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To cite this version:

Sara Navarro-Jaén, Mirella Virginie, Julien Bonin, Marc Robert, Robert Wojcieszak, et al.. Highlights and challenges in the selective reduction of carbon dioxide to methanol. Nature Reviews Chemistry, 2021, 10.1038/s41570-021-00289-y . hal-03319801

HAL Id: hal-03319801
https://hal.univ-lille.fr/hal-03319801v1

Submitted on 13 Aug 2021

December 2nd, 2020

Highlights and Challenges in the Selective CO_2 Reduction to Methanol

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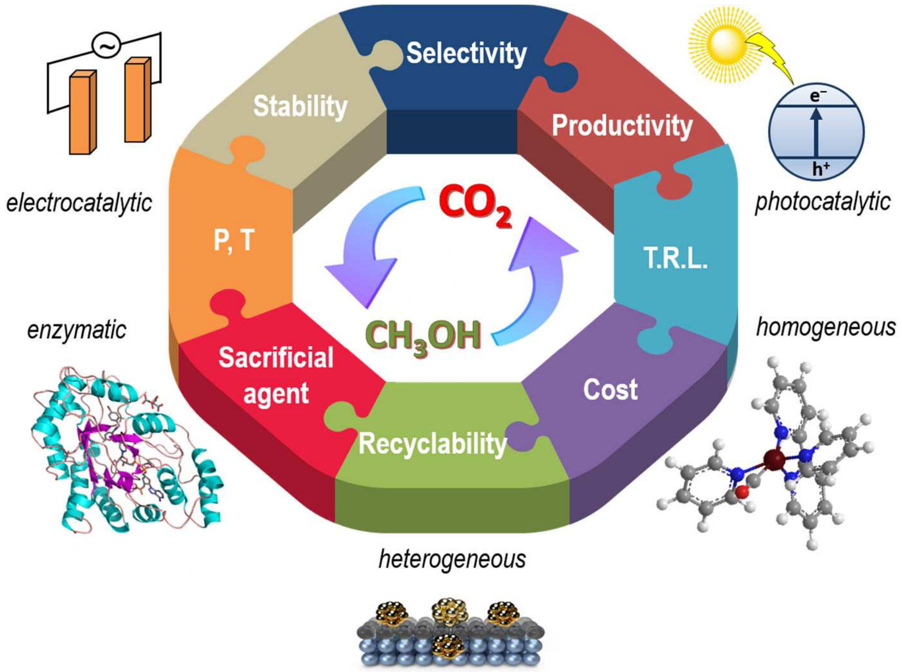

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Abstract. Carbon dioxide is an iconic greenhouse gas and a major factor for current global climate changes, making essential its capture and recycling into valuable products and fuels. Methanol is a key compound that could be obtained from the 6-electrons, 6-protons CO_2 reduction and that can be used both as a fuel and as a platform-molecule. The goal of this review is to present a comparative analysis of the CO_2 reduction routes to methanol *via* heterogeneous and homogeneous catalytic hydrogenation, as well as enzymatic, photo- and electro-catalysis. After identifying catalytic materials and reaction conditions, we provide a comparative assessment of their respective advantages and drawbacks in terms of selectivity, productivity, stability, operating conditions, cost and technical readiness level. Currently, heterogeneous hydrogenation catalysis and electrocatalysis have the highest potential for the CO_2 reduction to methanol at larger scale. Availability and price of sustainable electricity appear as essential prerequisites for efficient methanol synthesis from CO_2.

Keywords: CO_2 reduction; methanol; catalysis; photocatalysis; electrocatalysis

Atmospheric carbon dioxide (CO_2) concentration has reached[1] 417 ppm in May 2020. This gas is definitely the main greenhouse player, responsible for climate changes through transport, industry and household emissions. CO_2 is mainly generated by the combustion of non-renewable fossil fuels and by industrial activities such as iron, steel or cement production and petrochemical refining. Currently, there are two strategies to address the continuously increasing CO_2 content in the biosphere: carbon capture and storage (CCS)[2] and carbon capture and utilization (CCU)[3]. CCS relies on the CO_2 capture, including its separation, compression, transport, for permanent storage in a geological layer. However, such strategy relies on *putting the dust under the carpet*, while its technological and economic feasibility at larger scale has not been demonstrated. CCU involves either direct technological utilization of CO_2 (in soft drinks or fire extinguishers for example) or its chemical and/or biological conversion into value-added products and fuels[3–5].

The CO_2 chemical conversion could contribute to lower consumption of hydrocarbon-based fuels (gasoline, diesel, jet fuels), which are currently manufactured from fossil feedstocks[6] and which are major sources of greenhouse gas emissions. The synthesis of fuels and chemicals from CO_2 can also enhance carbon- and energy-efficiency of existing technologies and elaboration of new sustainable “green” industrial processes[7,8]. However, CO_2 is a very stable molecule, having the most oxidized state of carbon. The linear geometry and the strength of the double C=O bond (*ca.* 750 kJ mol^{-1}) require external energy for the CO_2 activation and conversion, which can come from either energy-dense feedstocks (*e.g.* hydrogen, reduced nucleotides), thermal energy (heat), light irradiation or electricity. In recent years, solar energy and renewable electricity have gradually become more and more economically competitive compared to the conventional fossil-based energy sources[9].

To address the perspective of an on-going shift from fossil to renewable energy supplies, development of chemical catalytic processes for the CO_2 reduction to methanol (CH_3OH) that would be simultaneously energy-efficient, highly selective and zero-waste is highly desirable. Various catalytic approaches, including heterogeneous and homogeneous catalytic hydrogenation, enzymatic, photo- and electro- catalysis, have been explored and have shown promise.

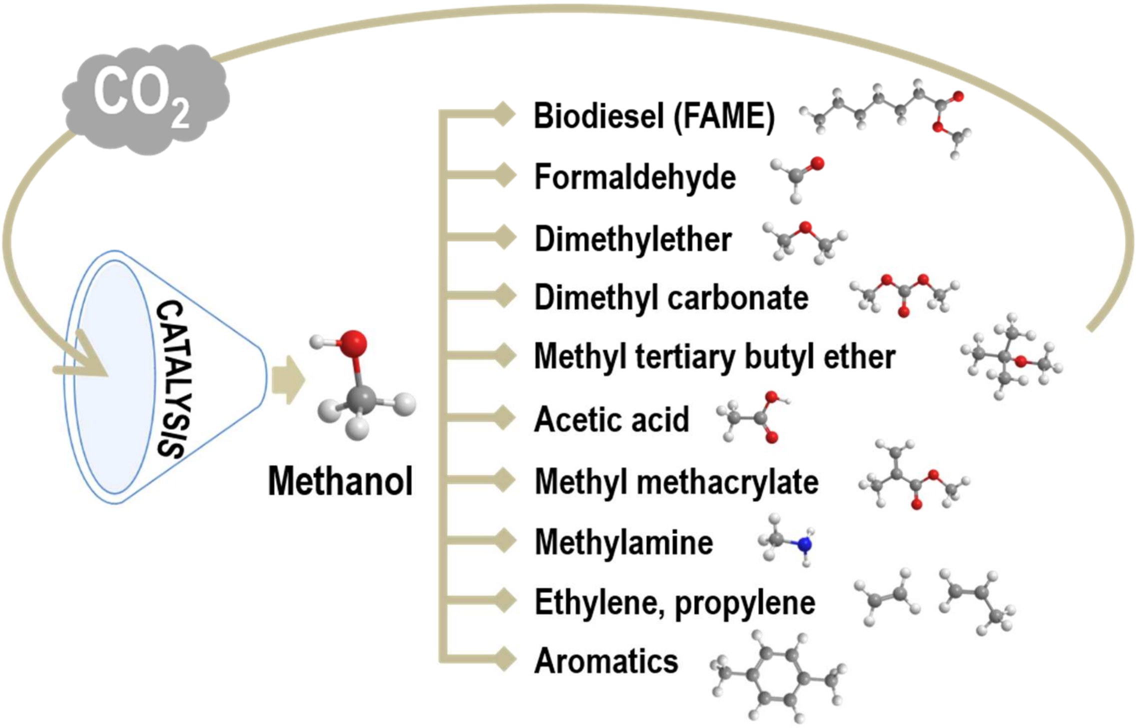

Fig. 1. Carbon cycle of methanol, a platform molecule for chemical industry.

Among the various reduction products possibly obtained from CO_2 reduction, methanol is a major target, having numerous applications in chemistry (**Fig. 1**). It can account alone for about 30% of the most widely used chemicals: dimethyl ether, dimethyl carbonate, formaldehyde, aromatics, ethylene, propylene, methyl tertiary butyl ether, methylamine, methyl methacrylate and acetic acid. Methanol is also used for the production of fatty acid methyl esters (FAME), which are the main components of biodiesel, and it can be used for direct blending of gasoline. Moreover, methanol is liquid at ambient temperatures and is thus easy to store and to handle. Last but not least, it can be directly used to feed fuel cells.

Worldwide, the methanol production capacity is of *ca.* 110 million metric tons per year[10]. Methanol production already involves utilization of 2 million tons of CO_2[11]. The CO_2 reduction to CH_3OH is often considered as the core of the "methanol economy"[4]. Since 2012, a demonstration plant[12] in Iceland is producing about 4000 tons of methanol/year from CO_2 and renewable H_2 over a heterogeneous Cu-ZnO catalyst, and is thus recycling 5500 tons of CO_2/year. Other industrial facilities for the CO_2 conversion to CH_3OH are under development in Germany[13] and China[14].

In this review, we draw a comparative qualitative and quantitative analysis of the CO_2 reduction routes to methanol *via* heterogeneous, homogeneous, enzymatic, photo- and electrocatalysis. Analysis of current trends is mainly based on the literature published in the last 5 years.

Heterogeneous hydrogenation catalysis. On an industrial scale, methanol is mostly produced from syngas, a mixture of CO, H_2 and some traces of CO_2, which is generated from fossil fuels (*e.g.* coal or natural gas). Therefore, the emerging environmental paradigm envisages anthropogenic CO_2 and "green" H_2 as ideal feedstock to produce "green" methanol in the near future[15–18]:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{298\ K,\ 5\ MPa} = -40.9\ kJ\cdot mol^{-1} \qquad \text{(Eq. 1)}$$

However, the CO_2 hydrogenation to methanol is more challenging than that of CO due to the thermodynamic and chemical stability of the CO_2 molecule[16], whereas the competitive reverse water-gas shift (RWGS) reaction (Eq. 2) can also take place, in particular at higher reaction temperatures:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{298\ K,\ 5\ MPa} = 49.8\ kJ\cdot mol^{-1} \qquad \text{(Eq. 2)}$$

Taking these aspects into consideration, design of appropriate stable catalysts able to activate the CO_2 molecule and to favour its conversion into CH_3OH is essential.

Cu-based catalysts. Although numerous systems have been studied for the conversion of CO_2 into methanol, major effort has been put on the Cu-based catalysts. Copper alone presents low activity for methanol synthesis, making the addition of promoters necessary to boost its performance[19,20]. The traditional Cu-ZnO catalyst (50-70% mol CuO, 20-50% ZnO, 5-20%

Al_2O_3, ZrO_2, …) achieves conversion efficiencies of about 30% and methanol selectivity between 30-70% at 220-300°C and < 50 bar[21]. Its low price, high activity and possibility to operate at mild temperature and pressure [22,23] have attracted the attention of numerous research groups.

Despite tremendous efforts in understanding the catalyst structure and reactivity, the nature of the active site is still a matter of intense debate[18,24,25]. The active site is commonly thought to result from the intimate Cu-ZnO synergy, *i.e.* formation of a Cu-Zn alloy or presence of oxygen vacancies generated by means of a junction of both metals (**Fig. 2a**)[18–20,26]. Thus, improving the Cu-ZnO interaction and maximizing the Cu surface area, which can be achieved by carefully controlling the synthesis and activation conditions[23,27] are determinant factors to obtainthe enhanced catalytic performance. In this sense, co-precipitation of metal hydroxycarbonates produced *via* the reaction of the metal precursors and a basic precipitating agent is the most explored synthesis method[23]. Temperature, pH and aging time are crucial factors that determine the hydroxycarbonate phase. The formation of zincian malachite [$(Cu_{1-x}Zn_x)_2(OH)_2CO_3$, $x \leq 0.27$] is generally associated to a greater Zn incorporation in the catalyst structure, which drives the enhanced catalytic behaviour[28]. Recently, it has been found that supercritical CO_2 allows the formation of stable amorphous georgeite [$Cu_7(CO_3)_5(OH)_4 \cdot 5H_2O$], which can further improve the activity and stability of the Cu-ZnO system[29].

Al_2O_3 has been the most popular catalyst promoter for the methanol synthesis from syngas[30], but its hydrophilicity seems to be detrimental for methanol synthesis from CO_2. Production of large amounts of water indeed induces catalyst sintering and subsequent deactivation[31,32]. ZrO_2 has been widely explored due to its weaker hydrophilic character, its basicity, which favours the CO_2 adsorption, enhanced activity and selectivity in the methanol synthesis from CO_2 (**Fig. 2b**)[23,32,33].

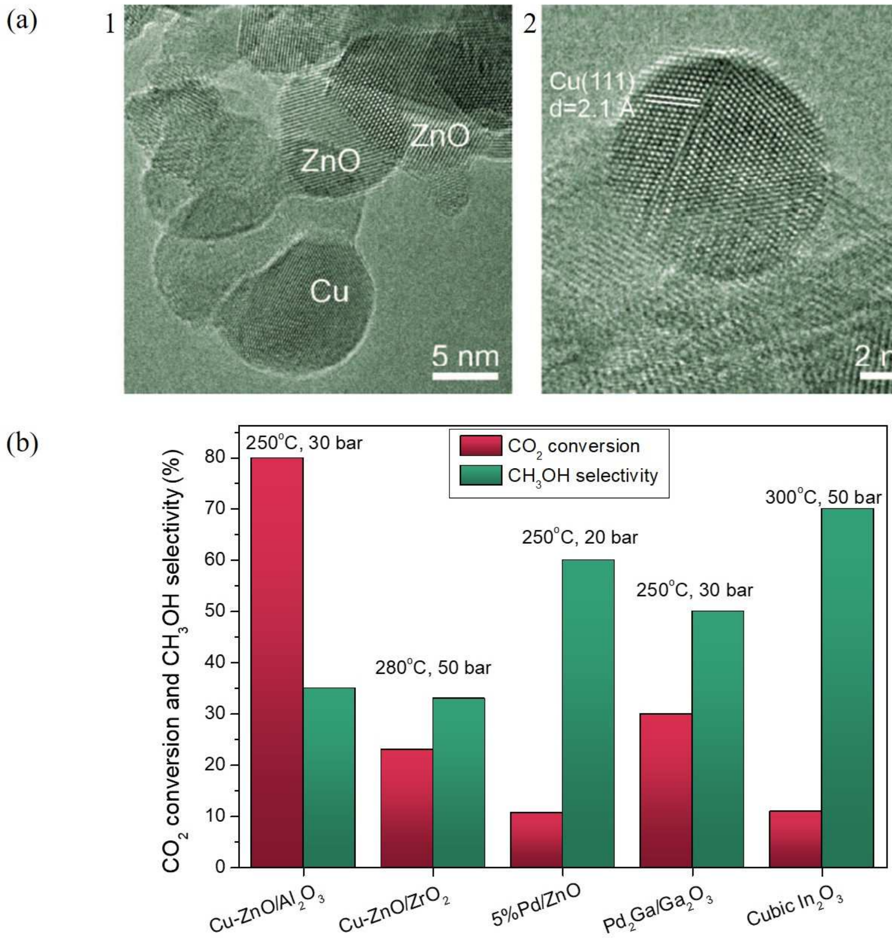

Fig. 2. (a) Transmission electron micrograph of a Cu-ZnO/Al_2O_3 catalyst during exposure to H_2 at 300 °C, showing (1) arrangement of the catalyst nanoparticles and (2) exposed Cu nanoparticles surfaces with direct gas accessibility [34]. (b) Comparison of catalytic performance (CO_2 conversion: red bars, CH_3OH selectivity: green bars) for selected heterogeneous catalysts [35–38].

Another strategy aims at improving the Cu-ZnO/ZrO_2 catalytic and mechanical properties by adding different mesoporous supports. For instance, addition of SBA-15 allows obtaining highly dispersed metal particles as well as confinement of the active phase inside the SBA-15 channels. Methanol space-time-yield of 376 $mg_{CH3OH}\cdot h^{-1}\cdot g_{cat}^{-1}$ was obtained, significantly larger than the 10 $mg_{CH3OH}\cdot h^{-1}\cdot g_{cat}^{-1}$ measured in the absence of support[39]. Hydrotalcites enhance methanol selectivity to 78.3% at 250°C and 30 bar, in contrast to 68.6% reached with CuZnO/ZrO_2 only, by virtue of the hydrotalcite CO_2 adsorption capacity, which increases the CO_2 concentration near the active sites[40]. A series of amorphous mesoporous aluminosilicates has been also studied, evincing the possibility of controlling specific area of metallic copper by adjusting the Si/Al ratio and increasing methanol production with the increase in the Al content[41].

Noble metal and bimetallic catalysts. Due to their well-known activity in the CO_2 hydrogenation reactions, Pd catalysts have also been explored for methanol synthesis[23]. The selectivity is generally directed by the support and promoters[37]. The Pd/ZnO catalysts can convert 11% CO_2 with 60% selectivity towards methanol at 250°C and 20 bar. The enhancement of the catalytic performance has been attributed to the formation of a PdZn alloy. In this sense, CO_2 is adsorbed on ZnO and H_2 is dissociated on the surface of Pd, giving rise to the formation of surface formate species. If the alloy is not formed, formate species directly decompose instead of producing methanol, due to their low stability on Pd. However, the formation of PdZn is thought to passivate the surface and stabilize the formate intermediate, favouring methanol production. Methanol production is promoted by small particle sizes, whereas isolated Pd particles foster the competitive RWGS reaction[37].

Ga_2O_3 is also a promising solid support. Upon association with Pd, it leads to the 20% CO_2 conversion and 51.5% methanol selectivity. In this case, it is assumed that the active metal species for methanol production involve Pd^{n+} $(0 < n < 2)$. The excellent catalytic activity explained by the presence of an optimal amount of Pd^{n+} stabilized by Ga_xO_y on the surface of Pd [42]. However, the RWGS reaction occurs as well, giving rise to the undesired formation of CO. Addition of Ga_2O_3 as promoter to Pd/SiO_2 led to a 500-fold increase in methanol production relative to the parent catalyst[43].

Although scarcely studied, Au has also been considered as a potential catalytic material, and due to its relative inertness in the hydrogenation reactions, selection of the support is crucial. As an example, Au/TiO_2 and $Au/CeO_x/TiO_2$ have been compared, showing that lower CeO_x coverages improve the selectivity towards CH_3OH even at low pressure[44].

Bimetallic systems have been widely investigated and exhibited enhanced catalytic properties. For instance, PdCu is an interesting system considering the outstanding performance of both metals separately. The SiO_2-supported PdCu catalysts with Pd/(Pd+Cu) ratios ranging from 0.25 to 0.34 convert from 5 to 7% of CO_2 with a 20-30% methanol selectivity, whereas *ca.* 3% conversion is obtained with Pd or Cu alone. The bimetallic promoting effect is explained by the formation of PdCu and $PdCu_3$ alloys, which may provide a source of chemisorbed hydrogen, thus favouring methanol formation[45]. The SiO_2-supported InPd catalysts[46] have also shown promising results, with higher CO_2 conversion and better methanol selectivity than the single metals, thanks to the formation of an InPd alloy and to a synergistic effect between indium oxide and bimetallic alloy. Such enhancement has also been observed with InNi catalysts, suggesting that these results can be expanded to other alloy/oxide systems[46]. The SiO_2-supported NiGa intermetallic catalysts are as well suitable for methanol production even at low pressure (10 bar), their performance being enhanced by doping with Au or Cu[47].

Metal oxide catalysts. There has been a recent surge in the use of metal oxides as catalysts for methanol synthesis. For example, the ZnO-ZrO_2 solid solution has emerged as a highly selective and stable catalyst, reaching more than 10% conversion and around 90% selectivity during 500 hours at 320°C and 50 bar[48]. In a similar way, M_aZrO_x (M_a = Cd, Ga) solid solutions can achieve from 4.3 to 12.4% CO_2 conversion and 80% selectivity, values that stand significantly higher than those obtained with the individual oxides[49]. In both cases, the results were attributed to the synergy between the catalytic components. The cubic phase of In_2O_3 has been investigated, but although the methanol selectivity reaches almost 100%, low conversion was achieved[38]. In order to overcome this problem, the promotion with other components is envisaged. For instance, Pd enhanced the In_2O_3 performance through its H_2 splitting capacity[50].

The results reported so far demonstrate that the Cu-based catalysts remain the catalytic family *par excellence* for the hydrogenation of CO_2 into methanol. However, the oxidation and sintering of Cu species together with the low water tolerance constitute significant drawbacks in terms of activity and stability. Consequently, the research is still focused on the search for appropriate promoters and hydrophobic components able to improve the catalyst stability. Noble metal, bimetallic and oxide catalysts have been studied to a lower extent, understanding of their characteristics and components interaction being wide paths to be explored.

On the other hand, the reaction mechanism is still a matter of debate. Although it is generally accepted that the catalytic formulations must be constituted by metals and/or oxides able to adsorb CO_2 and dissociate H_2, the identification of active sites, understanding of the interaction between components and dynamic behaviour of the participant species remain unclear and need to be clarified in order to pave the way to new catalytic formulations.

Regarding the industrial application of the heterogeneously catalysed methanol synthesis from CO_2, some additional aspects need to be considered. A greater amount of hydrogen is required for the hydrogenation of CO_2 with respect to that from syngas. Thus, for the process to be sustainable, hydrogen needs to be produced from renewable sources, such as, for example, from water electrolysis. On the other hand, the CO_2 hydrogenation is thermodynamically limited. For instance, the methanol yield from CO_2 at 200°C is about 50% lower with respect to that obtained from syngas. In order to overcome these problems, optimization of operating conditions and reactor design is mandatory[16]. Furthermore, methanol synthesis from CO_2 competes starting from 240°C, with the production of CO through the undesired RWGS reaction. Despite these necessary improvements, heterogeneous catalysis for methanol synthesis is already a relatively mature technology.

Molecular catalysis

Molecular-based catalysts, such as enzymes or molecular complexes, have noticeable advantages, such as fine tuning of the steric, electronic, acid-basic and electrostatic properties at the catalytically active site and in its close environment.

Enzymatic processes. Catalytic transformations using enzymes include a possibility to perform the reactions in mild conditions, with high efficiency and low energy consumption, taking advantage of the enzyme selectivity and with almost no deleterious impacts on the environment[51]. The CO_2 reduction using enzymatic catalysis has been intensively studied in the last 5 years[52–58]. Direct CO_2-to-methanol transformation remains however a challenge. An alternative consists in developing multi-cascade enzymatic systems[59,60]. To date, such multi-enzymatic systems only showed a relatively low methanol productivity, with the yield of less than 1 $mmol \cdot L^{-1}$ after hours of reaction[60]. In addition, high concentration (up to 100 $mmol \cdot L^{-1}$) of cofactor is necessary, which makes such process quite costly.

Multi-enzymatic systems. Catalytic conversion of CO_2 to methanol involves three dehydrogenases and presence of a cofactor (typically NADH, reduced nicotinamide adenine dinucleotide)[60]. The nature of cofactor strongly affects the selectivity of CO_2 reduction [61], *i.e.* it can improve the rate of the reaction towards a target compound.

CO_2 is firstly reduced into formate (**Fig. 3a**) by $F_{ate}DH$ (formate dehydrogenase), followed by the two-electron reduction of formate to formaldehyde catalysed by the formaldehyde dehydrogenase enzyme ($F_{ald}DH$). In the final step, methanol is produced by the alcohol dehydrogenase enzyme (ADH). The active sites of relevant enzymes are displayed in **Fig. 3b-e**. The overall methanol yield achieved in this three-step process is *ca.* 44%[59]. This relatively low conversion could be explained by the fact that because of unfavourable thermodynamics, the CO_2 reduction to formic acid catalysed by $F_{ate}DH$ is 30 times slower than the reverse oxidation of formate to CO_2[59,62]. In other words, the formate formation is the bottleneck of the catalytic process. In order to increase the conversion to methanol, one may operate at higher CO_2 concentration, which could be achieved by using ionic liquids compatible with the enzymes as a CO_2 co-solvent[59]. An aqueous system, containing 20% of [choline][glutamate] ([CH][Glu]) ionic liquid was recently reported, showing a 3.5-fold increase in methanol yield, when compared to the reaction carried out without co-solvent[59]. This yield was further increased (*ca.* 5-fold) upon incorporating a NADH regeneration step. The presence of the [CH][Glu] allows stabilizing proper conformation of the enzyme and also decreases the binding free energy of CO_2 to the enzyme[59]. In addition, the yield of methanol strongly depends on the [CH][Glu] concentration. From 10 to 20% increase in the concentration shifts the reaction equilibrium towards higher methanol production due to the larger concentration of CO_2 at the enzymatic catalytic site[59]. However, when the [CH][Glu] concentration increases from 20% to 60%, an opposite effect is observed, which may be explained by higher ionic concentrations (electrostatic charges) in the enzyme. Pressure is an additional mean to increase the CO_2 concentration in the system. The methanol formation rate could be enhanced from 1.20 to 2.17 $\times 10^{-3}$ $\mu mol \cdot min^{-1}$, when CO_2 pressure was raised from 0.2 to 0.5 MPa. Further increase to 1.0 MPa[63] has no beneficial effect on the reaction rate as NADH availability became the rate limiting factor of the process.

Multi-enzymatic processes are highly pH-sensitive[64]. They usually require low pH values and elevated temperatures. These conditions are not compatible with the stability of most enzymes, thus leading to their denaturation and/or inactivation. A strategy to prevent such deactivation lies in stabilizing the enzyme, for example through immobilization. It was shown[65] that the methanol productivity could be significantly enhanced by encapsulation of the three dehydrogenases in a porous silica sol–gel matrix. Both immobilization and confinement favourably affect the reaction thermodynamics. Different carriers and immobilization approaches were applied to create nature-mimicking microenvironments for enzymes, for example with alginate–silica composites[66]. Specific and suitable microenvironment is obtained in these cases, namely higher hydrophilicity, short diffusion distance, moderate rigidity and flexibility. These synergistically combined factors being suitable for the activity and the stability/reusability of the enzymes[66].

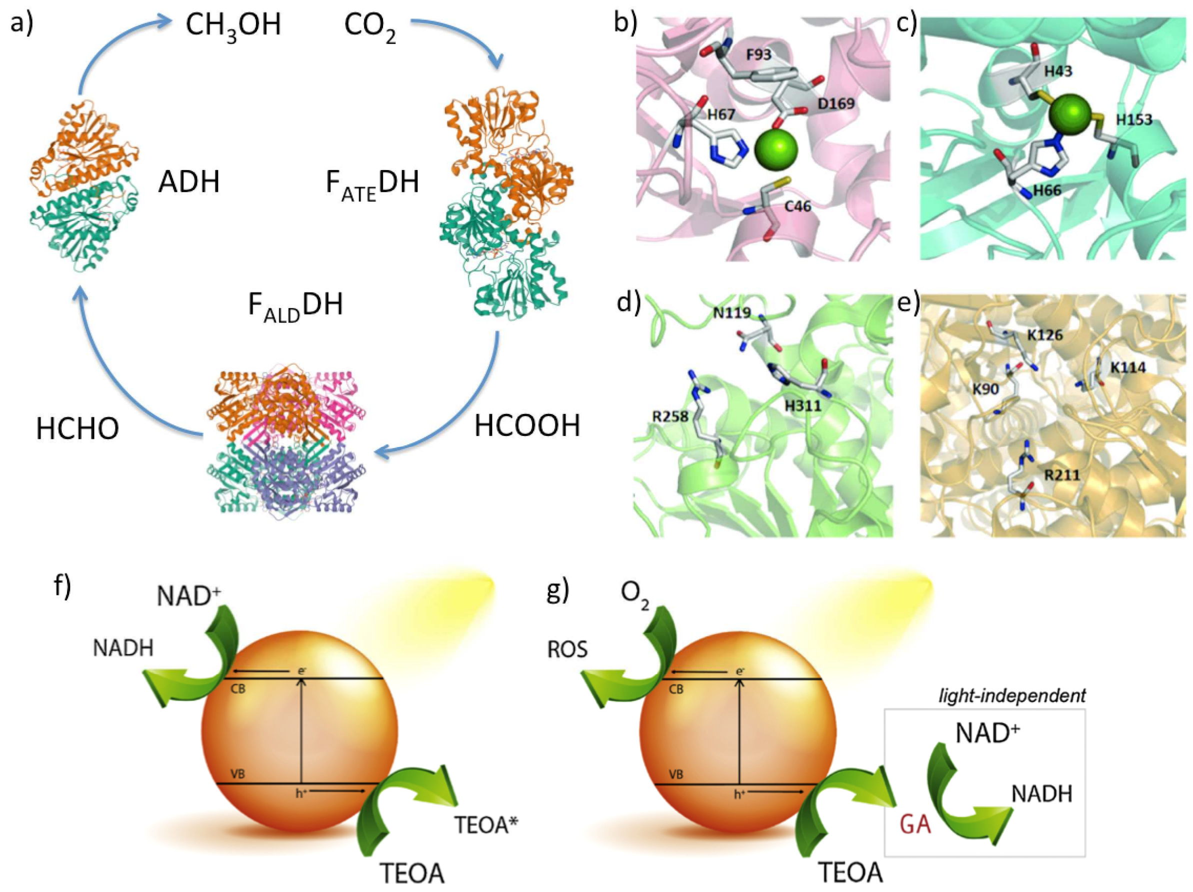

Fig. 3. a) Reaction pathway in enzymatic cascade for methanol synthesis from CO_2 using nicotinamide adenine dinucleotide hydrogenase (NADH), dependent formate dehydrogenase ($F_{ATE}DH$), formaldehyde dehydrogenase ($F_{ALD}DH$) and alcohol dehydrogenase (ADH) enzymes. [60] b) Representation of the active sites of the $F_{ALD}DH$. c) Representation of the active sites of the ADH, (d) Representation of the active sites of the $F_{ATE}DH$ e) Representation of the active sites of the glutamate dehydrogenase (GDH). The green spheres represent Zn^{2+} ions. [67] f) NADH cofactor photo-regeneration mechanism using semiconductor photocatalyst with simultaneous triethanolamine (TEOA) oxidation and NAD^+ reduction on the material surface (one-pot process). g) NADH cofactor photo-regeneration mechanism using semiconductor photocatalyst involving TEOA oxidation to glycolaldehyde (GA), an intermediate able to reduce NAD^+ after the light and photocatalyst removal (two-stage process). [68].

Cofactor regeneration. As already mentioned, use of NADH as a cofactor for dehydrogenase-catalysed reduction steps, is a drawback for the economic feasibility of enzymatic processes[69]. For the synthesis of one mole of methanol, three moles of NADH are consumed. This obviously hampers large scale application of enzymatic CO_2 conversion due to high cost of NADH[62]. A way to circumvent this problem is to implement a regeneration/reuse strategy. *In situ* cofactor regeneration is viewed as an ideal solution, for example by using photochemically induced regeneration (**Fig. 3 f, g**). The methanol production from CO_2 using four immobilized enzymes including $F_{ate}DH$, $F_{ald}DH$, ADH and glutamate dehydrogenase (GDH) was recently reported.[70] NADH was immobilized on a separate carrier and was regenerated by dehydrogenation of glutamate to 2-oxoglutarate. Even if the methanol yield was lower than in the case of the freely diffusing enzymes, the immobilized system showed largely improved stability and good recyclability. After seven cycles, more than 80% of original productivity was still maintained[70,71]. This led to a cumulative methanol yield of 127% (based on the amount of cofactor). The choice of the NADH regeneration system also plays a crucial role in reaching high efficiency and stability of the cascade enzymatic system in the CO_2 reduction to methanol. For example, phosphate dehydrogenase (PTDH) was found to be the most efficient agent for the NADH regeneration, with the activity 55 times higher than that of the free multi-enzymes $F_{ate}DH$, $F_{ald}DH$, ADH and PTDH system[72].

Homogeneous hydrogenation catalysis. The works reporting direct CO_2 hydrogenation to methanol using homogeneous metal complexes are not numerous[73–82]. Typically, a three-step cascade catalysis process is pursued: (i) formic acid formation from CO_2 hydrogenation; (ii) functionalization of formate to an activated ester, such as alkyl formate or carbonate or carbamate; and finally (iii) CH_3OH formation upon hydrogenation of the previous intermediate. The advantage of this cascade approach is that the rate and selectivity of each individual step can be individually tuned. However there is usually incompatibility for the catalysts in terms of reaction rate and reaction conditions, which is a major difficulty to achieve direct, one pot hydrogenation of CO_2 to methanol[78]. Conversion of CO_2 to formic acid derivative is favoured in basic medium in the presence of amines and amino alcohols, while subsequent reduction to methanol is favoured under acidic conditions[74]. The first CO_2-to-methanol reaction under basic conditions was successfully achieved[83] using a combination of dimethylamine and ruthenium catalyst and, so far, the best results in terms of activity were obtained using noble metal complexes and acidic conditions. Recently, a three-component catalyst made of a Ru catalyst, an Ir catalyst and a scandium salt (Sc(OTf)) was able to convert CO_2 to methanol with 402 TON at 155°C in ethanol as a solvent under high hydrogen pressure (*ca.* 83 bar).

Noble metal complexes (Ru). Typically, the catalytic reduction of CO_2 to methanol requires addition of an alcohol or amine to promote transformation of CO_2 to an intermediate species (alkyl formate, carbonate, urea). In a representative work, a highly active system including a Ru *triphos* (1,1,1-tris(diphenylphosphinomethyl)ethane) complex, [Ru(*triphos*)(TMM)] (TMM = trimethylenemethane), was shown to catalyze direct reduction of CO_2 to methanol (**Fig. 4a-c**)[84] reaching a TON of 603 in the presence of 1 equivalent of bis(trifluoromethane)-sulfonimide ($HNTf_2$), under high CO_2 pressure (60 bar) and ambient temperature[9]. The initial TOF of 70 h^{-1} was comparable to the results obtained with the most efficient heterogeneous catalysts. Moreover, the experiments indicated that the formato complex, [Ru(*triphos*)(η^2-O_2CH)(solvent)]$^+$ was the active catalyst for this reaction, while ([Ru(*triphos*)(H)$(CO)_2$]$^+$, [$Ru_2(\mu\text{-}H)_2$(*triphos*)$_2$] and [Ru(*triphos*)(H)(CO)(Cl)]) were inactive. In the proposed mechanism, hydride migration from Ru to the formic acid ligand in [Ru(*triphos*)(H)(H_2)(HCO_2H)]$^+$ is a key step in the formation of a Ru hydroxymethanolate species[85]. The nature of ligand plays an important role in the catalytic cycle, through both steric and electronic effects[73]. For example, tuning of the *triphos* ligand to cis,cis-1,3,5-tris-(diphenylphosphino)cyclohexane (*tdppcy*) gave high efficiency in direct methanol synthesis (**Fig. 4c**). Even if both ligands have comparable coordination geometries the *tdppcy* system is more rigid, which strongly alters the flexibility of the substituents on the phosphorus[76]. This rigidity allows a rotation along the P–C(cy)-axis, which at the same time reduces the conformational space and degrees of freedom of the phenyl groups.[76] The increase in the catalytic activity observed for *tdppcy* as compared to the *triphos* ligands (**Fig. 4a**) is then due to this specific rigidity of the P-substituents.[76] A highly active system with a TON close to 2000 using n($(PPh_3)_4Ru(H)_2$) complex was obtained using Lewis acid aluminum tristriflate as a co-catalyst and ethanol as a solvent. The modulation of the substituent on the ligands allowed to adjust to the polarity of various alcoholic solvents. High TON (*ca.* 2100) could be obtained in mixture alcohols[73].

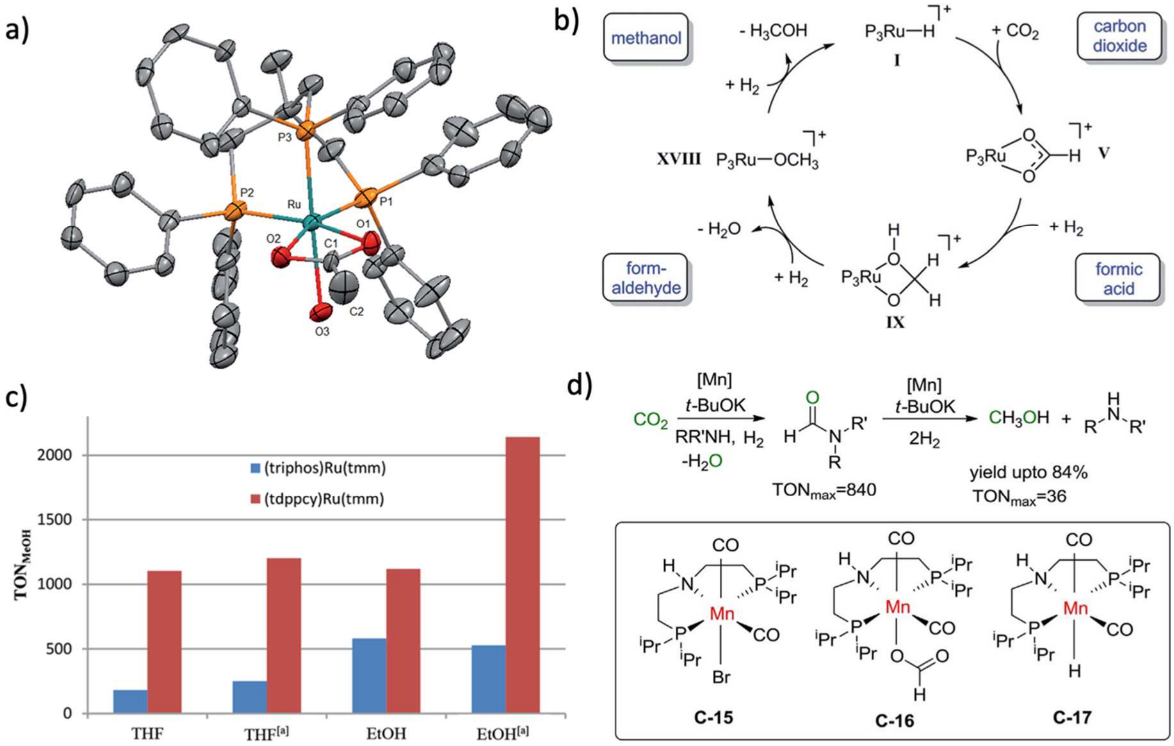

Fig. 4. a) Molecular structure of the triphos active cation (H_2O as a solvent) in the solid state as derived from single crystal X-ray diffraction (hydrogen atoms are omitted for clarity). Some selected bond lengths (A˚): Ru–P1 = 2.245(9); Ru–P2 = 2.255(3); Ru–P3 = 2.253(0); Ru–O1 = 2.171(2); Ru–O2 = 2.208(6); Ru–O3 = 2.204(7)[84], b) Basic catalytic cycle for the transformation of CO_2 to methanol at the Ru–*Triphos* fragment *via* formic acid and formaldehyde. P_3Ru denotes the *Triphos*–Ru(II) fragment comprising additional ligands to fill the coordination sphere, c) Comparison of defined precatalysts (triphos)Ru(tmm) and (*tdppcy*)Ru(tmm). Reaction conditions: n_{Ru} = 5 µmol, n_{Al} = 5 µmol (1 equiv), $V_{Solvent}$ = 4 mL, p(H_2/CO_2) [bar/bar] = 90/30, T = 120°C, t = 20 h. [a] 8 equiv of $Al(OTf)_3$ used[73], d) Structure and reaction pathway for the manganese-catalysed sequential CO_2 reduction to CH_3OH. In the first step of the reaction, N-formylation of an amine occurs in a mixture of CO_2:H_2 (1:1) at a pressure of 60–70 bar in THF at 110°C. This intermediate formamide is then hydrogenated to methanol at high pressure of hydrogen (80 bar) and T = 150°C.

Non-noble metal complexes (Co, Mn, Fe). A breakthrough in the direct methanol synthesis from CO_2 using non noble homogenous catalysts was achieved with cobalt/*triphos*-based systems [79], which can catalyse the reaction at 100°C with good activity. A high turnover number (TON) of 125 could be obtained after 96 hours of reaction. An inner-sphere mechanism was proposed, involving catalysis by the complex formed after the acetylacetonate ligands removal[79]. High temperature NMR studies showed that the initially formed cobalt–phosphine species were slowly transformed into various new catalytically active complexes[76]. The specific coordination of the *triphos* ligand is responsible for the remarkable reactivity of these catalysts, as it was already observed with the noble Ru complexes. However, novel versatile ligand structures are necessary for the development of more efficient homogeneous catalysts[73,76]. They should allow adapting the molecular catalyst for the multiphase and multistep reactions as well as permit the catalyst immobilization to facilitate the recovery and recycling. Recently, other transition metal (Mn[77, 86] and Fe[86]) complexes showed good activity as compared to the Co complexes described above. In both cases, formation of an intermediate (formamide and formaldehyde, respectively) was a key step of the reaction. In the case of a Mn-pincer complex (**Fig. 4d**), the first step is the N-formylation of the amine and then its hydrogenation to methanol. High yield of methanol could be obtained (up to 84% with respect to amine), but the reactions were performed at high pressure (60-80 bar of H_2), high temperature (150°C) and the final TON was quite low (36)[86]. The challenge in the processes carried out on the transient metal complexes is to decrease the H_2 pressure and temperature with the simultaneous TON increase. Lower temperature (80°C) was applied in the reaction carried out with C-scorpionate iron(II) catalyst[86]. A remarkable very high TON of 2283 (comparable to Ru complexes) was obtained with a TOF of 167 h^{-1} after 12 h of reaction. In this case, the reaction proceeds *via* hydride Fe complexes formation and CO_2 insertion into Fe-H bond to form the intermediate Fe-OC(O)H complex[86].

Photocatalysis. Photocatalysis refers to the acceleration of a light-induced chemical process in the presence of a catalyst. Water or molecular hydrogen usually are the reducing agents. They provide necessary protons, fuel electron transfers[87] and are oxidised to molecular oxygen and water, respectively. The term "artificial photosynthesis"[88,89] is used when the photocatalysis simultaneously involves the CO_2 reduction and water oxidation. Most commonly, photocatalytic reduction of CO_2 with water takes place at ambient temperature and pressure, while the hydrogen relevant processes necessitate more severe conditions[90–96] and can be often considered as a combination of photocatalysis and thermo-catalysis. Regarding this review, we will focus on the CO_2 photocatalytic reduction using water as a green and renewable reducing agent.

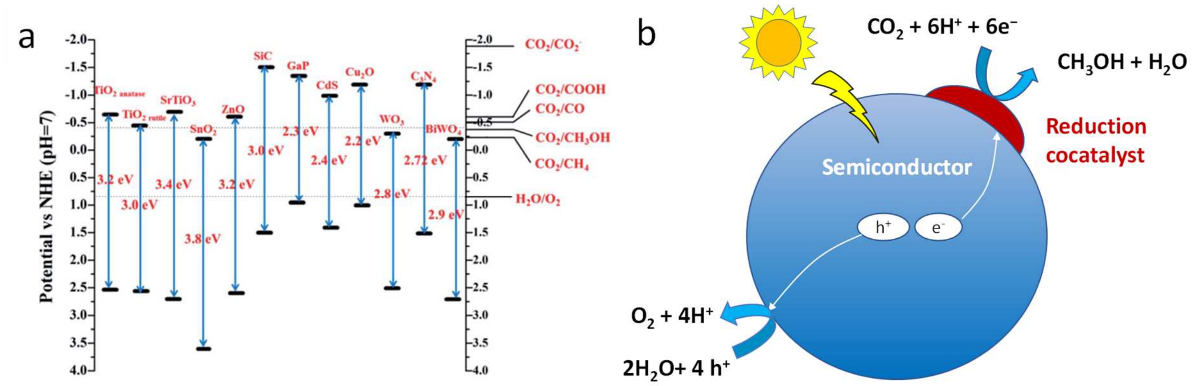

Fig. 5. Photocatalytic CO_2 reduction: (a) conduction band, valence band potentials and band gap energies of various semiconductor photocatalysts of compounds involved in CO_2 reduction relative to the redox potentials at pH 7 (adapted from [97–99]) (b) simplified structure and main components of photocatalyst.

Thermodynamics, mechanisms and kinetics of the CO_2 photoreduction. Photocatalysis typically involves photon absorption, which promotes the electrons (e^-) transfer from the valence band (VB) to the conduction band (CB), creating holes (h^+), followed by charge separation, transport and catalytic reactions. Holes participate in the oxidation of water, while electrons reduce CO_2. The electron-hole recombination can drastically lower the amount of useful charge carriers reaching the interface.

Photocatalytic conversion of CO_2 is strongly affected by both thermodynamics and kinetics in such a way, that several criteria must be fulfilled. First, the band gap energy must be higher that the variation of the overall free energy (**Fig. 5a**), taking into account the thereafter reactions (Eqs 3-6) involved in the CO_2 reduction by water:[100]

$H_2O \rightarrow H_2 + 1/2\ O_2$ $\Delta G_0 = 237\ kJ \cdot mol^{-1}$ (Eq. 3)

$CO_2 \rightarrow CO + ½\ O_2$ $\Delta G_0 = 514.2\ kJ \cdot mol^{-1}$ (Eq. 4)

$CO_2 + 2\ H_2O \rightarrow CH_3OH + 3/2\ O_2$ $\Delta G_0 = 689\ kJ \cdot mol^{-1}$ (Eq. 5)

$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$ $\Delta G_0 = 800\ kJ \cdot mol^{-1}$ (Eq. 6)

All of these reactions indeed correspond to the increase in the Gibbs free energy. Thus, without an external energy supply, the CO_2 reduction as well as water oxidation are thermodynamically unfavourable at ambient temperature. Second, the energy position of the conduction band minimum (CBM) of the semiconductor must be higher than the energy required for the CO_2 reductive reaction and most importantly higher than the energy levels of the reduction catalyst, whereas the position of valence band maximum (VBM) must be lower than the energy of the corresponding oxidative reactions (*e.g.* water oxidation (**Fig. 5a**)).[101] The apparent standard potentials *vs.* NHE at pH = 7 for CO_2 reduction reactions into the C_1 products (Eqs. 7-12), water splitting (Eq. 13) and proton reduction (Eq. 14) are outlined below[98,102,103]:

$CO_2 + e^- \rightarrow CO_2^{\bullet -}$ −1.90 V (Eq. 7)
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$ − 0.61 V (Eq. 8)
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ −0.53 V (Eq. 9)
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$ −0.48 V (Eq. 10)
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ −0.38 V (Eq. 11)
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ −0.24 V (Eq. 12)
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ +0.81 V (Eq. 13)
$2H^+ + 2e^- \rightarrow H_2$ −0.42 V (Eq. 14)

The single electron transfer to CO_2 is the most energy demanding process due to the need of bending the CO_2 linear geometry (-1.9 eV, Eq. 7). The proton-assisted transfers of two electrons to CO_2 with formation of CO or formic acid are more favourable (Eqs. 8, 9), but they involve multi-particle transfer and thus, may face kinetic limitations. Further reactions requiring the simultaneous transfer of 4 to 8 electrons and concomitant 4 to 8 protons (Eqs. 10-12) are even less probable in a single photochemical step, despite their favourably low potentials. The thermodynamic control of the selectivity of CO_2 reduction to methanol is rather difficult, since several reactions may occur with rather similar potentials. Kinetic challenge for the reduction to methanol lies in the competition the reduction of protons (Eq. 14) and various CO_2 reduction products such as CO[104], formic acid, formaldehyde or methane. Separation of methanol from O_2 simultaneously produced by water oxidation is an additional hurdle, the produced oxygen being able to initiate the reverse methanol oxidation reaction. Because of low methanol yield in most of photocatalytic processes, isotope labelling studies using $^{13}CO_2$ are mandatory to prove that methanol is indeed, produced from CO_2. Any study not reporting such control experiment should be taken with extreme caution. The photocatalysts for the CO_2 selective reduction to methane contain semiconductors and cocatalysts (**Figure 5b**).

Semiconductors. The following semiconductors have been most commonly used: titanium dioxide (TiO_2)[105], bismuth vanadate ($BiVO_4$)[106], copper oxide (Cu_2O)[107], zinc oxide (ZnO)[108], zinc sulfide (ZnS)[109], hematite (α-Fe_2O_3)[110], tungsten oxide (WO_3)[111], strontium titanate ($SrTiO_3$)[112,113], cadmium selenide (CdSe), gallium oxide (Ga_2O_3)[114] and zirconium dioxide (ZrO_2)[115], carbon nitride (C_3N_4)[116,117]. Narrow band gap semiconductors usually are preferred, since they can absorb visible light. However, the energy position of both CBM and VBM in these semiconductors may not allow simultaneous oxidation of water and reduction of CO_2. Thus, engineering of the semiconductor band structure is an extremely important task,[101] which can be achieved by doping[97], electronic promotion[118], isomorphous substitution[119], sensitization[120], variation of crystallite size, morphology changes[90,121,122] and heterostructuring[123]. Recombination of the photoexcited electron-hole pairs must be retarded, for example using traps for holes or electrons[124]. The trapping of charge carriers can be achieved by doping with different elements or small semiconductor nanoparticles (*e.g.* quantum dots[125–127]). Heterojunctions[128] with semiconductors, metals and carbon-based materials also are efficient to promote charge separation.

Reduction cocatalysts. The selectivity of CO_2 reduction is mainly affected by the active sites present provided by a co-catalyst, rather than by the semiconductor. If the latter contains copper[129–134], zinc[48,135,136], copper-zinc[137–144], silver[145,146], bismuth[147] and indium[136,148], methanol generally has been proposed to be the main reaction product. The presence of metals with strong hydrogenating and deoxygenating properties such as Pt, Ni[149] usually results in higher selectivity to methane. Additionally, the selectivity of CO_2 reduction is also affected by the photoreactor characteristics, whose optimization can result in a more than ten-fold increase in the methanol yield[150]. Photoreactors can be divided into classes according to their operation mode (batch or flow reactors) or phase composition (gas-solid or gas-solid-liquid). Higher activity is usually observed in the gas-solid mode[97,151,152] thanks to a better separation of charge carriers, a less prominent competition from the water reduction and an easier separation of the small amount of the reaction products. Gaseous phase CO_2 reduction in the absence of sufficient concentration of water usually results in the production of CO and methane, while conducting the CO_2 reduction in the water liquid phase is more favourable for methanol synthesis[98].

Electrocatalysis. The electroreduction reaction (CO_2ERR)[153] proceeds under mild reaction conditions (no need for hydrogen feeding, ambient temperature and pressure) and possesses excellent compatibility with clean renewable energy sources (electricity generated by solar and wind can be used to activate the CO_2). The reduction to methanol requires transfers of 6 electrons (Eq. 11) and as in other methods, it needs an active and selective catalytic material[154,155].

Catalytic process is typically conducted in aqueous solutions containing inorganic salts (mostly constituted of bicarbonate[153,156,157]) at a close-to-neutral pH or in alkaline solution[158]. The electrolyte can also be an organic solvent or ionic liquids, which show interesting FE in methanol production[159,160]. Generally speaking, such media are known for higher CO_2 solubility and can stabilize charged CO_2 intermediates, facilitating CO_2 reduction[161,162].

***Heterogeneous electrocatalysts*.** A wide range of metal based electrocatalysts for the CO_2ERR have been investigated. Copper based catalysts have been mostly used for converting CO_2 with acceptable activity and efficiency into methanol[162,163,164,165]. As already mentioned for photocatalysis, few articles evidenced, upon using labelled $^{13}CO_2$ experiment, that methanol really comes from CO_2.

A series of Pd_xCu_y aerogels bimetallic electrocatalysts[160] have been developed and their activity measured in a 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) aqueous solution as electrolyte. The highest Faradaic efficiency (FE) for CH_3OH production (80.0%) at -2.1 V (*vs.* Ag/Ag^+) led to a current density of 31.8 $mA \cdot cm^{-2}$ after 24 h of electrolysis, both aerogel structure, amorphous Cu and fcc Pd nanostructure being retained. The aerogels have fine inorganic network structure with high porosity, and the synergistic effect between Pd and Cu on the aerogel surface contributes to the excellent catalytic performance. The electronic charge transfer from Pd to Cu leads to weakly-bonded H_2 and CO_2 species over the Pd-Cu alloys. Pd and Cu are less prone to poisoning by carbon monoxide and can promote methanol production[166,167] Nanostructured catalysts offer high electrochemically active surface area through the variation of the coordination number of active sites (corner, edge and surface sites), local electronic structure, different facets and defect sites. Consequently, the product yield is directly affected by nanoparticle size[168–170]. Solvothermal synthesis of $Cu_{2-x}Se_{(y)}$ nanocatalysts[162] has been studied in the [Bmim]PF_6 (30 wt %)/CH_3CN/H_2O (5 wt%) ternary electrolyte. The best catalyst exhibited a FE of 77.6% at -2.1 V (*vs.* Ag/Ag^+) with current density of 41.5 mA·cm^{-2} after 24h of operation without any change in composition and structure of the catalyst. High fraction of unsaturated Se atoms on small particles may be one of the main reasons for high current density and FE (**Fig. 6 a, b**).

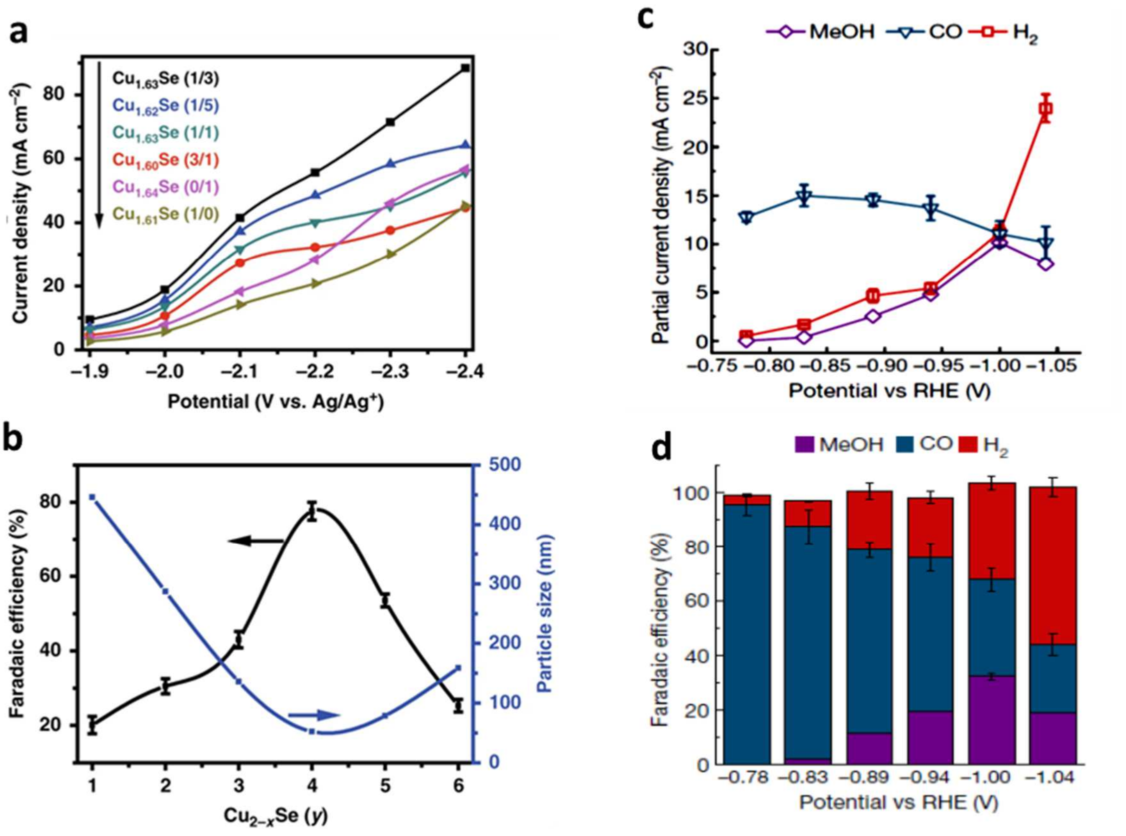

Fig. 6. a) Total current density over $Cu_{1.63}Se_{(1/3)}$ catalyst at different applied potentials.[162] b) Plots of particle size *vs.* FE of methanol on different $Cu_{1.63}Se_x$ catalysts. Data were obtained at ambient temperature and pressure with CO_2 stream of 10 sccm with 5 h electrolysis.[162] c) Partial current density for CO_2 electroreduction catalysed by CoPc–NH_2/CNT. Error bars represent one standard deviation from three measurements.[171] d) Faradaic efficiencies for CO_2RR using CoPc–NH_2/CNT as catalyst.[171]

Recently, incorporation of metal in carbon structure has been explored[158,172,173]. High surface area and well-conducting carbon materials are capable of stabilizing high metal loading, promoting transfer of electrons on the catalyst without impairing the electrical conductivity.

***Supported molecular electrocatalysts*.** In such systems, the catalysts are transition-metal complexes immobilized in thin conductive films deposited at a conductive surface. They may benefit from both high selectivity at the catalytic site and good stability of catalytic materials.

However, very few molecular catalysts are able to electroreduce CO_2 to methanol, and in fact only two examples, both related to Co phthalocyanines, are available in the literature.

Recently, cobalt phthalocyanine (CoPc) supported on carbon nanotubes has showed remarkable activity and selectivity in CO_2RR to methanol[171,174]. In a first study, unsubstituted cobalt phthalocyanine (CoPc) was supported onto multi-wall carbon nanotubes (MWCNT) and Nafion resin[174]. A global Faradaic efficiency of 19.5% and chemical selectivity of 7.5% for CH_3OH could be obtained in a sequential process converting first CO_2 to CO, then using CO as a substrate to generate methanol in alkaline conditions (pH 13). The fact that the methanol originates from CO_2 was carefully assessed by ^{1}H NMR. It was further shown that formaldehyde was also produced during electrolysis as a by- product. It is currently not known if this formaldehyde is an intermediate in the process or if on contrary, methanol comes from direct reduction of CO, with HCHO being only produced along a parallel pathway. Long term electrolysis led to deactivation of the catalyst through partial reduction of the ligand. In a subsequent study, amino groups were introduced at the phthalocyanine ligand (CoPc–NH_2), and the catalysts were highly dispersed in the conductive ink containing carbon nanotubes and Nafion, leading to higher stability over time and larger currents[171]. In 0.1 M $KHCO_3$ aqueous electrolyte at a potential of −1.00 V *vs.* RHE, methanol production could be sustained for 12 h with a FE of *ca.* 28 %, with corresponds to a partial current density of ca. 8.5 mA cm^{-2} (**Fig. 6 c, d**)[171]. It was not demonstrated that the methanol is issued from CO_2, but the results obtained in Ref 176 validate those obtained in this study. The mechanism proceeds *via* CO_2 reduction to CO intermediate and then methanol production, as with the non-substituted Co phthalocyanine[174].

Comparative assessment of the CO_2 reduction routes to methanol. Various routes have been explored for the selective CO_2 reduction to methanol. Their overview and comparison (**Table 1**) is based on several characteristics: reducing agent, maximum selectivity, productivity, stability, temperature, pressure, technological maturity and methanol cost. Molecular hydrogen is generally used as a reducing agent in homogeneous or heterogeneous catalysis, whereas water is employed in photo- or electro-catalysis. Enzymatic catalysis requires a cofactor (usually NADH) for the CO_2 reduction, which is expensive and must be regenerated for a subsequent cycle. Methanol selectivity above 90% can be reached in homogeneous, enzymatic, photocatalysis and 70% in heterogeneous catalysis and electrocatalytic processes. Higher selectivity is often either obtained at low CO_2 conversion, for example in photocatalysis, or by using multi-step processes as in homogeneous and enzymatic approach. In heterogeneous catalysis, CO is the main by-product. The methanol selectivity can be further improved, for example by increasing the total pressure up to 331 bar.[17] Productivity is another important figure of merit of any catalytic process and it can be expressed, depending on the process (homogeneous, heterogeneous, photo-, electro- enzymatic catalysis), in various units (such $mmol \cdot g_{cat}^{-1} \cdot h^{-1}$, TON or $\mu mol \cdot m^{-2}$, etc.). In order to compare different CO_2 reduction routes, we recalculated the productivities in a common unit, namely in the mol quantity of methanol produced per gram of catalyst per hour (**Table 1**). Surprisingly, the methanol productivity obtained in heterogeneous and homogeneous catalytic hydrogenation of CO_2, enzymatic and electrocatalysis are of the same order of magnitude, with exception of photocatalysis, for which it is one to two orders of magnitude less productive. Catalyst stability is commonly considered the determining parameter for any chemical process and in particular, for the synthesis of relatively cheap commodities such as methanol. Regarding this criteria, heterogeneous catalysis stands at the forefront of the various methods. For example, stable operation for methanol synthesis from CO_2 can surpass 3000 h[175]. In contrast, when conducting the reaction in a discontinuous mode (homogeneous or enzymatic catalysis), the catalyst stability is often limited to a few cycles or to a few tens of hours in the best cases for continuous operation in CO_2 photoand electrocatalysis. Moreover, the regeneration of deactivated homogeneous, electro- and photo- catalysts as well as enzymes is often difficult if not impossible.

Table 1

Comparison of different routes for CO_2 reduction to methanol

	Heterogeneous catalysis	**Homogeneous catalysis**	**Enzymatic catalysis**	**Photocatalysis**	**Electrocatalysis**
Reducing agent	hydrogen	hydrogen	cofactor	water	water
Catalysts	Cu/ZnO, Pd, Au, ZnO, M-ZrO_x, In_2O_3	Complexes of Mn, Cr, Ru, carbene	F_{ate}DH-F_{alt}DH-ADH	Cu, Zn, Ag, Bi, In + semiconductors	Cu-Pd, Cu-Se alloys, Co phthalocyanines
Maximum selectivity, %	> 70	> 90 in multistep reactions	> 90 in multistep reactions	> 99	> 70
Productivity mmol.g_{cat}^{-1}.h^{-1} and (characteristic units for each route)	2-20	10–98 (20-2000 TON)	> 6 (5-10 µmol /mg_{enzyme}^{-1} h^{-1})	0.02-0.5	> 22 (>30 µmol m^{-2} s^{-1})
Stability	> 3000 h	3-7 cycles	Up to 4 cycles	40 h or 4-10 cycles	4-120 h
Temperature	220-300°C	50-180°C	ambient-50°C	ambient	< 50°C
Pressure	30-50 bar ($H_2/CO_2 = 3$)	< 80 bar ($H_2/CO_2 = 3$)	< 10 bar	< 10 bar	atmospheric
TRL	6-7	2-3	2-3	2	3-4
Methanol cost[a], USD/ton	600-1700	n.d.	n.d.	> 1 000 000	> 700

[a] current methanol market cost is 250-400 USD/ton[176]

Both heterogeneous and homogeneous hydrogenation catalytic processes require the harshest conditions for methanol synthesis. Reaction typically occurs at 180-300°C and pressure up to

50-80 bar. Slightly lower temperature in homogeneous catalysis is due to the batch operation and longer CO_2 residence time compared to heterogeneous conditions, for which a flow reactor is used. Quasi ambient temperature and moderate pressure are major advantages of the enzymatic, photo- and electro-catalysis.

Technology Readiness Level (TRL[177]) is a recognized measure of the maturity of a technological process. The CO_2 hydrogenation to methanol *via* heterogeneous catalysis currently presents the highest TRL of 6-7[178–180]. Using this process, large demonstration facilities such as the CRI plant[12] in Iceland have been deployed. The second route in terms of maturity (TRL of 3-4) is electrocatalytic CO_2 reduction[179,181]. The latter is highly modular and can be attractive for decentralized operation[14]. Other routes such as homogeneous catalysis, photo-[179] and enzymatic catalysis are still at the level of the experimental proof-of-concept reached at the laboratory scale (*ca.* TRL 2-3).

The TRL levels for the various CO_2 reduction routes are closely linked to the methanol cost which is significantly higher, for all the discussed paths, than the current market price (**Table 1**). Heterogeneous CO_2 hydrogenation catalysis[180–185] and CO_2 electrocatalysis[186,187] provide methanol with a cost most closely approaching the market values. In the former, the methanol price is affected, up to 80-90%, by the price of sustainable hydrogen[5,179,188]. To reduce the methanol cost in electrocatalysis, the catalyst stability must be significantly increased (up to several thousand hours), the same being true regarding both cathodic and anodic sides.[187] At the current scientific and TRL levels, methanol produced *via* photocatalysis has an extremely high cost (**Table 1**). To manufacture economically competitive methanol, a 15% solar-to-fuels efficiency is required[189] and the photocatalytic activity must be raised by several orders of magnitude (from *ca.* 0.02-0.5 to 10 mmol $g_{cat}^{-1}\cdot h^{-1}$), which can only be envisioned in a long-term perspective. It seems difficult to fairly evaluate the methanol cost produced *via* homogeneous catalytic hydrogenation or enzymatic catalysis. The high price of enzymes and large quantities of cofactors limits the economic feasibility and scale up. Regeneration of metal complexes and their separation from methanol are major challenges for the cost reduction in homogeneous catalysis.

Conclusion. Among the different routes for the CO_2 reduction that have been discussed in this review, heterogeneous catalysis and direct electrocatalysis stand out of the pack. Methanol synthesis from CO_2 hydrogenation using heterogeneous catalysts has currently reached high scientific and technological maturity, while the CO_2 electrocatalytic approach seems to be very promising as a mid-term perspective. It is important to emphasize that sustainable electricity is a key prerequisite in both approaches, especially in the former case, since it must employ "green" hydrogen produced by water electrolysis.

Because of thermodynamic limitations, the state-of the-art CO_2 hydrogenation to methanol *via* heterogeneous catalysis requires high pressures (30-50 bar). In addition, water, which is a reaction by-product, inhibits the catalytic activity. The single pass methanol yield can be increased by selective water removal from the reactor using a combination of methanol synthesis and water adsorption/absorption or by using water selective membranes. Another target would be the development of new low-temperature catalysts operating at lower pressure, which could enable higher CO_2 conversion, higher methanol selectivity and zero CO production. In the conventional CO_2-to-methanol process, Cu-based catalysts remain the catalytic family *par excellence*. However, deactivation of copper catalysts constitutes an important drawback. Identification of active sites, understanding of the interaction between components and dynamic behaviour of the participant species need to be clarified. The cost and availability of sustainable hydrogen can also become an obstacle for implementation of larger scale CO_2 hydrogenation processes.

In the electrocatalytic approach, future trends may focus on the design of nanostructured high-performance catalysts and molecular supported catalysts with well controlled microenvironment at the active site, so as to reach higher methanol selectivity. Following the strategy reminiscent of enzymatic catalysis, electrocatalysis could benefit from a sequential approach upon combining two successive reactions, first CO_2 to CO and then CO to methanol, with optimization of each step, as it has been recently proposed[174] for a Co based molecular supported catalyst. Strategies to avoid poisoning and thus catalytic material degradation is of great importance. Currently, most CO_2RR electrocatalysts were tested only over few hours (up to 50 h typically), while for industrial application, thousand hours per year are expected. New developments in cell design (gas-diffusion cells, liquid-flow cells, solid polymer electrolytes), electrode structures and catalyst robustness are still required to improve performances under various operating regimes.

Acknowledgements

S. N.-J., M. V., R. W. and A. Y. K. acknowledge financial support from the European Union ("Electron to Value-Added Chemicals (E2C)" Interreg 2 Seas Project). Partial financial support to M. R. from the Institut Universitaire de France (IUF) is gratefully acknowledged.

Author contributions

All authors contributed to writing, editing and reviewing the manuscript before submission.

Competing interests

The authors declare no competing interests.

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