 (P-25) catalysts. Intensity of light: 265 μW/cm^2. Reaction time: 6 h. Source: adapted from Ref. [111].

mmol/g_{Ti} h	Photocatalyst			
	TiO_2 (P-25)	Ti-β(F)	TS-1 (Ti-silicalite)	Ti-β(OH)
CH_4	0.30	0.69	1.25	5.81
CH_3OH	–	0.49	0.41	0.68

A recent trend regards the development of nanophotocatalysts stabilized inside micro- and mesoporous materials. The use of nanoparticle semiconductors can provide a higher activity for CO_2 reduction compared to the corresponding bulk semiconductor. Studies have been carried out on TiO_2 nanoparticles as well as on various binary oxides including extremely small TiO_2 moieties such as TiO_2/SiO_2, TiO_2/Al_2O_3 and TiO_2/B_2O_3 [111]. In these systems, the photocatalytic activity increased as the diameter of the TiO_2 particles decreased, especially below 10 nm, but the absorption and photoluminescence spectra has blue shifts as the diameter of TiO_2 becomes smaller. In other words, there is an increase of the surface area, but a shift in the opposite direction to visible, e.g. there is a less efficient use of the sunlight radiation.

Ti-containing micro- and mesoporous zeolites have been indicated as efficient and selective photocatalytic reactivity for the reduction of CO_2 with H_2O using UV radiation. An example is reported in Table 4 that shows the yields of the main products in the photocatalytic reduction of CO_2 with H_2O at 50 °C. UV irradiation of Ti-β zeolite photocatalysts in the presence of CO_2 and H_2O led to the formation of CH_4 and CH_3OH as well as trace amounts of CO, C_2H_4 and O_2. Table 4 compares the results obtained with conventional TiO_2 (P-25 Degussa, now Evonik) with those of two types of Ti-β zeolites synthesized under hydrothermal conditions using conventional basic conditions (OH^- ions) or a fluorine-medium. It should be noted, however, that the positive effect of fluorine ions on photocatalytic activity is known, because changes the hydrophobicity of the surface of TiO_2. Therefore, the difference in the behavior is probably related to this aspect and not to the differences in the synthesis of the zeolite. The behavior of titanium-silicalite (TS-1) is also compared. Note that the results refer to the activity per gram of Ti and that this amount is much less (few wt.%) in Ti-containing zeolites with respect to TiO_2 (P-25) which thus shows a still better activity per gram of catalyst.

To evidence also that in TiO_2 nanoparticles loaded with noble metals in low amounts (typically 0.5 wt.%), a "short-circuited photoelectrochemical cell" providing both the oxidizing and reducing sites for the reaction could exists. Schematic representations of photoelectrochemical cells (PEC) and Pt-loaded TiO_2 particle systems (Pt/TiO_2) are depicted in Fig. 9. This evidences that

Table 3
Selected recent studies on CO_2 reduction photocatalysts. Source: adapted from Usubharatana et al. [37].

Photocatalyst	Reductant	Light source	Primary product(s)	Comments	Ref.
Ti-MCM-41	Water vapor	266-nm emission of a pulsed Nd:YAG laser at 10 Hz	CO, O_2	CO_2 reduced to CO as a single-photon two electron-transfer product, with O_2 as a coproduct	[112]
TiO_2 (P-25)	Aqueous $NaHCO_3$	15-W (maximum) source at 365 nm	CH_4, CH_3OH	More effective at higher acidity	[113]
Cu/TiO_2	Water, NaOH	Hg lamp; UV-C (254 nm), UV-A (365 nm)	Methanol	Activity increases with copper dispersion and smaller copper particles on titania	[114]
Ti-containing mesoporous silica thin film	Water vapor	100-W high pressure Hg lamp	CH_4, CH_3OH	More active and selective to methanol than Ti-MCM-41	[115]
Pt/$K_2Ti_6O_{13}$ with Fe-based catalyst	Water	300-W Xe lamp, 150-W Hg lamp	H_2, CH_4, HCHO, HCOOH, CH_3OH, C_2H_5OH	Methanol and ethanol produced when hybrid catalyst was used	[116]

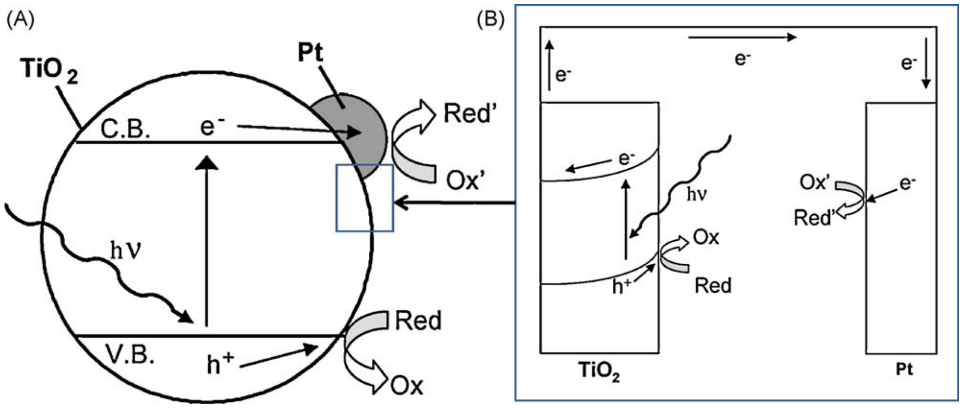

Fig. 9. Schematic representations of (A) the Pt-loaded TiO_2 (Pt/TiO_2) particle system and (B) the "short-circuited" photoelectrochemical cell (PEC). Source: adapted from Ref. [111].

often a clear distinction between the mechanisms of photoreduction and photoelectrochemical reduction of CO_2 is not possible, particularly on metal-doped semiconductor materials.

The reaction mechanism in the photoreduction of CO_2 involves two important species, $H^{\bullet}$ (hydrogen atom) and $^{\bullet}CO_2^{-}$ (carbon dioxide anion radical), produced by electron transfer from the conduction band as follows:

$$H^+ + e^- \rightarrow H^{\bullet} \tag{10a}$$

$$CO_2 + e^- \rightarrow {}^{\bullet}CO_2^{-} \tag{10b}$$

Two and other multielectron reactions compete with these processes:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad \text{carbon monoxide} \tag{11a}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \quad \text{formic acid} \tag{11b}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O \quad \text{formaldehyde} \tag{11c}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad \text{methanol} \tag{11d}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad \text{methane} \tag{11e}$$

However, the solubility of CO_2 in water is particularly low, and the CO_2 photoreduction process is competing with H_2 and H_2O_2 formation, which consumes H^+ and e^- as follows:

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \quad \text{water decomposition} \tag{12a}$$

$$4H^+ + 4e^- \rightarrow 2H_2 \quad \text{hydrogen formation} \tag{12b}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \text{hydrogen peroxide formation} \tag{12c}$$

There are thus intrinsic limitations to improve the productivity to fuels in CO_2 photocatalytic reduction. To note that methanol and formaldehyde are the easier products of CO_2 reduction in water solution. It should be thus carefully checked (for example, in the cited case of the Grimes and co-workers [110] results) whether they do not form really or may be not detected, remaining adsorbed on the photocatalyst, for example. In all cases, being present many competitive reactions in water solution, and being all the species very reactive, the possibility to form longer chain hydrocarbons or alcohols is limited. Finally, a highly diluted water solution containing the liquid fuels (methanol, for example) form and the recovery of these chemicals is expensive. Therefore, although the direct CO_2 reduction of semiconductor-based materials is conceptually attracting, this approach has limited perspectives of applications. The physical separation of the water photodissociation from the CO_2 reduction stages, such as in the PEC approach, could instead overcome some of these limitations.

Because of these limitations, some researchers have attempted to replace water with other reductants. If low-dielectric constant solvents or low-polarity solvents are used, $^{\bullet}CO_2^{-}$ anion radicals can be strongly adsorbed on the surface through the carbon atom of another $^{\bullet}CO_2^{-}$ anion radical because these radicals are not well dissolved in low-polarity solvents. Here, CO is produced as the major reduction product of CO_2. If a high-dielectric constant solvent is used (e.g. water), the $^{\bullet}CO_2^{-}$ anion radicals can be greatly stabilized by the solvent, resulting in weak interactions with the photocatalyst surface. Subsequently, the carbon atom of the radical tends to react with a proton to produce formic acid.

The use of photocatalysis in supercritical CO_2 has been also attempted to improve the performances [117]. Formic acid was obtained as product, but the results were not particularly good. It must be finally remarked that the proper choice of photoreactor is an important parameter to consider, because the performances could be greatly depend on this factor.

3.4.3. Thermochemical conversion of CO_2

Different thermochemical cycles have been proposed to use the thermal energy of solar furnaces or nuclear reactors to supply the energy required for splitting carbon dioxide

$$CO_2 \leftrightharpoons CO + 1/2O_2 \qquad \Delta G = 0 \text{ at } 3350\,K \tag{13}$$

When this reaction is coupled with the thermochemical water splitting to produce H_2 and O_2, the CO/H_2 mixture obtained maybe then converted by established routes to methanol, FT products, etc. However, if CO_2 gas stream is heated and photolyzed by intense solar radiation and then allowed to cool slowly, it will react back to the initial CO_2 by a series of elementary chemical reactions. The back reaction to CO_2 can be significantly reduced by quenching adding CO_2, water, or a mixture of them. A three-fold quench with pure CO_2 will stop the reactions and preserve over 90% of the initial photolytic CO [118].

The concept has been further developed and the results of the first prototype were published by Traynor and Jensen [119] of Los Alamos Renewable Energy Corporation. In the first prototype system, a solar focusing mirror and secondary concentrator were used to provide high solar intensity around a ceramic rod. This high temperature, high solar irradiance environment provided strong heating of CO_2 with the resultant dissociation to CO and oxygen. Quenching of the back reaction was provided by the geometry and gas dynamics of the system and by cool gas quencher jets just downstream. The best-measured net conversion of CO_2 to CO was near 6%, which is compared to a plant design target of 12%. The peak observed conversion of solar energy to chemical energy was 5%.

In 2005 Los Alamos Renewable Energy (LARE) announced the process called SOLAREC^{TM} (Solar Reduction of Carbon). In the LARE reactor, CO_2 is fed into a reaction chamber that is sealed at one end by a quartz window 8 cm in diameter. The chamber is fixed at the focal point of a mirrored dish that concentrates sunlight through the chamber's window onto a ceramic rod set inside the chamber to collect the heat. As the gas comes into contact with the rod its temperature rises to around 2400 °C, causing the molecules to break down and release CO and oxygen.

One of the drawbacks of this approach is the high operating temperature. High temperatures lead to heavy thermal losses, which in turn can reduce efficiency. Though the sun's energy is free, equipment to generate and withstand these temperatures is expensive to build, making efficient operation vital if the process is to be cost-effective.

Sandia (Albuquerche, US) is developing an alternative system indicated as CR5 (short for counter-rotating ring receiver reactor recuperator) which operates at less extreme temperatures. Like the LARE reactor it has a concentrator dish that focuses the sun's rays. In this case, the high temperatures are generated on one side of a stack of 14 rings made of a cobalt ferrite ceramic, a material that when heated releases oxygen from its molecular lattice without destroying the lattice's integrity. The rings, which are about 30 cm in diameter, rotate at around one revolution per minute inside a sealed double chamber.

Sunlight focused through a window in the hot side of the chamber heats the rings to 1500 °C, causing the ceramic lattice to liberate oxygen atoms. As the rings rotate, the heated section passes to the rear of the chamber, where it cools to around 1100 °C as it is bathed in CO_2. At this temperature the deoxygenated ceramic reacts with the CO_2 molecules to grab back the oxygen atom missing from its lattice, leaving behind a molecule of CO. As the ring continues to rotate, the reoxygenated section passes back into the hot side of the chamber and the cycle begins again.

Proper heating and cooling of the rings is crucial to the operation of the process. On the heated side, the rings must reach the correct temperature for the ceramic to liberate oxygen, and they must cool by several hundred degrees by the time they reach the cool side in order to react with the CO_2. To help achieve this, alternate rings rotate in opposite directions, so as the hot section of each ring moves towards the cool side of the chamber it is cooled by neighbouring rings moving in the opposite direction. Both hot and cooler sides of the chamber are maintained at equal pressure to minimize the flow of gases between them.

The CR5 was originally developed to produce hydrogen using steam in the cool chamber, but was then converted to split CO_2, because could offer a more efficient way of capturing solar energy. Burning the CO formed in the solar reactor should deliver 10% of the energy that was required to produce it. They calculate that the prototype will be able to produce about 100 L of CO per hour.

The concept of using metal-oxide materials which spontaneously reduce at high temperature (using solar energy) and are then are reoxidized by interaction with H_2O to form H_2 (or alternative with CO_2 to produce CO) has been significantly investigated in literature and recently reviewed by Agrafiotis et al. [120].

$$MO_{red} + CO_2(H_2O) \rightarrow MO_{ox} + CO(H_2) \tag{14a}$$

$$MO_{ox} \rightarrow MO_{red} + 1/2O_2 \qquad (\text{about}1000\text{–}1200\,^{\circ}\text{C}) \tag{14b}$$

It is clear that the two concepts should be coupled to develop with the same solar reactor both CO from CO_2 and H_2 from H_2O, and then use them is a conventional catalytic reactor to produce fuels (methanol, FT hydrocarbons, etc.). The real issue is the high temperatures which are requested and the stability of associated materials.

4. Conclusions

Large amounts of CO_2 will be available in a near future due to the planned CSS plants and therefore carbon dioxide can be a zero cost (or even with negative value) feedstock for innovative conversion processes. Although several opportunities exist also for the conversion of carbon dioxide to chemicals, this review is focused on the possibilities for the conversion to fuels, because the market for chemicals is two orders of magnitude lower with respect to that for fuels. It is remarked, however, that the requisites for this objectives are (i) minimize as much as possible the consumption of hydrogen (or hydrogen sources), (ii) produce fuels that can be easy stored and transported, and (iii) use renewable energy sources. From this perspective, the preferable option is to produce alcohols (preferably ≥C2) using solar energy to produce the protons and electrons necessary for the reaction of CO_2 reduction. It is evidenced, however, that this is still a long-term objective, even if already some good advances in this direction exist. On the contrary, the conversion of CO_2 to methanol or syngas is already at a pilot plant scale and may be thus commercially implemented, if process economics will be proven. There is still limited information on these aspects, and in any case the economy of the process will strongly depends on the value (or negative value) of CO_2, and the availability (and cost) of energy and hydrogen. These aspects will greatly depend on a number of aspects making not possible a generalization.

This review has shortly analyzed the state of the art on the different options for the conversion of carbon dioxide to fuels, with a focus on the catalytic aspects. Some relevant option, such as the use of micro-algae or other bio-catalysis based processes, or the use of microwave and plasma processes were not addressed due to size limits in the manuscript.

Hydrogenation of CO_2 to form fuels is the most investigated area. By coupling conventional methanol process to RWGS it is possible to feed even pure CO_2 to produce methanol. This reaction scheme has been implemented at a pilot plant level and results are quite encouraging. A further step would be to use multifunctional catalysts to produce directly DME, which is a preferable energy carrier.

Hydrogenation of carbon dioxide to hydrocarbons is possible, but requires much higher consumption of H_2 and therefore is less interesting. Conversion of CO_2 to other oxygenates such as ethanol and DME is attracting, but further development in the catalysts is necessary. There is large interest on the conversion of carbon dioxide to formic acid, but a conditioning factor is the availability of efficient technologies to use formic acid as energy carrier, as well as the toxic character of formic acid.

Dry reforming of methane with CO_2 is a known technology. Tri-reforming is an extension of the concept to operate autothermically and with the advantage of not requiring a pure CO_2 stream to operate. Pilot plant studies have shown stability of operations (suing noble metals supported on MgO) for over 7000 h, although larger scale demonstration could be necessary.

There are also various processes at an earlier stage, particularly biological and photo/electrocatalytic processes, which need to be studied representing the future in medium-long term. Therefore, the area of carbon dioxide conversion to fuels and chemicals is a very active R&D sector, and we should anticipate it represents a challenging possibility for companies to develop complementary strategies to CSS to reduce greenhouse gas emissions.

Acknowledgements

The manuscript was prepared in the frame of the activities of the project “ELCAT” (FP6-NEST-A-2400) and the Network of Excellence “IDECAT” (NMP3-CT-2005-011730) supported by the European Commission, and the European Laboratory of Catalysis and Surface Science (ELCASS) whose partners (FHI-MPG, and LMSPC-ECPM-ULP) are gratefully acknowledged.

References

[1] G. Centi, G. Cum, J.L.G. Fierro, J.M. López Nieto, in Direct Conversion of Methane, Ethane and Carbon Dioxide to Fuels and Chemicals, CAP Report, The Catalyst Group Resources, 2008.
[2] S.K. Ritter, What can we do with carbon dioxide? Chem. Eng. News 85 (18) (2007) 11.
[3] D. Graham-Rowe, Turning CO_2 back into hydrocarbons, New Scientist 2645 (March) (2008) 32.
[4] International Energy Agency (IEA), World Energy Outlook, 2008.
[5] G. Centi, S. Perathoner, Carbon dioxide utilization for global sustainability, Stud. Surf. Sci. Catal. 153 (2004) 1.
[6] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W.M. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, Chem. Rev. 101 (4) (2001) 953.
[7] M. Aresta, A. Dibenedetto, F. Nocita, C. Pastore, A.M. Venezia, F. Chirikalova, V.I. Kononenko, V.G. Shevchenko, I.A. Chupova, Catal. Today 115 (2006) 117.
[8] M. Aresta, A. Dibenedetto, Dalton Trans. 28 (2007) 2975.
[9] T. Sakakura, J.-C. Choi, H. Yasuda, Chem. Rev. 107 (6) (2007) 2365.
[10] C. Song, A.M. Gaffney, K. Fujimoto (Eds.), CO_2 Conversion and Utilization (ACS Symposium Series), American Chemical Society, Washington, DC, 2002.
[11] I. Omae, Catal. Today 115 (1–4) (2006) 33.
[12] S.-i. Fujita, B.M. Bhanage, M. Arai, in: L.P. Bevy (Ed.), Progress in Catalysis Research, Nova Science Pub., Hauppauge, NY, 2005, p. 57.
[13] P.G. Jessop, F. Joo, C.-C. Tai, Coord. Chem. Rev. 248 (21–24) (2004) 2425.
[14] G. Centi, R.A. van Santen (Eds.), Catalysis for Renewables, Wiley VCH Pub., Weinheim, Germany, 2007.
[15] F. Cavani, G. Centi, S. Perathoner, F. Trifirò, Sustainable Industrial Chemistry—Principles, in: Tools and Industrial Examples, Wiley VCH, Weinheim, Germany, 2009.
[16] B. Wang, Y. Li, N. Wu, C.Q. Lan, Appl. Microbiol. Biotechnol. 79 (5) (2008) 707.
[17] A.T. Bell, B.C. Gates, D. Ray, Basic Research Needs: Catalysis for Energy (PNNL-17214), U.S. Department of Energy, Report from a Workshop held in August 6–8, 2007, Bethesda, Maryland (US) (http://www.sc.doe.gov/bes/reports/list.html).
[18] G. Centi, S. Perathoner, Z. Rak, Appl. Catal., B: Environ. 41 (2003) 143.
[19] G. Centi, S. Perathoner, G. Winè, M. Gangeri, Green Chem. 9 (2007) 671.
[20] M. Gangeri, S. Perathoner, S. Caudo, G. Centi, J. Amadou, D. Bégin, C. Pham-Huu, M.J. Ledoux, J.-P. Tessonnier, D.S. Su, R. Schlögl, Catal. Today 143 (1–2) (2009) 57.
[21] G. Centi, S. Perathoner, Top. Catal. 52 (8) (2009) 948–961.
[22] E.E. Benson, C.P. Kubiak, A.J. Sathrum, J.M. Smieja, Chem. Soc. Rev. 38 (1) (2009) 89.
[23] K.M.K. Yu, I. Curcic, J. Gabriel, S.C.E. Tsang, ChemSusChem 1 (11) (2008) 893.
[24] C. Minero, V. Maurino, in: G. Centi, R.A. Van Santen (Eds.), Catalysis for Renewables: From Feedstock to Energy Production, Wiley-VCH, Weinheim, Germany, 2007, p. 351 (Chapter 16).
[25] G.A. Olah, A. Goeppert, G.K.S. Prakash, J. Org. Chem. 74 (2) (2009) 487.
[26] (a) C. Song, Catal. Today 115 (2006) 2;
(b) C.S. Song, W. Pan, Catal. Today 98 (4) (2004) 463.
[27] J. Louie, Curr. Org. Chem. 9 (7) (2005) 605.
[28] Y. Sun, Carbon dioxide utilization for global sustainability, Stud. Surf. Sci. Catal. 153 (2004) 9.
[29] M. Aresta, A. Dibenedetto, Catal. Today 98 (4) (2004) 455.
[30] M. Ricci, in: M. Aresta (Ed.), Carbon Dioxide Recovery and Utilization, Kluwer Acad. Pub. (now Springer-Verlag, Germany), Dordrecht, The Netherlands, 2003, p. 395.
[31] D.J. Darensbourg, Chem. Rev. 107 (6) (2007) 2388.
[32] S. Fukuoka, M. Tojo, H. Hachiya, M. Aminaka, K. Hasegawa, Poymer J. (Tokyo, Japan) 39 (2) (2007) 91.
[33] R. Zevenhoven, S. Eloneva, S. Teir, Catal. Today 115 (1–4) (2006) 73.
[34] A.A. Lemonidou, J. Valla, I.A. Vasalos, in: Aresta M. (Ed.), Carbon Dioxide Recovery and Utilization, Kluwer Acad. Pub. (now Springer-Verlag, Germany), Dordrecht, The Netherlands, 2003, p. 373.
[35] M. Saito, Catal. Surveys Jpn. 2 (2) (1998) 175.
[36] S. Tan, L. Zou, E. Hu, Res. J. Chem. Environ. 9 (1) (2005) 66.
[37] P. Usubharatana, D. McMartin, A. Veawab, P. Tontiwachwuthikul, Ind Eng. Chem. Res. 45 (8) (2006) 2558.
[38] Y.H. Hu, E. Ruckenstein, Adv. Catal. 48 (2004) 297.
[39] G. Shaub, D. Unruh, M. Rohde, Carbon dioxide utilization for global sustainability, Stud. Surf. Sci. Catal. 153 (2004) 17.
[40] T. Kodama, Prog. Energy Combust. Sci. 29 (6) (2003) 567.
[41] A. Dibenedetto, I. Tommasi, in: M. Aresta (Ed.), Carbon Dioxide Recovery and Utilization, Kluwer Acad. Pub., Dordrecht, The Netherlands, 2003, p. 315.
[42] Z. Jiang, W. Songwei, Carbon dioxide utilization for global sustainability, Stud. Surf. Sci. Catal. 153 (2004) 475.
[43] K. Skjanes, P. Lindblad, J. Muller, Biomol. Eng. 24 (4) (2007) 405.
[44] J.L.G. Fierro, in: J.L.G. Fierro (Ed.), Metal Oxides Chemistry and Applications, CRC Taylor & Francis Pub., Boca Raton, FL, USA, 2006 , p. 569 (Chapter 18).
[45] P.G. Jessop, Prepr. Pap. – Am. Chem. Soc., Div. Fuel Chem. 49 (1) (2004) 1.
[46] S. Zhang, Y. Chen, F. Li, X. Lu, W. Dai, R. Mori, Catal. Today 115 (1–4) (2006) 61.
[47] M.P. Rohde, D. Unruh, G. Schaub, Catal. Today 106 (1–4) (2005) 143.
[48] M.P. Rohde, D. Unruh, G. Schaub, Ind Eng. Chem. Res. 44 (25) (2005) 9653.
[49] M. Saito, M. Takeuchi, T. Fujitani, J. Toyir, S. Luo, J. Wu, H. Mabuse, K. Ushikoshi, K. Mori, T. Watanabe, Appl. Organometal. Chem. 14 (2000) 763.
[50] M. Saito, K. Murata, Catal. Survey Asia 8 (4) (2004) 285.
[51] D. Mignard, C. Pritchard, Chem. Eng. Res. Des. 84 (A9) (2006) 828.
[52] A.F. Ghenciu, Curr. Opin. Solid State Mater. Sci. 6 (2002) 389.
[53] Y. Tanaka, T. Utaka, R. Kikuchi, K. Sasaki, K. Eguchi, Appl. Catal., A: Gen. 238 (2003) 11.
[54] Q.F. Li, M.F. Stephanopoulos, Appl. Catal., B: Environ. 27 (2000) 179.
[55] S.L. Swartz, M.M. Seabaugh, C.T. Holt, W.J. Dawson, Fuel Cell. Bull. 4 (30) (2001) 7.
[56] A. Goguet, S.O. Shekhtman, R. Burch, C. Hardacre, F.C. Meunier, G.S. Yablonsky, J. Catal. 237 (2006) 102.
[57] R.J. Gorte, S. Zhao, Catal. Today 104 (2005) 18.
[58] G. Jacobs, U.M. Graham, E. Chenu, P.M. Patterson, A. Dozier, B.H. Davis, J. Catal. 229 (2005) 499.
[59] F.C. Meunier, D. Tibiletti, A. Goguet, S. Shekhtman, C. Hardacre, R. Burch, Catal. Today 126 (1–2) (2007) 143.
[60] D. Mignard, M. Sahibzada, J.M. Duthie, H.W. Whittington, Int. J. Hydrogen Energy 28 (2003) 455.
[61] G.A. Olah, A. Goeppert, G.K.S. Prakash, Beyond Oil and Gas: The Methanol Economy, Wiley-VCH Pub., Weinheim, Germany, 2006.
[62] T. Maki, T. Ueyama, K. Mae, Chem. Eng. Technol. 28 (2005) 494.
[63] Y. Kawamura, N. Ogura, T. Yamamoto, A. Igarashi, Chem. Eng. Sci. 61 (2006) 1092.
[64] M. Lachowska, J. Skrzypek, Stud. Surf. Sci. Catal. 153 (2004) 173.
[65] C. Yang, Z. Ma, N. Zhao, W. Wei, T. Hu, Y. Sun, Catal. Today 115 (2006) 222.
[66] X.-M. Liu, G.Q. Lu, Z.-F. Yan, J. Beltramini, Ind. Eng. Chem. Res. 42 (2003) 6518.
[67] J. Wu, M. Saito, M. Takeuchi, T. Watanabe, Appl. Catal., A: Gen. 218 (1–2) (2001) 235.
[68] J.E. Miller, Initial Case for Splitting Carbon Dioxide to Carbon Monoxide and Oxygen, SANDIA Report SAND2007-8012, Sandia National Laboratories (US), December 2007.
[69] J.S.M. Zadeh, K.J. Smith, J. Catal. 183 (2) (1999) 232.
[70] Y. Zhang, G. Jacobs, D.E. Sparks, M.E. Dry, B.H. Davis, Catal. Today 71 (3–4) (2002) 411.
[71] X. Zhang, B. Dai, A. Zhu, W. Gong, C.J. Liu, Catal. Today 72 (2002) 223.
[72] T. Riedel, M. Claeys, H. Schulz, G. Schaub, S.-S. Nam, K.-W. Jun, M.-J. Choi, G. Kishan, K.-W. Lee, Appl. Catal., A: Gen. 186 (1–2) (1999) 201.
[73] H. Schulz, T. Riedel, G. Schaub, Top. Catal. 32 (3–4) (2005) 117.
[74] F. Tihay, A.C. Roger, G. Pourroy, A. Kiennemann, Energy Fuels 16 (5) (2002) 1271.
[75] R. Bai, Y. Tan, Y. Han, Fuel Proc. Technol. 86 (3) (2004) 293.
[76] X. Ni, Y. Tan, Y. Han, N. Tsubaki, Catal. Comm. 8 (11) (2007) 1711.
[77] H. Arakawa, Advances in chemical conversion for mitigating carbon dioxide, Stud. Surf. Sci. Catal. 114 (1998) 19.
[78] X. Pan, Z. Fan, W. Chen, Y. Ding, H. Luo, X. Bao, Nat. Mater. 6 (2007) 507.
[79] Z. Fan, W. Chen, X. Pan, X. Bao, Catal. Today (2009), doi:10.1016/j.cattod.2009.03.004.
[80] H. Kurakata, Y. Izumi, K.-I. Aika, Chem. Commun. (1996) 389.
[81] Y. Izumi, Platinum Met. Rev. 41 (4) (1997) 166.
[82] S. Ogo, R. Kabe, H. Hayashi, R. Harada, S. Fukuzumi, Dalton Trans. 39 (2006) 4657.
[83] J. Stevens, Chemical Technology, 11, RSC Pub., Cambridge, UK, 3, 2006, p. T42.
[84] Z. Zhang, Y. Xie, W. Li, S. Hu, J. Song, T. Jiang, B. Han, Angew. Chem. Int. Ed. 47 (6) (2008) 1127.
[85] (a) F. Yagi, R. Kanai, S. Wakamatsu, R. Kajiyama, Y. Suehiro, M. Shimura, Catal. Today 104 (1) (2005) 2;
(b) F. Yagi, S. Hodoshima, S.i. Wakamatsu, R. Kanai, K. Kawazuishi, Y. Suehiro, M. Shimura, in: F.B. Noronha, M. Schmal, E.F. Sousa-Aguiar (Eds.), Studies Surface Science and Catal. Natural Gas Conversion VIII, vol. 167, Elsevier Pub., Amsterdam, 2007, p. 385.
[86] M.C.J. Bradford, M.A. Vannice, Catal. Rev. – Sci. Eng. 41 (1) (1999) 1.
[87] D.J. Moon, Catal. Surveys Asia 12 (3) (2008) 188.
[88] A.P.E. York, T.-c. Xiao, M.L.H. Green, J.B. Claridge, Catal. Rev. – Sci. Eng. 49 (4) (2007) 511.
[89] T. Borowiecki, J. Ryczkowski, in: L.P. Bevy (Ed.), Focus on Catalysis Research, Nova Science Pub., Hauppauge, NY, 2006, p. 101.
[90] H.S. Roh, H.S. Potdar, K.W. Jun, J.W. Kim, Y.S. Oh, Appl. Catal., A: Gen. 276 (2004) 231.
[91] V.M. Gonzalez-Dela Cruz, J.P. Holgado, R. Pereniguez, A. Caballero, J. Catal. 257 (2) (2008) 307.
[92] K.O. Christensen, D. Chen, R. Lødeng, A. Holmen, Appl. Catal., A: Gen. 314 (1) (2006) 9.
[93] D. Chen, K.O. Christensen, E. Ochoa-Fernández, Z. Yu, B. Tøtdal, N. Latorre, A. Monzón, A. Holmen, J. Catal. 229 (2005) 82.
[94] T. Horiuchi, K. Sakuma, T. Fukui, Y. Kubo, T. Osaki, T. Mori, Appl. Catal. 144 (1996) 111.
[95] X. Zhu, P. Huo, Y.-p. Zhang, D.-g. Cheng, C.-j. Liu, Appl. Catal., B: Environ. 81 (1–2) (2008) 132.

[96] Y.-X. Pan, C.-J. Liu, P. Shi, Peng, J. Power Sources 176 (1) (2008) 46.
[97] J.R.H. Ross, Catal. Today 100 (1–2) (2005) 151.
[98] X. Song, Z. Guo, Energy Convers. Manage. 47 (2006) 560.
[99] (a) M. Halmann, A. Steinfeld, Energy 31 (15) (2006) 3171;
(b) M. Halmann, A. Steinfeld, Catal. Today 115 (2006) 170.
[100] D.L. DuBois, Electrochemical reactions of carbon dioxide, Encyclopedia Electrochem. 7a (2006) 202.
[101] M. Gattrell, N. Gupta, A. Co, J. Electroanal. Chem. 594 (2006) 1.
[102] Y. Hori, CO_2 Reduction Catalyzed by Metal Electrodes, Handb. Fuel Cells – Fundam. Technol. Appl. 2 (2003) 720.
[103] Y. Hori, H. Konishi, T. Futamura, A. Murata, O. Koga, H. Sakurai, K. Oguma, Electrochim. Acta 50 (2005) 5354.
[104] J. Salimon, M. Kalaji, J. Chem. 5 (1) (2003) 023.
[105] J. Qu, X. Zhang, Y. Wang, C. Xie, Electrochim. Acta 50 (16–17) (2005) 3576.
[106] M. Jitaru, J. Univ. Chem. Technol. Metall. 42 (4) (2007) 333.
[107] H. Shibata, J.A. Moulijn, G. Mul, Catal. Lett. 123 (3–4) (2008) 186.
[108] M. Gangeri, S. Perathoner, S. Caudo, G. Centi, J. Amadou, D. Begin, C. Pham-Huu, M.J. Ledoux, J.-P. Tessonnier, D.S. Su, R. Schlögl, Catal. Today 143 (1–2) (2009) 57.
[109] G. Centi, S. Perathoner, G. Winè, M. Gangeri, Converting CO_2 to fuel: a dream or a challenge? Prepr. Symp. – Am. Chem. Soc. Div. Fuel Chem. 51 (2006) 745.
[110] O.K. Varghese, M. Paulose, T.J. LaTempa, C.A. Grimes, Nano Lett. 9 (2) (2009) 731.
[111] M. Kitano, M. Matsuoka, M. Ueshima, M. Anpo, Appl. Catal., A: Gen. 325 (2007) 1.
[112] W. Lin, H. Han, H. Frei, J. Phys. Chem. B 108 (2004) 18269.
[113] Y. Ku, W.-H. Lee, W.-Y. Wang, J. Mol. Catal. A 212 (2004) 191.
[114] I.-H. Tseng, J.C.S. Wu, H.-Y. Chou, J. Catal. 221 (2004) 432.
[115] Y. Shioya, K. Ikeue, M. Ogawa, M. Anpo, Appl. Catal., A: Gen. 254 (2003) 251.
[116] H. Hori, K. Koike, Y. Suzuki, M. Ishizuka, J. Tanaka, K. Takeuchi, Y. Sasaki, J. Mol. Catal. A 179 (2002) 1.
[117] S. Kaneco, H. Kurimoto, Y. Shimizu, K. Ohta, T. Mizuno, Energy 24 (1999) 21.
[118] J.L. Lyman, R. Jensen, J. Sci. Total Environ. 277 (1–3) (2001) 7.
[119] A.J. Traynor, R.J. Jensen, Ind. Eng. Chem. Res. 41 (2002) 1935.
[120] C.C. Agrafiotis, C. Pagkoura, S. Lorentzou, M. Kostoglou, A.G. Konstandopoulos, Catal. Today 127 (2007) 265.