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Highlights and Challenges in the Selective CO₂ Reduction to Methanol

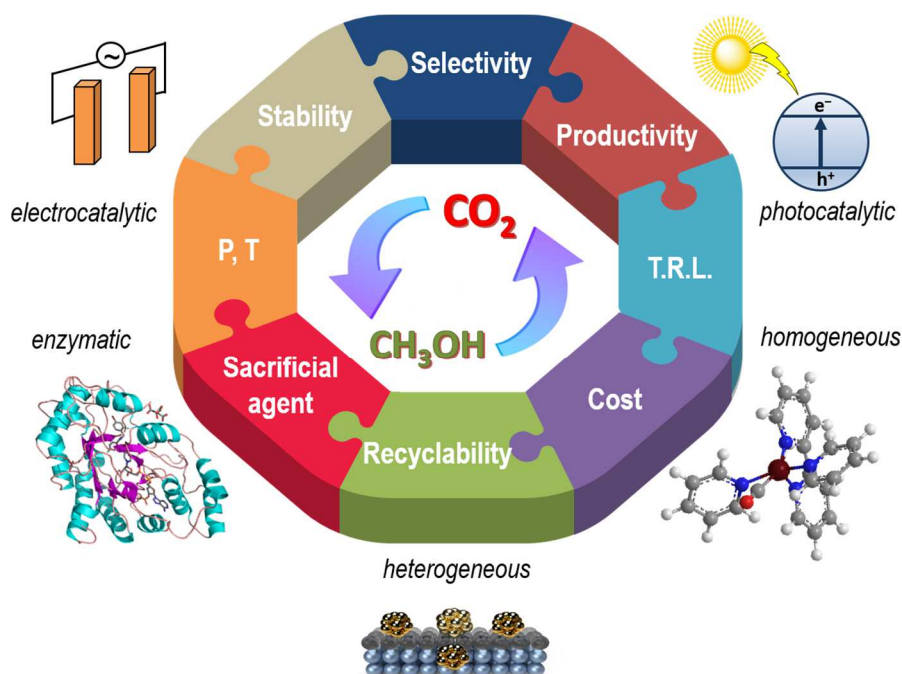
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TOC image

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 CO₂ 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 CO₂ 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 CO₂ reduction to methanol at larger scale. Availability and price of sustainable electricity appear as essential prerequisites for efficient methanol synthesis from CO₂.

Keywords: CO₂ reduction; methanol; catalysis; photocatalysis; electrocatalysis

Atmospheric carbon dioxide (CO₂) concentration has reached¹ 417 ppm in May 2020. This gas is definitely the main greenhouse player, responsible for climate changes through transport, industry and household emissions. CO₂ 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 CO₂ content in the biosphere: carbon capture and storage (CCS)² and carbon capture and utilization (CCU)³. CCS relies on the CO₂ 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 CO₂ (in soft drinks or fire extinguishers for example) or its chemical and/or biological conversion into value-added products and fuels³⁻⁵.

The CO₂ chemical conversion could contribute to lower consumption of hydrocarbon-based fuels (gasoline, diesel, jet fuels), which are currently manufactured from fossil feedstocks⁶ and which are major sources of greenhouse gas emissions. The synthesis of fuels and chemicals from CO₂ can also enhance carbon- and energy-efficiency of existing technologies and elaboration of new sustainable “green” industrial processes^{7,8}. However, CO₂ 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 CO₂ 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 sources⁹.

To address the perspective of an on-going shift from fossil to renewable energy supplies, development of chemical catalytic processes for the CO₂ reduction to methanol (CH₃OH) 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.

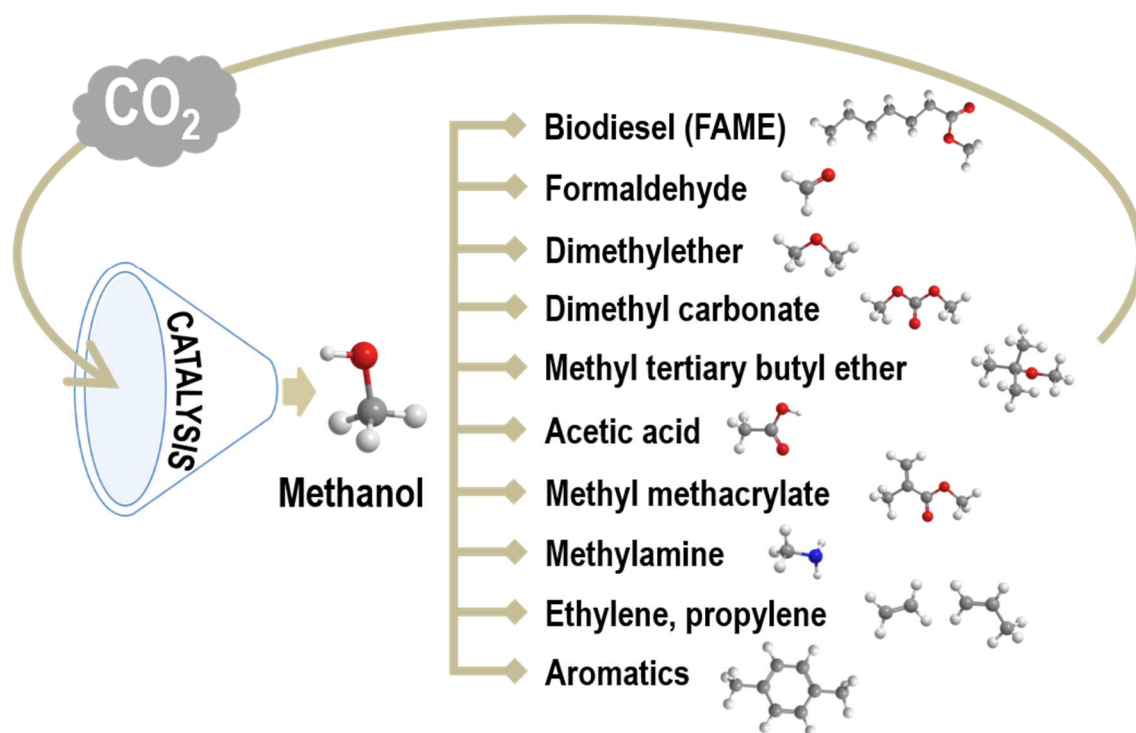


Fig. 1. Carbon cycle of methanol, a platform molecule for chemical industry.

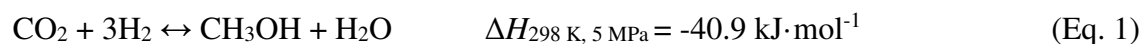
Among the various reduction products possibly obtained from CO_2 reduction, methanol is a major target, having numerous applications in chemistry (**Fig. 1**). It can account alone for about 30% of the most widely used chemicals: dimethyl ether, dimethyl carbonate, formaldehyde, aromatics, ethylene, 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 year¹⁰. Methanol production already involves utilization of 2 million tons of CO_2 ¹¹. The CO_2 reduction

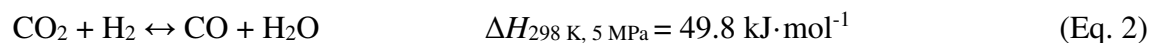
to CH₃OH is often considered as the core of the “methanol economy”⁴. Since 2012, a demonstration plant¹² in Iceland is producing about 4000 tons of methanol/year from CO₂ and renewable H₂ over a heterogeneous Cu-ZnO catalyst, and is thus recycling 5500 tons of CO₂/year. Other industrial facilities for the CO₂ conversion to CH₃OH are under development in Germany¹³ and China¹⁴.

In this review, we draw a comparative qualitative and quantitative analysis of the CO₂ 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, H₂ and some traces of CO₂, which is generated from fossil fuels (*e.g.* coal or natural gas). Therefore, the emerging environmental paradigm envisages anthropogenic CO₂ and “green” H₂ as ideal feedstock to produce “green” methanol in the near future^{15–18}:



However, the CO₂ hydrogenation to methanol is more challenging than that of CO due to the thermodynamic and chemical stability of the CO₂ molecule¹⁶, whereas the competitive reverse water-gas shift (RWGS) reaction (Eq. 2) can also take place, in particular at higher reaction temperatures:



Taking these aspects into consideration, design of appropriate stable catalysts able to activate the CO₂ molecule and to favour its conversion into CH₃OH is essential.

Cu-based catalysts. Although numerous systems have been studied for the conversion of CO₂ 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%

Al₂O₃, ZrO₂, ...) achieves conversion efficiencies of about 30% and methanol selectivity between 30-70% at 220-300°C and < 50 bar²¹. 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 obtain the 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 method²³. 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)₂CO₃, x ≤ 0.27] is generally associated to a greater Zn incorporation in the catalyst structure, which drives the enhanced catalytic behaviour²⁸. Recently, it has been found that supercritical CO₂ allows the formation of stable amorphous georgeite [Cu₇(CO₃)₅(OH)₄·5H₂O], which can further improve the activity and stability of the Cu-ZnO system²⁹.

Al₂O₃ has been the most popular catalyst promoter for the methanol synthesis from syngas³⁰, but its hydrophilicity seems to be detrimental for methanol synthesis from CO₂. Production of large amounts of water indeed induces catalyst sintering and subsequent deactivation^{31,32}. ZrO₂ has been widely explored due to its weaker hydrophilic character, its basicity, which favours the CO₂ adsorption, enhanced activity and selectivity in the methanol synthesis from CO₂ (**Fig. 2b**)^{23,32,33}.

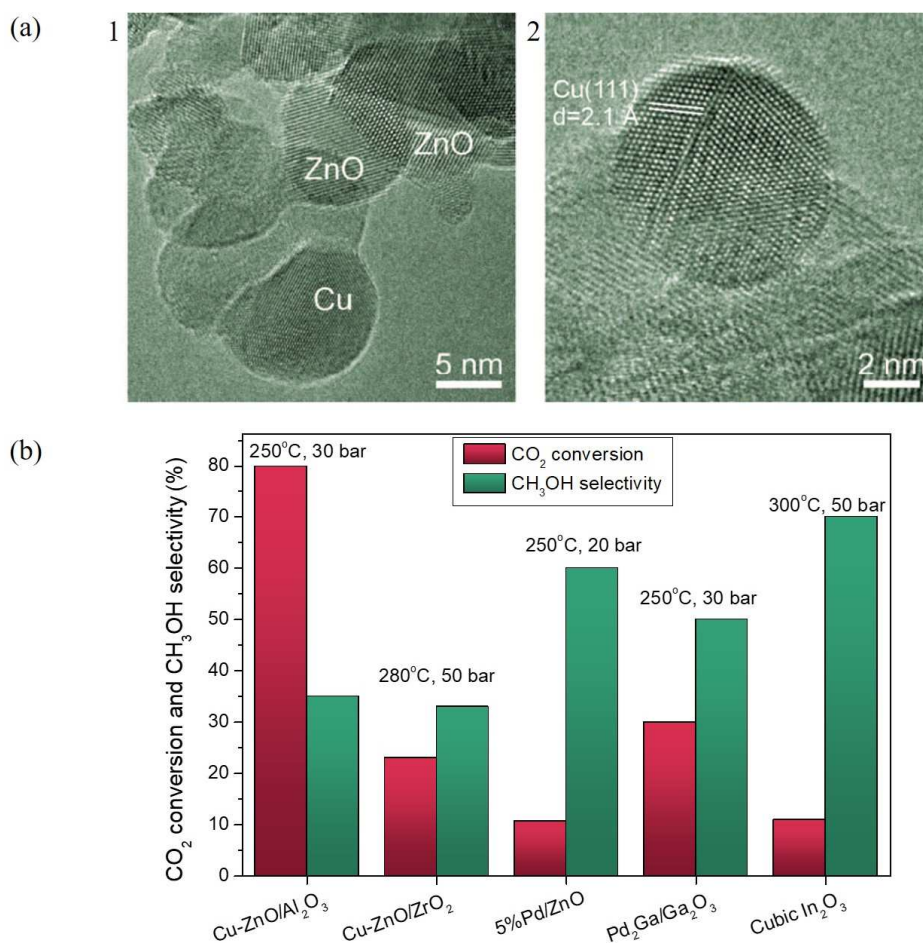


Fig. 2. (a) Transmission electron micrograph of a Cu-ZnO/Al₂O₃ catalyst during exposure to H₂ at 300 °C, showing (1) arrangement of the catalyst nanoparticles and (2) exposed Cu nanoparticles surfaces with direct gas accessibility³⁴. (b) Comparison of catalytic performance (CO₂ conversion: red bars, CH₃OH selectivity: green bars) for selected heterogeneous catalysts^{35–38}.

Another strategy aims at improving the Cu-ZnO/ZrO₂ 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}·h⁻¹·g_{cat}⁻¹ was obtained, significantly larger than the 10 mg_{CH₃OH}·h⁻¹·g_{cat}⁻¹ measured in the absence of support³⁹. Hydrotalcites enhance methanol selectivity to 78.3% at 250°C and 30 bar, in contrast to 68.6% reached with CuZnO/ZrO₂ only, by virtue of the hydrotalcite CO₂ adsorption capacity, which increases the CO₂ concentration near the active sites⁴⁰. 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 content⁴¹.

Noble metal and bimetallic catalysts. Due to their well-known activity in the CO₂ hydrogenation reactions, Pd catalysts have also been explored for methanol synthesis²³. The selectivity is generally directed by the support and promoters³⁷. The Pd/ZnO catalysts can convert 11% CO₂ 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, CO₂ is adsorbed on ZnO and H₂ 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 reaction³⁷.

Ga₂O₃ is also a promising solid support. Upon association with Pd, it leads to the 20% CO₂ conversion and 51.5% methanol selectivity. In this case, it is assumed that the active metal species for methanol production involve Pdⁿ⁺ (0 < n < 2). The excellent catalytic activity explained by the presence of an optimal amount of Pdⁿ⁺ stabilized by Ga_xO_y on the surface of Pd⁴². However, the RWGS reaction occurs as well, giving rise to the undesired formation of CO. Addition of Ga₂O₃ as promoter to Pd/SiO₂ led to a 500-fold increase in methanol production relative to the parent catalyst⁴³.

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/TiO₂ and Au/CeO_x/TiO₂ have been compared, showing that lower CeO_x coverages improve the selectivity towards CH₃OH even at low pressure⁴⁴.

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 SiO₂-supported PdCu catalysts with Pd/(Pd+Cu) ratios ranging from 0.25 to 0.34 convert from 5 to 7% of CO₂ 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 PdCu₃ alloys, which may provide a source of chemisorbed hydrogen, thus favouring methanol formation⁴⁵. The SiO₂-supported InPd catalysts⁴⁶ have also shown promising results, with higher CO₂ 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 systems⁴⁶. The SiO₂-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 Cu⁴⁷.

Metal oxide catalysts. There has been a recent surge in the use of metal oxides as catalysts for methanol synthesis. For example, the ZnO-ZrO₂ 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 bar⁴⁸. In a similar way, M_aZrO_x (M_a = Cd, Ga) solid solutions can achieve from 4.3 to 12.4% CO₂ conversion and 80% selectivity, values that stand significantly higher than those obtained with the individual oxides⁴⁹. In both cases, the results were attributed to the synergy between the catalytic components. The cubic phase of In₂O₃ has been investigated, but although the methanol selectivity reaches almost 100%, low conversion was achieved³⁸. In order to overcome this problem, the promotion with other components is envisaged. For instance, Pd enhanced the In₂O₃ performance through its H₂ splitting capacity⁵⁰.

The results reported so far demonstrate that the Cu-based catalysts remain the catalytic family *par excellence* for the hydrogenation of CO₂ 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 CO₂ and dissociate H₂, 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 CO₂, some additional aspects need to be considered. A greater amount of hydrogen is required for the hydrogenation of CO₂ 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 CO₂ hydrogenation is thermodynamically limited. For instance, the methanol yield from CO₂ 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 mandatory¹⁶. Furthermore, methanol synthesis from CO₂ 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 environment⁵¹. The CO₂ reduction using enzymatic catalysis has been intensively studied in the last 5 years^{52–58}. Direct CO₂-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·L⁻¹ after hours of reaction⁶⁰. In addition, high concentration (up to 100 mmol·L⁻¹) of cofactor is necessary, which makes such process quite costly.

Multi-enzymatic systems. Catalytic conversion of CO₂ 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 CO₂ reduction⁶¹, *i.e.* it can improve the rate of the reaction towards a target compound.

CO₂ 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 CO₂ reduction to formic acid catalysed by F_{ate}DH is 30 times slower than the reverse oxidation of formate to CO₂^{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 CO₂ concentration, which could be achieved by using ionic liquids compatible with the enzymes as a CO₂ co-solvent⁵⁹. 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-solvent⁵⁹. 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 CO₂ to the enzyme⁵⁹. 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 CO₂ at the enzymatic catalytic site⁵⁹. 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 CO₂ concentration in the system. The methanol formation rate could be enhanced from 1.20 to $2.17 \times 10^{-3} \mu\text{mol} \cdot \text{min}^{-1}$, when CO₂ pressure was raised from 0.2 to 0.5 MPa. Further increase to 1.0 MPa⁶³ 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-sensitive⁶⁴. 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 shown⁶⁵ 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 composites⁶⁶. 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 enzymes⁶⁶.

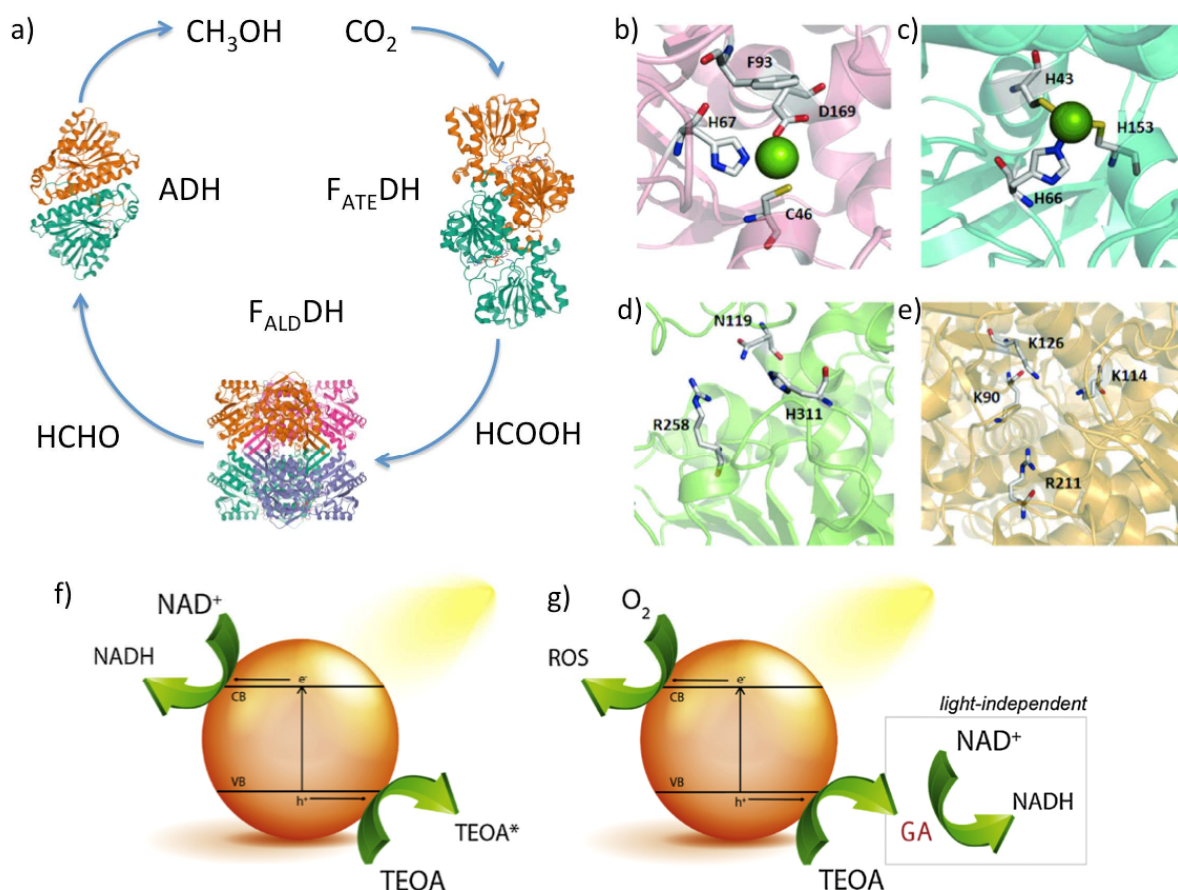


Fig. 3. a) Reaction pathway in enzymatic cascade for methanol synthesis from CO_2 using nicotinamide adenine dinucleotide hydrogenase (NADH), dependent formate dehydrogenase ($\text{F}_{\text{ATE}}\text{DH}$), formaldehyde dehydrogenase ($\text{F}_{\text{ALD}}\text{DH}$) and alcohol dehydrogenase (ADH) enzymes.⁶⁰ b) Representation of the active sites of the $\text{F}_{\text{ALD}}\text{DH}$. c) Representation of the active sites of the ADH, (d) Representation of the active sites of the $\text{F}_{\text{ATE}}\text{DH}$ 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 processes⁶⁹.

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 NADH⁶². 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 CO₂ 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 CO₂ 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 system⁷².

Homogeneous hydrogenation catalysis. The works reporting direct CO₂ 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 CO₂ hydrogenation; (ii) functionalization of formate to an activated ester, such as alkyl formate or carbonate or carbamate; and finally (iii) CH₃OH 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 CO₂ to methanol⁷⁸. Conversion of CO₂ 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 conditions⁷⁴. The first CO₂-to-methanol reaction under basic conditions was successfully achieved⁸³ 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 CO₂ 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 CO₂ to methanol requires addition of an alcohol or amine to promote transformation of CO₂ 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 CO₂ to methanol (**Fig. 4a-c**)⁸⁴ reaching a TON of 603 in the presence of 1 equivalent of bis(trifluoromethane)-sulfonimide (HNTf₂), under high CO₂ pressure (60 bar) and ambient temperature⁹. 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 formate complex, [Ru(*triphos*)(η^2 -O₂CH)(solvent)]⁺ was the active catalyst for this reaction, while ([Ru(*triphos*)(H)(CO)₂]⁺, [Ru₂(μ -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)(H₂)(HCO₂H)]⁺ is a key step in the formation of a Ru hydroxymethanolate species⁸⁵. The nature of ligand plays an important role in the catalytic cycle, through both steric and electronic effects⁷³. 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 phosphorus⁷⁶. 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 tris(triflate) 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 alcohols⁷³.

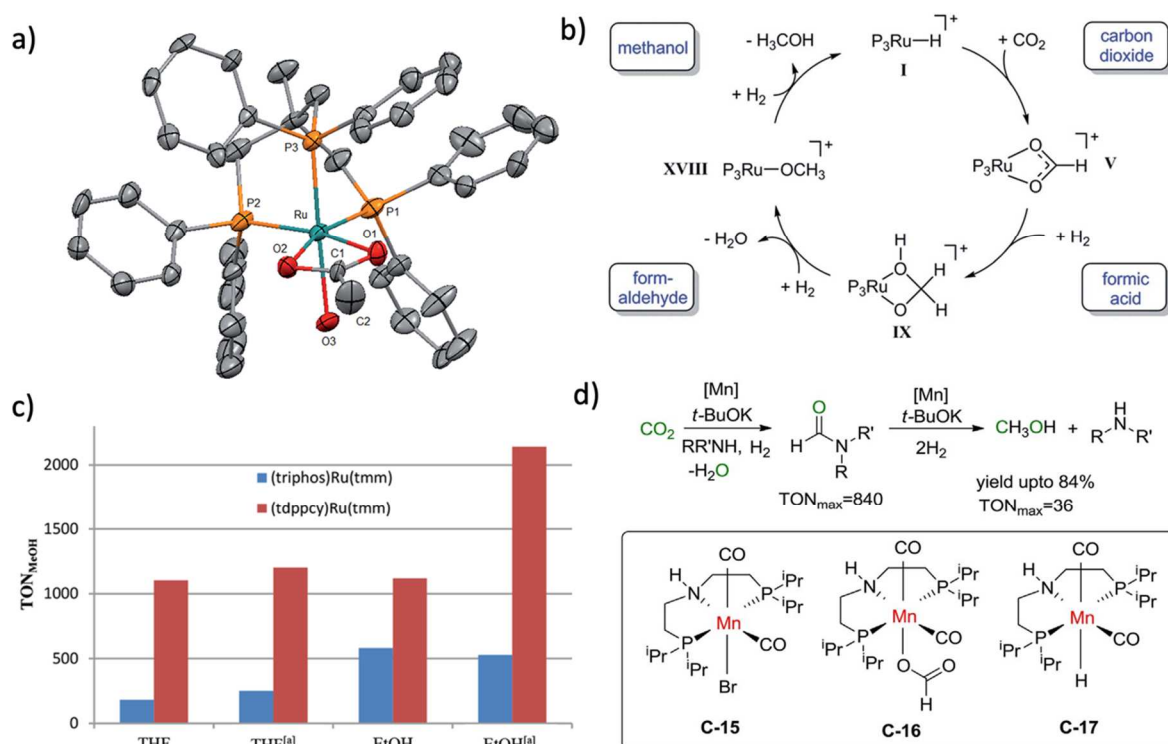


Fig. 4. a) Molecular structure of the triphos active cation (H₂O as a solvent) in the solid state as derived from single crystal X-ray diffraction (hydrogen atoms are omitted for clarity). Some selected bond lengths (Å): Ru–P1 = 2.245(9); Ru–P2 = 2.255(3); Ru–P3 = 2.253(0); Ru–O1 = 2.171(2); Ru–O2 = 2.208(6); Ru–O3 = 2.204(7)⁸⁴, b) Basic catalytic cycle for the transformation of CO₂ to methanol at the Ru-Triphos fragment *via* formic acid and formaldehyde. P₃Ru 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: $n_{Ru} = 5 \mu mol$, $n_{Al} = 5 \mu mol$ (1 equiv), $V_{Solvent} = 4 mL$, $p(H_2/CO_2)$ [bar/bar] = 90/30, $T = 120^\circ C$, $t = 20 h$. [a] 8 equiv of Al(OTf)₃ used⁷³, d) Structure and reaction pathway for the manganese-catalysed sequential CO₂ reduction to CH₃OH. In the first step of the reaction, N-formylation of an amine occurs in a mixture of CO₂:H₂ (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 $T = 150^\circ C$.

Non-noble metal complexes (Co, Mn, Fe). A breakthrough in the direct methanol synthesis from CO₂ using non noble homogenous catalysts was achieved with cobalt/*triphos*-based systems⁷⁹, 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 removal⁷⁹. High temperature NMR studies showed that the initially formed cobalt–phosphine species were slowly transformed into various new catalytically active complexes⁷⁶. 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 Fe⁸⁶) 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 H₂), 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 H₂ pressure and temperature with the simultaneous TON increase. Lower temperature (80°C) was applied in the reaction carried out with C-scorpionate iron(II) catalyst⁸⁶. 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 CO₂ insertion into Fe-H bond to form the intermediate Fe-OC(O)H complex⁸⁶.

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 transfers⁸⁷ and are oxidised to molecular oxygen and water, respectively. The term “artificial photosynthesis”^{88,89} is used when the photocatalysis simultaneously involves the CO₂ reduction and water oxidation. Most commonly, photocatalytic reduction of CO₂ 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 CO₂ photocatalytic reduction using water as a green and renewable reducing agent.

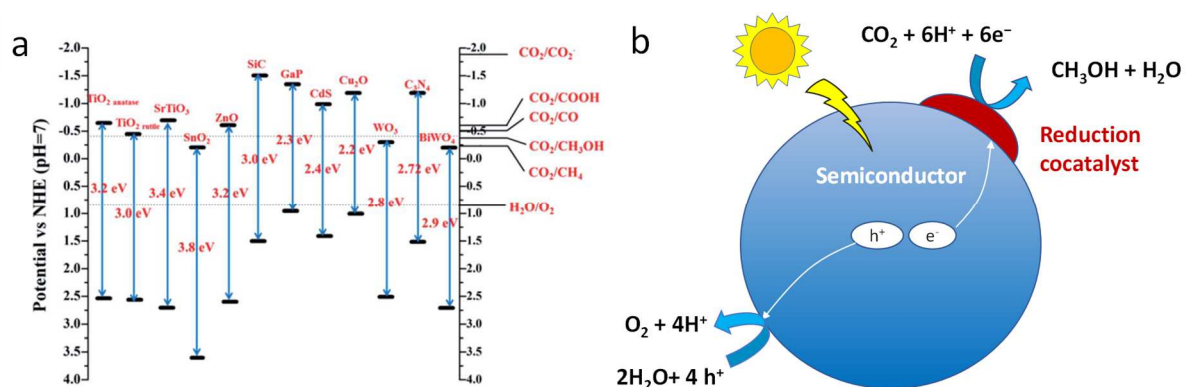


Fig. 5. Photocatalytic CO₂ reduction: (a) conduction band, valence band potentials and band gap energies of various semiconductor photocatalysts of compounds involved in CO₂ reduction relative to the redox potentials at pH 7 (adapted from ^{97–99}) (b) simplified structure and main components of photocatalyst.

Thermodynamics, mechanisms and kinetics of the CO₂ 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 CO₂. The electron-hole recombination can drastically lower the amount of useful charge carriers reaching the interface.

Photocatalytic conversion of CO₂ 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 than the variation of the overall free energy (**Fig. 5a**), taking into account the thereafter reactions (Eqs 3-6) involved in the CO₂ reduction by water:¹⁰⁰



All of these reactions indeed correspond to the increase in the Gibbs free energy. Thus, without an external energy supply, the CO₂ 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 CO₂ 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 CO₂ reduction reactions into the C₁ products (Eqs. 7-12), water splitting (Eq. 13) and proton reduction (Eq. 14) are outlined below^{98,102,103}:



The single electron transfer to CO₂ is the most energy demanding process due to the need of bending the CO₂ linear geometry (-1.9 eV, Eq. 7). The proton-assisted transfers of two electrons

to CO₂ 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 CO₂ 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 CO₂ reduction products such as CO¹⁰⁴, formic acid, formaldehyde or methane. Separation of methanol from O₂ 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 ¹³CO₂ are mandatory to prove that methanol is indeed, produced from CO₂. Any study not reporting such control experiment should be taken with extreme caution. The photocatalysts for the CO₂ selective reduction to methane contain semiconductors and cocatalysts (**Figure 5b**).

Semiconductors. The following semiconductors have been most commonly used: titanium dioxide (TiO₂)¹⁰⁵, bismuth vanadate (BiVO₄)¹⁰⁶, copper oxide (Cu₂O)¹⁰⁷, zinc oxide (ZnO)¹⁰⁸, zinc sulfide (ZnS)¹⁰⁹, hematite (α-Fe₂O₃)¹¹⁰, tungsten oxide (WO₃)¹¹¹, strontium titanate (SrTiO₃)^{112,113}, cadmium selenide (CdSe), gallium oxide (Ga₂O₃)¹¹⁴ and zirconium dioxide (ZrO₂)¹¹⁵, carbon nitride (C₃N₄)^{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 CO₂. Thus, engineering of the semiconductor band structure is an extremely important task,¹⁰¹ which can be achieved by doping⁹⁷, electronic promotion¹¹⁸, isomorphous substitution¹¹⁹, sensitization¹²⁰, variation of crystallite size, morphology changes^{90,121,122} and heterostructuring¹²³. Recombination of the photoexcited electron-hole pairs must be retarded,

for example using traps for holes or electrons¹²⁴. The trapping of charge carriers can be achieved by doping with different elements or small semiconductor nanoparticles (*e.g.* quantum dots^{125–127}). Heterojunctions¹²⁸ with semiconductors, metals and carbon-based materials also are efficient to promote charge separation.

Reduction cocatalysts. The selectivity of CO₂ 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}, bismuth¹⁴⁷ 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, Ni¹⁴⁹ usually results in higher selectivity to methane. Additionally, the selectivity of CO₂ reduction is also affected by the photoreactor characteristics, whose optimization can result in a more than ten-fold increase in the methanol yield¹⁵⁰. 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 CO₂ reduction in the absence of sufficient concentration of water usually results in the production of CO and methane, while conducting the CO₂ reduction in the water liquid phase is more favourable for methanol synthesis⁹⁸.

Electrocatalysis. The electroreduction reaction (CO₂ERR)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 CO₂). 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 solution¹⁵⁸. 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 CO₂ solubility and can stabilize charged CO₂ intermediates, facilitating CO₂ reduction^{161,162}.

Heterogeneous electrocatalysts. A wide range of metal based electrocatalysts for the CO₂ERR have been investigated. Copper based catalysts have been mostly used for converting CO₂ with acceptable activity and efficiency into methanol^{162,163,164,165}. As already mentioned for photocatalysis, few articles evidenced, upon using labelled ¹³CO₂ experiment, that methanol really comes from CO₂.

A series of Pd_xCu_y aerogels bimetallic electrocatalysts¹⁶⁰ have been developed and their activity measured in a 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄) aqueous solution as electrolyte. The highest Faradaic efficiency (FE) for CH₃OH production (80.0%) at -2.1 V (vs. Ag/Ag⁺) led to a current density of 31.8 mA·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 H₂ and CO₂ 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) nanocatalysts¹⁶² has been studied in the [Bmim]PF₆ (30 wt %)/CH₃CN/H₂O (5 wt%) ternary electrolyte. The best catalyst exhibited a FE of 77.6% at -2.1 V (vs. Ag/Ag⁺) with current

density of $41.5 \text{ mA} \cdot \text{cm}^{-2}$ 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).

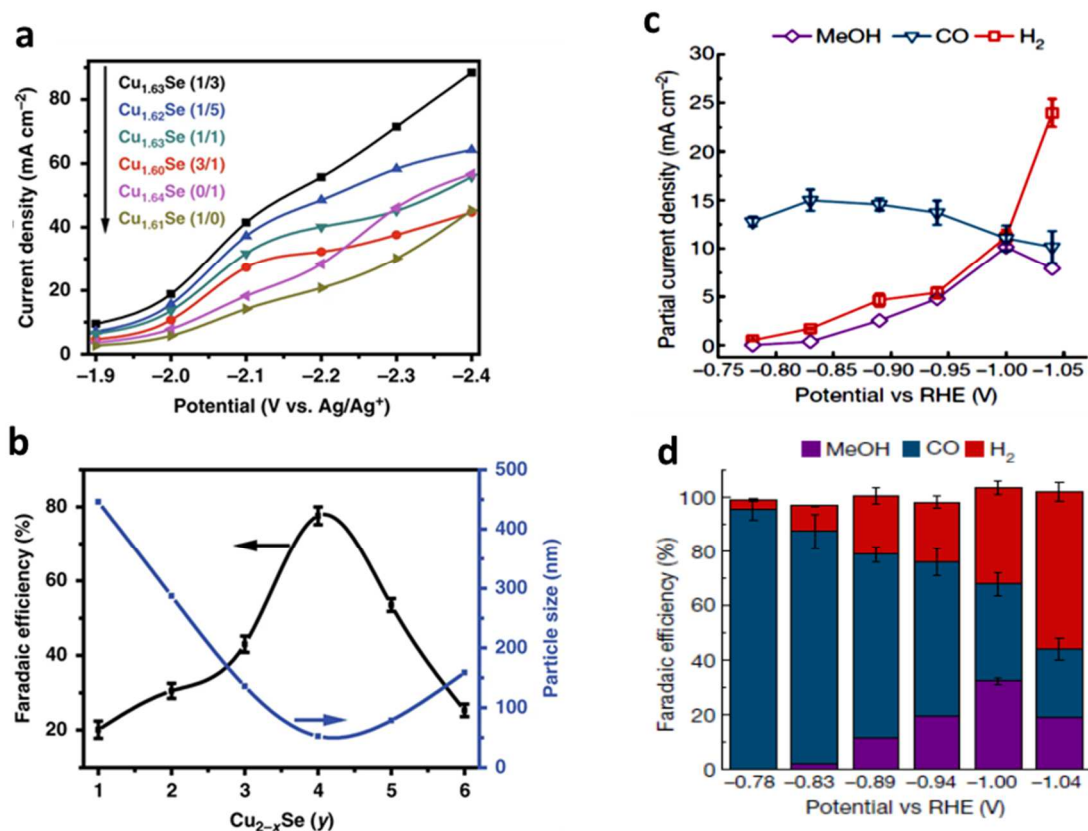


Fig. 6. a) Total current density over Cu_{1.63}Se_(1/3) catalyst at different applied potentials.¹⁶² b) Plots of particle size vs. FE of methanol on different Cu_{1.63}Se_x catalysts. Data were obtained at ambient temperature and pressure with CO₂ stream of 10 sccm with 5 h electrolysis.¹⁶² c) Partial current density for CO₂ electroreduction catalysed by CoPc-NH₂/CNT. Error bars represent one standard deviation from three measurements.¹⁷¹ d) Faradaic efficiencies for CO₂RR using CoPc-NH₂/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 CO₂ 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 CO₂RR to methanol^{171,174}. In a first study, unsubstituted cobalt phthalocyanine (CoPc) was supported onto multi-wall carbon nanotubes (MWCNT) and Nafion resin¹⁷⁴. A global Faradaic efficiency of 19.5% and chemical selectivity of 7.5% for CH₃OH could be obtained in a sequential process converting first CO₂ to CO, then using CO as a substrate to generate methanol in alkaline conditions (pH 13). The fact that the methanol originates from CO₂ was carefully assessed by ¹H 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–NH₂), and the catalysts were highly dispersed in the conductive ink containing carbon nanotubes and Nafion, leading to higher stability over time and larger currents¹⁷¹. In 0.1 M KHCO₃ 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 CO₂, but the results obtained in Ref 176 validate those obtained in this study. The mechanism proceeds *via* CO₂ reduction to CO intermediate and then methanol production, as with the non-substituted Co phthalocyanine¹⁷⁴.

Comparative assessment of the CO₂ reduction routes to methanol. Various routes have been explored for the selective CO₂ 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 CO₂ 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 CO₂ 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·g_{cat}⁻¹·h⁻¹, TON or μmol·m⁻², etc.). In order to compare different CO₂ 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 CO₂, 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 CO₂ can surpass 3000 h¹⁷⁵. 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 CO₂ photo-

and 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 CO₂ 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 ₂ O 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/ton¹⁷⁶

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 CO₂ 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 (TRL¹⁷⁷) is a recognized measure of the maturity of a technological process. The CO₂ hydrogenation to methanol *via* heterogeneous catalysis currently presents the highest TRL of 6-7¹⁷⁸⁻¹⁸⁰. Using this process, large demonstration facilities such as the CRI plant¹² in Iceland have been deployed. The second route in terms of maturity (TRL of 3-4) is electrocatalytic CO₂ reduction^{179,181}. The latter is highly modular and can be attractive for decentralized operation¹⁴. 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 CO₂ 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 CO₂ hydrogenation catalysis¹⁸⁰⁻¹⁸⁵ and CO₂ 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 required¹⁸⁹ and the photocatalytic activity must be raised by several orders of magnitude (from *ca.* 0.02-0.5 to 10 mmol g_{cat}⁻¹·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 CO₂ reduction that have been discussed in this review, heterogeneous catalysis and direct electrocatalysis stand out of the pack.

Methanol synthesis from CO₂ hydrogenation using heterogeneous catalysts has currently reached high scientific and technological maturity, while the CO₂ 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 CO₂ 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 CO₂ conversion, higher methanol selectivity and zero CO production. In the conventional CO₂-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 CO₂ 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 micro-

environment 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 CO₂ to CO and then CO to methanol, with optimization of each step, as it has been recently proposed¹⁷⁴ for a Co based molecular supported catalyst. Strategies to avoid poisoning and thus catalytic material degradation is of great importance. Currently, most CO₂RR 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.

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Author contributions

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

Competing interests

The authors declare no competing interests.

References

1. Global Monitoring Laboratory. <https://www.esrl.noaa.gov/gmd/ccgg/trends/>.
2. D'Alessandro, D. M., Smit, B. & Long, J. R. Carbon dioxide capture: Prospects for new materials. *Angew. Chemie - Int. Ed.* **49**, 6058–6082 (2010).
3. Aresta, M., Dibenedetto, A. & Angelini, A. Catalysis for the valorization of exhaust carbon: From CO₂ to chemicals, materials, and fuels. technological use of CO₂. *Chem. Rev.* **114**, 1709–1742 (2014).
4. Goeppert, A., Czaun, M., Jones, J. P., Surya Prakash, G. K. & Olah, G. A. Recycling of carbon dioxide to methanol and derived products-closing the loop. *Chem. Soc. Rev.* **43**, 7995–8048 (2014).
5. Ordonsky, V. V., Dros, A.-B., Schwiedernoch, R. & Khodakov, A. Y. Challenges and Role of Catalysis in CO₂ Conversion to Chemicals and Fuels. in *Nanotechnology in Catalysis* 803–850 (Wiley-VCH Verlag GmbH & Co. KGaA, 2017). doi:10.1002/9783527699827.ch30.
6. Centi, G. & Perathoner, S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catal. Today* **148**, 191–205 (2009).
7. Centi, G., Quadrelli, E. A. & Perathoner, S. Catalysis for CO₂ conversion: A key technology for rapid introduction of renewable energy in the value chain of chemical industries. *Energy Environ. Sci.* **6**, 1711–1731 (2013).
8. Artz, J. *et al.* Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment. *Chem. Rev.* **118**, 434–504 (2018).
9. Wang, W. H., Himeda, Y., Muckerman, J. T., Manbeck, G. F. & Fujita, E. CO₂ Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO₂ Reduction. *Chem. Rev.* **115**, 12936–12973 (2015).
10. The methanol Industry. *Methanol Institute* <https://www.methanol.org/the-methanol->

industry/.

11. Alper, E. & Yuksel Orhan, O. CO₂ utilization: Developments in conversion processes. *Petroleum* **3**, 109–126 (2017).
12. Carbon Recycling International (CRI). <https://www.carbonrecycling.is>.
13. Methanol from CO₂. <http://www.mefco2.eu/>.
14. Norskov, J. K., Latimer, A. A. & Dickens C.F. Research needs towards sustainable production of fuels and chemicals. in *Energy-X* <https://www.energy-x.eu/research-needs-report/> (2019).
15. Ali, K. A., Abdullah, A. Z. & Mohamed, A. R. Recent development in catalytic technologies for methanol synthesis from renewable sources: A critical review. *Renew. Sustain. Energy Rev.* **44**, 508–518 (2015).
16. Zhong, J. *et al.* State of the art and perspectives in heterogeneous catalysis of CO₂ hydrogenation to methanol. *Chem. Soc. Rev.* **49**, 1385–1413 (2020).
17. Prieto, G. Carbon Dioxide Hydrogenation into Higher Hydrocarbons and Oxygenates: Thermodynamic and Kinetic Bounds and Progress with Heterogeneous and Homogeneous Catalysis. *ChemSusChem* **10**, 1056–1070 (2017).
18. Jiang, X., Nie, X., Guo, X., Song, C. & Chen, J. G. Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis. *Chem. Rev.* **120**, 7984–8034 (2020).
19. Le Valant, A. *et al.* The Cu-ZnO synergy in methanol synthesis from CO₂, Part 1: Origin of active site explained by experimental studies and a sphere contact quantification model on Cu + ZnO mechanical mixtures. *J. Catal.* **324**, 41–49 (2015).
20. Dang, S. *et al.* A review of research progress on heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation. *Catal. Today* **330**, 61–75 (2019).
21. Ye, R.-P. *et al.* CO₂ hydrogenation to high-value products via heterogeneous catalysis.

- Nat. Commun.* **10**, 5698 (2019).
22. Bansode, A., Tidona, B., Von Rohr, P. R. & Urakawa, A. Impact of K and Ba promoters on CO₂ hydrogenation over Cu/Al₂O₃ catalysts at high pressure. *Catal. Sci. Technol.* **3**, 767–778 (2013).
 23. Álvarez, A. *et al.* Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO₂ Hydrogenation Processes. *Chem. Rev.* **117**, 9804–9838 (2017).
 24. Kattel, S., Ramírez, P. J., Chen, J. G., Rodríguez, J. A. & Liu, P. Active sites for CO₂ hydrogenation to methanol on Cu/ZnO catalysts. *Science* **355**, 1296–1299 (2017).
 25. Mota, N., Guil-Lopez, R., Pawelec, B. G., Fierro, J. L. G. & Navarro, R. M. Highly active Cu/ZnO-Al catalyst for methanol synthesis: Effect of aging on its structure and activity. *RSC Adv.* **8**, 20619–20629 (2018).
 26. Zabilskiy, M. *et al.* The unique interplay between copper and zinc during catalytic carbon dioxide hydrogenation to methanol. *Nat. Commun.* **11**, 1–8 (2020).
 27. Kondrat, S. A. *et al.* Preparation of a highly active ternary Cu-Zn-Al oxide methanol synthesis catalyst by supercritical CO₂ anti-solvent precipitation. *Catal. Today* **317**, 12–20 (2018).
 28. Zwiener, L. *et al.* Evolution of zincian malachite synthesis by low temperature co-precipitation and its catalytic impact on the methanol synthesis. *Appl. Catal. B Environ.* **249**, 218–226 (2019).
 29. Kondrat, S. A. *et al.* Stable amorphous georgeite as a precursor to a high-activity catalyst. *Nature* **531**, 83–87 (2016).
 30. Dasireddy, V. D. B. C. & Likozar, B. The role of copper oxidation state in Cu/ZnO/Al₂O₃ catalysts in CO₂ hydrogenation and methanol productivity. *Renew. Energy* **140**, 452–460 (2019).

31. Behrens, M. Promoting the Synthesis of Methanol: Understanding the Requirements for an Industrial Catalyst for the Conversion of CO₂. *Angew. Chemie - Int. Ed.* **55**, 14906–14908 (2016).
32. Guil-López, R. *et al.* Methanol Synthesis from CO₂: A Review of the Latest Developments in Heterogeneous Catalysis. *Materials (Basel)*. **12**, 3902 (2019).
33. Wang, Y. *et al.* Exploring the ternary interactions in Cu-ZnO-ZrO₂ catalysts for efficient CO₂ hydrogenation to methanol. *Nat. Commun.* **10**, 1166 (2019).
34. Kuld, S. *et al.* Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. *Sci. Reports* **352**, 969–974 (2016).
35. Li, L. *et al.* Ga-Pd/Ga₂O₃ Catalysts: The Role of Gallia Polymorphs, Intermetallic Compounds, and Pretreatment Conditions on Selectivity and Stability in Different Reactions. *ChemCatChem* **4**, 1764–1775 (2012).
36. Angelo, L. *et al.* Study of CuZn MO_x oxides (M = Al, Zr, Ce, CeZr) for the catalytic hydrogenation of CO₂ into methanol. *Comptes Rendus Chim.* **18**, 250–260 (2015).
37. Bahruji, H. *et al.* Pd/ZnO catalysts for direct CO₂ hydrogenation to methanol. *J. Catal.* **343**, 133–146 (2016).
38. Dang, S. *et al.* Rationally designed indium oxide catalysts for CO₂ hydrogenation to methanol with high activity and selectivity. *Sci. Adv.* **6**, eaaz2060 (2020).
39. Mureddu, M., Ferrara, F. & Pettinau, A. Highly efficient CuO/ZnO/ZrO₂@SBA-15 nanocatalysts for methanol synthesis from the catalytic hydrogenation of CO₂. *Appl. Catal. B Environ.* **258**, (2019).
40. Fang, X. *et al.* Improved methanol yield and selectivity from CO₂ hydrogenation using a novel Cu-ZnO-ZrO₂ catalyst supported on Mg-Al layered double hydroxide (LDH). *J. CO₂ Util.* **29**, 57–64 (2019).
41. Jiang, Q. *et al.* Tuning the highly dispersed metallic Cu species via manipulating

- Brønsted acid sites of mesoporous aluminosilicate support for CO₂ hydrogenation reactions. *Appl. Catal. B Environ.* **269**, 118804 (2020).
42. Fujitani, T. *et al.* Development of an active Ga₂O₃ supported palladium catalyst for the synthesis of methanol from carbon dioxide and hydrogen. *Appl. Catal. A, Gen.* **125**, 0–3 (1995).
 43. Bonivardi, A. L., Chiavassa, D. L., Querini, C. A. & Baltanás, M. A. Enhancement of the catalytic performance to methanol synthesis from CO₂/H₂ by gallium addition to palladium/silica catalysts. *Stud. Surf. Sci. Catal.* **130**, 3747–3752 (2000).
 44. Yang, X. *et al.* Low pressure CO₂ hydrogenation to methanol over gold nanoparticles activated on a CeO_x/TiO₂ Interface. *J. Am. Chem. Soc.* **137**, 10104–10107 (2015).
 45. Jiang, X., Koizumi, N., Guo, X. & Song, C. Bimetallic Pd-Cu catalysts for selective CO₂ hydrogenation to methanol. *Appl. Catal. B Environ.* **170–171**, 173–185 (2015).
 46. Snider, J. L. *et al.* Revealing the Synergy between Oxide and Alloy Phases on the Performance of Bimetallic In-Pd Catalysts for CO₂ Hydrogenation to Methanol. *ACS Catal.* **9**, 3399–3412 (2019).
 47. Duyar, M. S., Gallo, A., Snider, J. L. & Jaramillo, T. F. Low-pressure methanol synthesis from CO₂ over metal-promoted Ni-Ga intermetallic catalysts. *J. CO₂ Util.* **39**, 101151 (2020).
 48. Wang, J. *et al.* A highly selective and stable ZnO-ZrO₂ solid solution catalyst for CO₂ hydrogenation to methanol. *Sci. Adv.* **3**, e1701290 (2017).
 49. Wang, J. *et al.* High-Performance MaZrO_x (Ma = Cd, Ga) Solid-Solution Catalysts for CO₂ Hydrogenation to Methanol. *ACS Catal.* **9**, 10253–10259 (2019).
 50. Frei, M. S. *et al.* Atomic-scale engineering of indium oxide promotion by palladium for methanol production via CO₂ hydrogenation. *Nat. Commun.* **10**, 1–11 (2019).
 51. Shi, J. *et al.* Enzymatic conversion of carbon dioxide. *Chem. Soc. Rev.* **44**, 5981–6000

- (2015).
52. Kuk, S. K. *et al.* Photoelectrochemical Reduction of Carbon Dioxide to Methanol through a Highly Efficient Enzyme Cascade. *Angew. Chemie Int. Ed.* **56**, 3827–3832 (2017).
 53. Oliveira, A. R. *et al.* Toward the Mechanistic Understanding of Enzymatic CO₂ Reduction. *ACS Catal.* **10**, 3844–3856 (2020).
 54. Katagiri, T. & Amao, Y. Double-Electron Reduced Diphenylviologen as a Coenzyme for Biocatalytic Building Carbon–Carbon Bonds from CO₂ as a Carbon Feedstock. *ACS Sustain. Chem. Eng.* **7**, 9080–9085 (2019).
 55. Zhang, S. *et al.* Artificial Thylakoid for the Coordinated Photoenzymatic Reduction of Carbon Dioxide. *ACS Catal.* **9**, 3913–3925 (2019).
 56. Cai, Z. *et al.* Chloroplast-Inspired Artificial Photosynthetic Capsules for Efficient and Sustainable Enzymatic Hydrogenation. *ACS Sustain. Chem. Eng.* **6**, 17114–17123 (2018).
 57. Ma, K., Yehezkeli, O., Park, E. & Cha, J. N. Enzyme Mediated Increase in Methanol Production from Photoelectrochemical Cells and CO₂. *ACS Catal.* **6**, 6982–6986 (2016).
 58. Schwarz, F. M., Schuchmann, K. & Müller, V. Hydrogenation of CO₂ at ambient pressure catalyzed by a highly active thermostable biocatalyst. *Biotechnol. Biofuels* **11**, (2018).
 59. Zhang, Z. *et al.* Efficient ionic liquid-based platform for multi-enzymatic conversion of carbon dioxide to methanol. *Green Chem.* **20**, 4339–4348 (2018).
 60. Singh, R. K. *et al.* Insights into Cell-Free Conversion of CO₂ to Chemicals by a Multienzyme Cascade Reaction. *ACS Catal.* **8**, 11085–11093 (2018).
 61. Kuwabata, S., Tsuda, R. & Yoneyama, H. Electrochemical conversion of carbon dioxide to methanol with the assistance of formate dehydrogenase and methanol dehydrogenase

- as biocatalysts. *J. Am. Chem. Soc.* **116**, 5437–5443 (1994).
62. Rusching, U., Muller, U., Willnow, P. & Hopner, T. CO₂ Reduction to Formate by NADH Catalysed by Formate Dehydrogenase from *Pseudomonas oxalaticus*. *Eur. J. Biochem.* **70**, 325–330 (1976).
 63. Wang, Y., Li, M., Zhao, Z. & Liu, W. Effect of carbonic anhydrase on enzymatic conversion of CO₂ to formic acid and optimization of reaction conditions. *J. Mol. Catal. B Enzym.* **116**, 89–94 (2015).
 64. Baskaya, F. S., Zhao, X., Flickinger, M. C. & Wang, P. Thermodynamic Feasibility of Enzymatic Reduction of Carbon Dioxide to Methanol. *Appl. Biochem. Biotechnol.* **162**, 391–398 (2010).
 65. Obert, R. & Dave, B. C. Enzymatic conversion of carbon dioxide to methanol: Enhanced methanol production in silica sol-gel matrices. *Journal of the American Chemical Society* vol. 121 12192–12193 (1999).
 66. Xu, S., Lu, Y., Li, J., Jiang, Z. & Wu, H. Efficient Conversion of CO₂ to Methanol Catalyzed by Three Dehydrogenases Co-encapsulated in an Alginate–Silica (ALG–SiO₂) Hybrid Gel. *Ind. Eng. Chem. Res.* **45**, 4567–4573 (2006).
 67. Marques Netto, C. G. C., Andrade, L. H. & Toma, H. E. Carbon dioxide/methanol conversion cycle based on cascade enzymatic reactions supported on superparamagnetic nanoparticles. *An. Acad. Bras. Cienc.* **90**, 593–606 (2017).
 68. Kinastowska, K. *et al.* Photocatalytic cofactor regeneration involving triethanolamine revisited: The critical role of glycolaldehyde. *Appl. Catal. B Environ.* **243**, 686–692 (2019).
 69. Beller, M. & Bornscheuer, U. T. CO₂ fixation through hydrogenation by chemical or enzymatic methods. *Angew. Chemie - Int. Ed.* **53**, 4527–4528 (2014).
 70. El-Zahab, B., Donnelly, D. & Wang, P. Particle-tethered NADH for production of

- methanol from CO₂ catalyzed by coimmobilized enzymes. *Biotechnol. Bioeng.* **99**, 508–514 (2008).
71. Shi, J. *et al.* Enzymatic conversion of carbon dioxide. *Chem. Soc. Rev.* **44**, 5981–6000 (2015).
 72. Cazelles, R. *et al.* Reduction of CO₂ to methanol by a polyenzymatic system encapsulated in phospholipids–silica nanocapsules. *New J. Chem.* **37**, 3721 (2013).
 73. Schieweck, B. G., Jürling-Will, P. & Klankermayer, J. Structurally Versatile Ligand System for the Ruthenium Catalyzed One-Pot Hydrogenation of CO₂ to Methanol. *ACS Catal.* **10**, 3890–3894 (2020).
 74. Kar, S., Kothandaraman, J., Goeppert, A. & Prakash, G. K. S. Advances in catalytic homogeneous hydrogenation of carbon dioxide to methanol. *J. CO₂ Util.* **23**, 212–218 (2018).
 75. Kar, S., Goeppert, A. & Prakash, G. K. S. Integrated CO₂ Capture and Conversion to Formate and Methanol: Connecting Two Threads. *Acc. Chem. Res.* **52**, 2892–2903 (2019).
 76. Liu, W., Sahoo, B., Junge, K. & Beller, M. Cobalt Complexes as an Emerging Class of Catalysts for Homogeneous Hydrogenations. *Acc. Chem. Res.* **51**, 1858–1869 (2018).
 77. Sen, R., Goeppert, A., Kar, S. & Prakash, G. K. S. Hydroxide Based Integrated CO₂ Capture from Air and Conversion to Methanol. *J. Am. Chem. Soc.* **142**, 4544–4549 (2020).
 78. Chu, W.-Y., Culakova, Z., Wang, B. T. & Goldberg, K. I. Acid-Assisted Hydrogenation of CO₂ to Methanol in a Homogeneous Catalytic Cascade System. *ACS Catal.* **9**, 9317–9326 (2019).
 79. Schneidewind, J., Adam, R., Baumann, W., Jackstell, R. & Beller, M. Low-Temperature Hydrogenation of Carbon Dioxide to Methanol with a Homogeneous Cobalt Catalyst.

- Angew. Chemie Int. Ed.* **56**, 1890–1893 (2017).
80. Liu, Z., Wang, K., Chen, Y., Tan, T. & Nielsen, J. Third-generation biorefineries as the means to produce fuels and chemicals from CO₂. *Nat. Catal.* **3**, 274–288 (2020).
 81. Li, H. *et al.* Synergetic interaction between neighbouring platinum monomers in CO₂ hydrogenation. *Nat. Nanotechnol.* **13**, 411–417 (2018).
 82. Balaraman, E., Gunanathan, C., Zhang, J., Shimon, L. J. W. & Milstein, D. Efficient hydrogenation of organic carbonates, carbamates and formates indicates alternative routes to methanol based on CO₂ and CO. *Nat. Chem.* **3**, 609–614 (2011).
 83. Rezayee, N. M., Huff, C. A. & Sanford, M. S. Tandem Amine and Ruthenium-Catalyzed Hydrogenation of CO₂ to Methanol. *J. Am. Chem. Soc.* **137**, 1028–1031 (2015).
 84. Wesselbaum, S. *et al.* Hydrogenation of carbon dioxide to methanol using a homogeneous ruthenium–Triphos catalyst: from mechanistic investigations to multiphase catalysis. *Chem. Sci.* **6**, 693–704 (2015).
 85. Kar, S., Goeppert, A., Kothandaraman, J. & Prakash, G. K. S. Manganese-Catalyzed Sequential Hydrogenation of CO₂ to Methanol via Formamide. *ACS Catal.* **7**, 6347–6351 (2017).
 86. Ribeiro, A. P. C., Martins, L. M. D. R. S. & Pombeiro, A. J. L. Carbon dioxide-to-methanol single-pot conversion using a C-scorpionate iron(ii) catalyst. *Green Chem.* **19**, 4811–4815 (2017).
 87. Yu, X., Moldovan, S., Ordonsky, V. V. & Khodakov, A. Y. Design of core–shell titania–heteropolyacid–metal nanocomposites for photocatalytic reduction of CO₂ to CO at ambient temperature. *Nanoscale Adv.* **1**, 4321–4330 (2019).
 88. Dau, H., Fujita, E. & Sun, L. Artificial Photosynthesis: Beyond Mimicking Nature. *ChemSusChem* vol. 10 4228–4235 (2017).
 89. Butburee, T., Chakthranont, P., Phawa, C. & Faungnawakij, K. Beyond Artificial

- Photosynthesis: Prospects on Photobiorefinery. *ChemCatChem* **12**, 1873–1890 (2020).
90. Yan, T. *et al.* Polymorph selection towards photocatalytic gaseous CO₂ hydrogenation. *Nat. Commun.* **10**, 1–10 (2019).
91. Jia, J. *et al.* Heterogeneous catalytic hydrogenation of CO₂ by metal oxides: Defect engineering-perfecting imperfection. *Chemical Society Reviews* **46**, 4631–4644 (2017).
92. Yan, X. *et al.* Nickel@Siloxene catalytic nanosheets for high-performance CO₂ methanation. *Nat. Commun.* **10**, 2608 (2019).
93. Jia, J. *et al.* Visible and Near-Infrared Photothermal Catalyzed Hydrogenation of Gaseous CO₂ over Nanostructured Pd@Nb₂O₅. *Adv. Sci.* **3**, 1600189 (2016).
94. Wang, J. *et al.* A highly selective and stable ZnO-ZrO₂ solid solution catalyst for CO₂ hydrogenation to methanol. *Sci. Adv.* **3**, 1701290–1701300 (2017).
95. Guan, G., Kida, T. & Yoshida, A. Reduction of carbon dioxide with water under concentrated sunlight using photocatalyst combined with Fe-based catalyst. *Applied Catalysis B: Environmental* **41**, 387–396 (2003).
96. Wang, L. *et al.* Photocatalytic Hydrogenation of Carbon Dioxide with High Selectivity to Methanol at Atmospheric Pressure. *Joule* **2**, 1369–1381 (2018).
97. Xie, S., Zhang, Q., Liu, G. & Wang, Y. Photocatalytic and photoelectrocatalytic reduction of CO₂ using heterogeneous catalysts with controlled nanostructures. *Chem. Commun.* **52**, 35–59 (2016).
98. Habisreutinger, S. N., Schmidt-Mende, L. & Stolarczyk, J. K. Photocatalytic reduction of CO₂ on TiO₂ and other semiconductors. *Angew. Chemie - Int. Ed.* **52**, 7372–7408 (2013).
99. Zhao, G., Huang, X., Wang, X. & Wang, X. Progress in catalyst exploration for heterogeneous CO₂ reduction and utilization: A critical review. *Journal of Materials Chemistry A*, **5**, 21625–21649 (2017).

100. Stolarczyk, J. K., Bhattacharyya, S., Polavarapu, L. & Feldmann, J. Challenges and Prospects in Solar Water Splitting and CO₂ Reduction with Inorganic and Hybrid Nanostructures. *ACS Catal.* **8**, 3602–3635 (2018).
101. Kowalska, E., Wei, Z. & Janczarek, M. Band-gap Engineering of Photocatalysts: Surface Modification versus Doping. in *Visible Light-Active Photocatalysis* 447–484 (Wiley-VCH Verlag GmbH & Co. KGaA, 2018). doi:10.1002/9783527808175.ch16.
102. Kubacka, A., Fernández-García, M. & Colón, G. Advanced Nanoarchitectures for Solar Photocatalytic Applications. *Chem. Rev.* **112**, 1555–1614 (2012).
103. Lehn, J.-M. & Ziessel, R. Photochemical generation of carbon monoxide and hydrogen by reduction of carbon dioxide and water under visible light irradiation. *Proc. Natl. Acad. Sci.* **79**, 701–704 (1982).
104. Navalón, S., Dhakshinamoorthy, A., Álvaro, M. & Garcia, H. Photocatalytic CO₂ Reduction using Non-Titanium Metal Oxides and Sulfides. *ChemSusChem* **6**, 562–577 (2013).
105. Ma, Y. *et al.* Titanium Dioxide-Based Nanomaterials for Photocatalytic Fuel Generations. *Chem. Rev.* **114**, 9987–10043 (2014).
106. Malathi, A., Madhavan, J., Ashokkumar, M. & Arunachalam, P. A review on BiVO₄ photocatalyst: Activity enhancement methods for solar photocatalytic applications. *Appl. Catal. A Gen.* **555**, 47–74 (2018).
107. Wu, Y. A. *et al.* Facet-dependent active sites of a single Cu₂O particle photocatalyst for CO₂ reduction to methanol. *Nat. Energy* **4**, 957–968 (2019).
108. Bae, K.-L., Kim, J., Lim, C. K., Nam, K. M. & Song, H. Colloidal zinc oxide-copper(I) oxide nanocatalysts for selective aqueous photocatalytic carbon dioxide conversion into methane. *Nat. Commun.* **8**, 1156 (2017).
109. Zhou, R. & Guzman, M. I. CO₂ Reduction under Periodic Illumination of ZnS. *J. Phys.*

- Chem. C* **118**, 11649–11656 (2014).
110. Jiang, Z. *et al.* A Hierarchical Z-Scheme α -Fe₂O₃ /g-C₃N₄ Hybrid for Enhanced Photocatalytic CO₂ Reduction. *Adv. Mater.* **30**, 1706108 (2018).
 111. Wang, H., Zhang, L., Wang, K., Sun, X. & Wang, W. Enhanced photocatalytic CO₂ reduction to methane over WO₃·0.33H₂O via Mo doping. *Appl. Catal. B Environ.* **243**, 771–779 (2019).
 112. Terranova, U., Viñes, F., de Leeuw, N. H. & Illas, F. Mechanisms of carbon dioxide reduction on strontium titanate perovskites. *J. Mater. Chem. A* **8**, 9392–9398 (2020).
 113. Shoji, S., Yamaguchi, A., Sakai, E. & Miyauchi, M. Strontium Titanate Based Artificial Leaf Loaded with Reduction and Oxidation Cocatalysts for Selective CO₂ Reduction Using Water as an Electron Donor. *ACS Appl. Mater. Interfaces* **9**, 20613–20619 (2017).
 114. Pan, Y.-X. *et al.* Photocatalytic CO₂ reduction highly enhanced by oxygen vacancies on Pt-nanoparticle-dispersed gallium oxide. *Nano Res.* **9**, 1689–1700 (2016).
 115. Kohno, Y., Tanaka, T., Funabiki, T. & Yoshida, S. Photoreduction of CO₂ with H₂ over ZrO₂. A study on interaction of hydrogen with photoexcited CO₂. *Phys. Chem. Chem. Phys.* **2**, 2635–2639 (2000).
 116. Lin, J., Pan, Z. & Wang, X. Photochemical Reduction of CO₂ by Graphitic Carbon Nitride Polymers. *ACS Sustain. Chem. Eng.* **2**, 353–358 (2014).
 117. Sun, Z., Wang, H., Wu, Z. & Wang, L. g-C₃N₄ based composite photocatalysts for photocatalytic CO₂ reduction. *Catal. Today* **300**, 160–172 (2018).
 118. Sun, Z. *et al.* Enriching CO₂ Activation Sites on Graphitic Carbon Nitride with Simultaneous Introduction of Electron-Transfer Promoters for Superior Photocatalytic CO₂-to-Fuel Conversion. *Adv. Sustain. Syst.* **1**, 1700003 (2017).
 119. Dong, Y. *et al.* Tailoring Surface Frustrated Lewis Pairs of In₂O_{3-x}(OH)_y for Gas-Phase Heterogeneous Photocatalytic Reduction of CO₂ by Isomorphous Substitution of In³⁺

- with Bi³⁺. *Adv. Sci.* **5**, 1700732 (2018).
120. Zhang, X., Peng, T. & Song, S. Recent advances in dye-sensitized semiconductor systems for photocatalytic hydrogen production. *J. Mater. Chem. A* **4**, 2365–2402 (2016).
 121. Truong, Q. D., Hoa, H. T., Vo, D. V. N. & Le, T. S. Controlling the shape of anatase nanocrystals for enhanced photocatalytic reduction of CO₂ to methanol. *New J. Chem.* **41**, 5660–5668 (2017).
 122. Xu, Q., Yu, J., Zhang, J., Zhang, J. & Liu, G. Cubic anatase TiO₂ nanocrystals with enhanced photocatalytic CO₂ reduction activity. *Chem. Commun.* **51**, 7950–7953 (2015).
 123. Yuan, Y. P., Ruan, L. W., Barber, J., Joachim Loo, S. C. & Xue, C. Hetero-nanostructured suspended photocatalysts for solar-to-fuel conversion. *Energy and Environmental Science* vol. 7 3934–3951 (2014).
 124. Qian, R. *et al.* Charge carrier trapping, recombination and transfer during TiO₂ photocatalysis: An overview. *Catal. Today* **335**, 78–90 (2019).
 125. Wang, Y. *et al.* Unique hole-accepting carbon-dots promoting selective carbon dioxide reduction nearly 100% to methanol by pure water. *Nat. Commun.* **11**, 2531 (2020).
 126. Hori, Y. *et al.* Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal electrodes in aqueous media. *Curr. Opin. Green Sustain. Chem.* **16**, 1833–1839 (2019).
 127. Zeng, Z. *et al.* Boosting the Photocatalytic Ability of Cu₂O Nanowires for CO₂ Conversion by MXene Quantum Dots. *Adv. Funct. Mater.* **29**, 1–9 (2019).
 128. Wang, H. *et al.* Semiconductor heterojunction photocatalysts: Design, construction, and photocatalytic performances. *Chem. Soc. Rev.* **43**, 5234–5244 (2014).
 129. Gusain, R., Kumar, P., Sharma, O. P., Jain, S. L. & Khatri, O. P. Reduced graphene oxide-CuO nanocomposites for photocatalytic conversion of CO₂ into methanol under

- visible light irradiation. *Appl. Catal. B Environ.* **181**, 352–362 (2016).
130. Jiang, W.-X., Liu, W.-X., Wang, C.-L., Zhan, S.-Z. & Wu, S.-P. A bis(thiosemicarbazonato)-copper complex, a new catalyst for electro-and photo-reduction of CO₂ to methanol † Diacetyl-2-(4-N-methyl-3-thiosemicarbazone)-3-(4-N-amino-3-thiosemicarbazone) (H₂ ATSM) reacts with. *New J. Chem* **44**, 2721 (2020).
 131. Navaee, A. & Salimi, A. Sulfur doped-copper oxide nanoclusters synthesized through a facile electroplating process assisted by thiourea for selective photoelectrocatalytic reduction of CO₂. *J. Colloid Interface Sci.* **505**, 241–252 (2017).
 132. Tseng, I.-H., Wu, J. C. S. & Chou, H.-Y. Effects of sol-gel procedures on the photocatalysis of Cu/TiO₂ in CO₂ photoreduction. *J. Catal.* **221**, 432–440 (2004).
 133. Xiang, T. *et al.* Selective photocatalytic reduction of CO₂ to methanol in CuO-loaded NaTaO₃ nanocubes in isopropanol. *Beilstein J. Nanotechnol* **7**, 776–783 (2016).
 134. Yisilamu, G. *et al.* Preparation of Cuprous Oxide Nanoparticles Coated with Aminated Cellulose for the Photocatalytic Reduction of Carbon Dioxide to Methanol. *Energy Technol.* **6**, 1168–1177 (2018).
 135. Madhusudan, P. *et al.* Graphene-Zn_{0.5}Cd_{0.5}S nanocomposite with enhanced visible-light photocatalytic CO₂ reduction activity. *Appl. Surf. Sci.* **506**, (2020).
 136. Yang, C., Li, Q., Xia, Y., Lv, K. & Li, M. Enhanced visible-light photocatalytic CO₂ reduction performance of ZnIn₂S₄ microspheres by using CeO₂ as cocatalyst. *Appl. Surf. Sci.* **464**, 388–395 (2019).
 137. Christoforidis, K. C. & Fornasiero, P. Photocatalysis for Hydrogen Production and CO₂ Reduction: The Case of Copper-Catalysts. *ChemCatChem* **11**, 368–382 (2019).
 138. Alves Melo Júnior, M., Morais, A. & Nogueira, A. F. Boosting the solar-light-driven methanol production through CO₂ photoreduction by loading Cu₂O on TiO₂-pillared K₂Ti₄O₉. *Microporous Mesoporous Mater.* **234**, 1–11 (2016).

139. Gao, P. *et al.* Influence of Zr on the performance of Cu/Zn/Al/Zr catalysts via hydrotalcite-like precursors for CO₂ hydrogenation to methanol. *J. Catal.* **298**, 51–60 (2013).
140. Li, B. *et al.* Preparation of Cu₂O modified TiO₂ nanopowder and its application to the visible light photoelectrocatalytic reduction of CO₂ to CH₃OH. *Chem. Phys. Lett.* **700**, 57–63 (2018).
141. Guan, G., Kida, T., Harada, T., Isayama, M. & Yoshida, A. Photoreduction of carbon dioxide with water over K₂Ti₆O₁₃ photocatalyst combined with Cu/ZnO catalyst under concentrated sunlight. *Appl. Catal. A Gen.* **249**, 11–18 (2003).
142. Kumar, P. *et al.* Core–shell structured reduced graphene oxide wrapped magnetically separable rGO@CuZnO@Fe₃O₄ microspheres as superior photocatalyst for CO₂ reduction under visible light. *Appl. Catal. B Environ.* **205**, 654–665 (2017).
143. Wang, Z. jun *et al.* Photo-assisted methanol synthesis via CO₂ reduction under ambient pressure over plasmonic Cu/ZnO catalysts. *Appl. Catal. B Environ.* **250**, 10–16 (2019).
144. Yendrapati Taraka, T. P., Gautam, A., Jain, S. L., Bojja, S. & Pal, U. Controlled addition of Cu/Zn in hierarchical CuO/ZnO p-n heterojunction photocatalyst for high photoreduction of CO₂ to MeOH. *J. CO₂ Util.* **31**, 207–214 (2019).
145. Zheng, Y. *et al.* Nano Ag-Decorated MoS₂ Nanosheets from 1T to 2H Phase Conversion for Photocatalytically Reducing CO₂ to Methanol. *Energy Technol.* **7**, 1900582 (2019).
146. Yu, B. *et al.* Photocatalytic reduction of CO₂ over Ag/TiO₂ nanocomposites prepared with a simple and rapid silver mirror method. *Nanoscale* **8**, 11870–11874 (2016).
147. Wang, X. *et al.* BiVO₄ /Bi₄Ti₃O₁₂ heterojunction enabling efficient photocatalytic reduction of CO₂ with H₂O to CH₃OH and CO. *Appl. Catal. B Environ.* **270**, (2020).
148. Gondal, M. A., Dastageer, M. A., Oloore, L. E., Baig, U. & Rashid, S. G. Enhanced photo-catalytic activity of ordered mesoporous indium oxide nanocrystals in the

- conversion of CO₂ into methanol. *J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.* **52**, 785–793 (2017).
149. Meng, A., Wu, S., Cheng, B., Yu, J. & Xu, J. Hierarchical TiO₂ /Ni(OH)₂ composite fibers with enhanced photocatalytic CO₂ reduction performance. *J. Mater. Chem. A* **6**, 4729–4736 (2018).
 150. Spadaro, L., Arena, F. & Palella, A. *Which Future Route in the Methanol Synthesis? Photocatalytic Reduction of CO₂, the New Challenge in the Solar Energy Exploitation. Methanol: Science and Engineering* (Elsevier B.V., 2018). doi:10.1016/B978-0-444-63903-5.00016-9.
 151. Edelmannová, M. *et al.* Photocatalytic hydrogenation and reduction of CO₂ over CuO/TiO₂ photocatalysts. *Appl. Surf. Sci.* **454**, 313–318 (2018).
 152. Xie, S., Wang, Y., Zhang, Q., Deng, W. & Wang, Y. MgO- and Pt-promoted TiO₂ as an efficient photocatalyst for the preferential reduction of carbon dioxide in the presence of water. *ACS Catal.* **4**, 3644–3653 (2014).
 153. Albo, J., Sáez, A., Solla-gullón, J., Montiel, V. & Irabien, A. Applied Catalysis B : Environmental Production of methanol from CO₂ electroreduction at Cu₂O and Cu₂O /ZnO-based electrodes in aqueous solution. *Appl. Catal. B Environ.* **176–177**, 709–717 (2015).
 154. Al-rowaili, F. N., Jamal, A., Shammakh, M. S. B. & Rana, A. A Review on Recent Advances for Electrochemical Reduction of Carbon Dioxide to Methanol Using Metal – Organic Framework (MOF) and Non-MOF Catalysts: Challenges and Future Prospects. *ACS Sustain. Chem. Eng* **6**, 15895–15914 (2018).
 155. Zhang, L., Zhao, Z. J. & Gong, J. Nanostructured Materials for Heterogeneous Electrocatalytic CO₂ Reduction and their Related Reaction Mechanisms. *Angew. Chemie - Int. Ed.* **56**, 11326–11353 (2017).

156. Albo, J. & Irabien, A. Cu₂O-loaded gas diffusion electrodes for the continuous electrochemical reduction of CO₂ to methanol. *J. Catal.* **343**, 232–239 (2016).
157. Albo, J., Beobide, G., Castaño, P. & Irabien, A. Methanol electrosynthesis from CO₂ at Cu₂O/ZnO prompted by pyridine-based aqueous solutions. *Biochem. Pharmacol.* **18**, 164–172 (2017).
158. Jiwanti, P. K., Natsui, K. & Einaga, Y. Selective production of methanol by the electrochemical reduction of CO₂ on boron-doped diamond electrodes in aqueous ammonia solution. *RSC Adv.* **6**, 102214–102217 (2016).
159. Jr, D. F., Gonçalves, W. D. G. & Dupont, J. CO₂ Electroreduction in Ionic Liquids. *Front. Chem.* **7**, 1–8 (2019).
160. Lu, L. *et al.* Highly Efficient Electroreduction of CO₂ to Methanol on Palladium–Copper Bimetallic Aerogels. *Angew. Chemie - Int. Ed.* **57**, 14149–14153 (2018).
161. Moura de Salles Pupo, Marilia Kortlever, R. Electrolyte Effects on the Electrochemical Reduction of CO₂. *ChemPhysChem* **20**, 2926–2935 (2019).
162. Yang, D. *et al.* Selective electroreduction of carbon dioxide to methanol on copper selenide nanocatalysts. *Nat. Commun.* **10**, 1–9 (2019).
163. Li, C. W., Ciston, J. & Kanan, M. W. Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature* **508**, 504–507 (2014).
164. Jiang, Y., Long, R. & Xiong, Y. Regulating C-C coupling in thermocatalytic and electrocatalytic CO_x conversion based on surface science. *Chem. Sci.* **10**, 7310–7326 (2019).
165. Raciti, D. & Wang, C. Recent Advances in CO₂ Reduction Electrocatalysis on Copper. *ACS Energy Lett.* **3**, 1545–1556 (2018).
166. Jiang, X. *et al.* Origin of Pd-Cu bimetallic effect for synergetic promotion of methanol formation from CO₂ hydrogenation. *J. Catal.* **369**, 21–32 (2019).

167. Bai, S. *et al.* Highly Active and Selective Hydrogenation of CO₂ to Ethanol by Ordered Pd–Cu Nanoparticles. *J. Am. Chem. Soc.* **139**, 6827–6830 (2017).
168. Feng, G. *et al.* Oxygenates from the Electrochemical Reduction of Carbon Dioxide. *Chem. - An Asian J.* **13**, 1992–2008 (2018).
169. Birdja, Y. Y. *et al.* Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels. *Nat. Energy* **4**, 732–745 (2019).
170. Perry, S. C., Leung, P. ki, Wang, L. & Ponce de León, C. Developments on carbon dioxide reduction: Their promise, achievements, and challenges. *Curr. Opin. Electrochem.* **20**, 88–98 (2020).
171. Wu, Y., Jiang, Z., Lu, X., Liang, Y. & Wang, H. Domino electroreduction of CO₂ to methanol on a molecular catalyst. *Nature* **575**, 639–642(2019).
172. Zhao, K., Liu, Y., Quan, X., Chen, S. & Yu, H. CO₂ Electroreduction at Low Overpotential on Oxide-Derived Cu/Carbons Fabricated from Metal Organic Framework. *ACS Appl. Mater. Interfaces* **9**, 5302–5311 (2017).
173. Huang, J., Guo, X., Yue, G., Hu, Q. & Wang, L. Boosting CH₃OH Production in Electrocatalytic CO₂ Reduction over Partially Oxidized 5 nm Cobalt Nanoparticles Dispersed on Single-Layer Nitrogen-Doped Graphene. *ACS Appl. Mater. Interfaces* **10**, 44403–44414 (2018).
174. Boutin, E. *et al.* Aqueous Electrochemical Reduction of Carbon Dioxide and Carbon Monoxide into Methanol with Cobalt Phthalocyanine. *Angew. Chemie - Int. Ed.* **58**, 16172–16176 (2019).
175. Toyir, J. *et al.* Sustainable process for the production of methanol from CO₂ and H₂ using Cu/ZnO-based multicomponent catalyst. *Phys. Procedia* **2**, 1075–1079 (2008).
176. Methanex Corporation. <https://www.methanex.com/our-business/pricing>.
177. EU HORIZON 2020, WORK PROGRAMME 2016– 2017 20. General Annexes.

https://ec.europa.eu/research/participants/data/ref/h2020/other/wp/2016-2017/annexes/h2020-wp1617-annex-ga_en.pdf.

178. Roy, S., Cherevotan, A. & Peter, S. C. Thermochemical CO₂ Hydrogenation to Single Carbon Products: Scientific and Technological Challenges. *ACS Energy Lett.* **3**, 1938–1966 (2018).
179. Jarvis, S. M. & Samsatli, S. Technologies and infrastructures underpinning future CO₂ value chains: A comprehensive review and comparative analysis. *Renewable and Sustainable Energy Reviews* vol. 85 46–68 (2018).
180. Pérez-Fortes, M., Schöneberger, J. C., Boulamanti, A. & Tzimas, E. Methanol synthesis using captured CO₂ as raw material: Techno-economic and environmental assessment. *Appl. Energy* **161**, 718–732 (2016).
181. Pérez-Fortes, M. & Tzimas, E. *Techno-economic and environmental evaluation of CO₂ utilisation for fuel production. Synthesis of methanol and formic acid. Scientific and Technical Research Series* (2016). doi:10.2790/89238.
182. Hank, C. *et al.* Economics & carbon dioxide avoidance cost of methanol production based on renewable hydrogen and recycled carbon dioxide-power-to-methanol. *Sustain. Energy Fuels* **2**, 1244–1261 (2018).
183. Bellotti, D., Rivarolo, M. & Magistri, L. Economic feasibility of methanol synthesis as a method for CO₂ reduction and energy storage. in *Energy Procedia* vol. 158 4721–4728 (Elsevier Ltd, 2019).
184. Bos, M. J., Kersten, S. R. A. & Brilman, D. W. F. Wind power to methanol: Renewable methanol production using electricity, electrolysis of water and CO₂ air capture. *Appl. Energy* **264**, 114672 (2020).
185. Broeren, M. Production of bio-methanol. *IEA-ETSAP and IRENA© Technology Brief 108 – January* (2013).

186. Lu, Q. & Jiao, F. Electrochemical CO₂ reduction: Electrocatalyst, reaction mechanism, and process engineering. *Nano Energy* **29**, 439–456 (2016).
187. Verma, S., Kim, B., Jhong, H. R. M., Ma, S. & Kenis, P. J. A. A gross-margin model for defining technoeconomic benchmarks in the electroreduction of CO₂. *ChemSusChem* **9**, 1972–1979 (2016).
188. Asif, M., Gao, X., Lv, H., Xi, X. & Dong, P. Catalytic hydrogenation of CO₂ from 600 MW supercritical coal power plant to produce methanol: A techno-economic analysis. *Int. J. Hydrogen Energy* **43**, 2726–2741 (2018).
189. Herron, J. A. & Maravelias, C. T. Assessment of Solar-to-Fuels Strategies: Photocatalysis and Electrocatalytic Reduction. *Energy Technol.* **4**, 1369–1391 (2016).