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Yakubu Adekunle Alli, Peter Olusakin Oladoye, Onome Ejeromedoghene, Owolabi Mutolib Bankole, Oyekunle Azeez Alimi, Elizabeth Oyinkansola Omotola, Clement Ajibade Olanrewaju, Karine Philippot, Adeyemi Adeleye, Adeniyi Sunday Ogunlaja

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1 **Nanomaterials as Catalysts for CO₂ Transformation into Value-added Products: A**
2 **Review**

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33 **Abstract**

34 Carbon dioxide (CO₂) is the most important greenhouse gas (GHG), accounting for
35 76% of all GHG emissions. The atmospheric CO₂ concentration has increased from 280
36 ppm in the pre-industrial era to about 417.86 ppm, and is projected to reach 570 ppm by
37 the end of the 21st century. In addition to reducing CO₂ emissions from anthropogenic
38 activities, strategies to adequately address climate change must include CO₂ capture. To
39 promote circular economy, captured CO₂ should be converted to value-added materials
40 such as fuels and chemical feedstock. Due to their tunable chemistry (which allows
41 them to be selective) and high surface area (which allows them to be efficient),
42 engineered nanomaterials are promising for CO₂ capturing and/or transformation. This
43 work critically reviewed the application of nanomaterials for the transformation of CO₂
44 into various fuels, like formic acid, carbon monoxide, methanol, and ethanol. We
45 discussed the literature on the use of metal-based nanomaterials, inorganic/organic
46 nanocomposites, as well as other routes suitable for CO₂ conversion such as the
47 electrochemical, non-thermal plasma, and hydrogenation routes. The characteristics,
48 steps, mechanisms, and challenges associated with the different transformation
49 technologies were also discussed. Finally, we presented a section on the future outlook
50 of the field, which includes recommendations for how to continue to advance the use of
51 nanotechnology for conversion of CO₂ to fuels.

52 **Keywords:** CO₂ based fuels, nanomaterials, global warming, catalysts

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78 5. Conclusions and future outlook

79

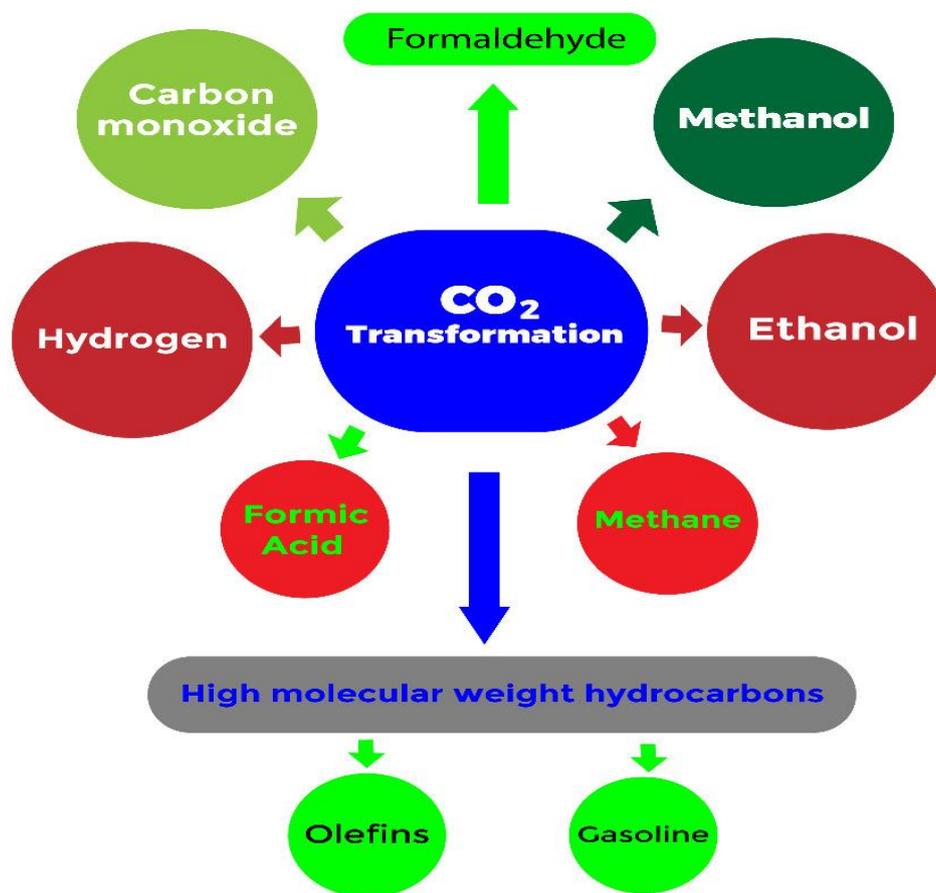
80 **1. Introduction**

81 One of the primary environmental concerns today is climate change. Indicators of
82 climate change include global warming, increased frequency and intensity of natural
83 disasters and extreme weather events such as wildfires which was responsible for the
84 loss of ~\$650 billion between 2016 to 2018, extreme droughts in Europe, heatwaves in
85 USA, and hurricanes in other parts of the world (Mustafa et al., 2020). Climate change
86 is mainly attributed to increased emission of greenhouse gases into the atmosphere
87 (Cassia et al., 2018; Solomon et al., 2010, 2009), which has led to the global surface
88 temperature of 0.88°C (1.58°F) in September 2022 which is above the average for the
89 20th century of 15.0°C (59.0°F), tying September 2021 as the sixth warmest for
90 September in the 143-year record. In addition, global CO₂ levels was 280 ppm in the
91 pre-industrial era; it has now increased to 417.86 ppm as at October 19, 2022 according
92 to the Global Monitoring Laboratory (daily global CO₂ trend) and it is projected to
93 reach 570 ppm by the end of the 21st century (Mustafa et al., 2020).

94 In order to ameliorate global warming and other climate change indicators, it is
95 imperative that emission of CO₂ is controlled, and the excess atmospheric CO₂ is
96 captured. Several strategies exist for achieving atmospheric CO₂ reduction. For
97 instance, afforestation is effective for CO₂ emission reduction and sequestration
98 (Halder et al., 2014; Jansen et al., 2015; Li et al., 2013; Mondal et al., 2012). More so,
99 various governmental and inter-governmental policies have been implemented to also
100 reduce the emissions of CO₂ by putting taxes on carbon sources and fossil fuels (Atsbha
101 et al., 2021; Herzer, 2022; Omoregbe et al., 2020; Peiseler & Cabrera Serrenho, 2022).
102 Chemical CO₂ conversion is also effective but is a herculean task due to the

103 characteristic thermodynamic stability of CO₂ molecule. The stability of CO₂ arises
104 from its structure (O=C=O) and possession of double covalent bonds with two oxygen
105 atoms (Ateka et al., 2022). The carbon in CO₂ is extremely inactive and is kinetically
106 inert owing to its occurrence at the highest oxidation state in CO₂ (Wang et al., 2022).
107 As a result, the transformation of CO₂ to useful fuels and/or chemicals demands the
108 input of substantial amount of energy to cleave the C-O bond (Pawelec et al., 2021; Sha
109 et al., 2020)

110 The energy requirement for CO₂ conversion is met through three major routes: (i) the
111 use of (nanomaterial-based) catalysts with active sites, (ii) the application of high
112 pressure and/or temperature, and (iii) application of energy from carbon-neutral and
113 renewable energy sources (Kamkeng et al., 2021). There are a number of technological
114 approaches that can be employed to execute transformation of CO₂. In terms of using
115 catalysts for CO₂ transformation, the processes and/or mechanisms involved may be
116 photocatalytic, electrocatalytic, thermal or non-thermal etc., to lower the energy barrier
117 and create alternative pathway for the catalytic CO₂ reduction (Ateka et al., 2022). For
118 example, in photo-catalyzed transformation using titanium dioxide (TiO₂; a common
119 photo-catalyst) as a catalyst, upon irradiation, a photo hole-electron pair is generated,
120 which interacts with CO₂ and H₂O molecules to produce hydrocarbons and other value-
121 added products. This is feasible only by appropriate catalyst selection, doping and
122 conditions (Low et al., 2017). Scheme 1 presents the various value added-products of
123 CO₂ transformation covered in this synthesis.



124

125 Scheme 1: Products obtained from the transformation of CO₂

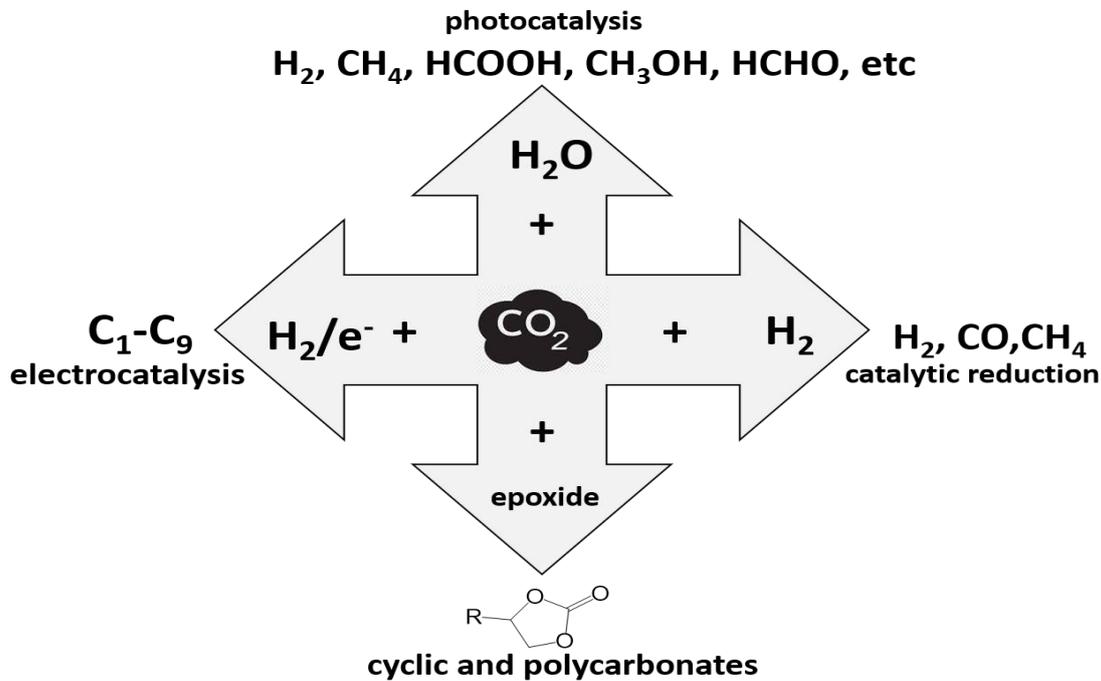
126 A number of comprehensive, systematic and/or critical reviews on the transformation
 127 of CO₂ have been published (Kamkeng et al., 2021; Low et al., 2017; Mustafa et al.,
 128 2020; Pawelec et al., 2021; Sha et al., 2020; Wang et al., 2011; Wu et al., 2017).
 129 Although a large proportion of them are detailed with respect to application and
 130 transformation of CO₂, recent advances in technologies for CO₂ conversion have not
 131 been sufficiently covered by the existing reviews. In addition, the technical challenges
 132 facing the real-world implementation of these technologies are yet to the
 133 comprehensively explored and presented. Therefore, this synthesis on CO₂ conversion

134 to valued-added products attempts to provide current and comprehensive understanding
135 on nano-enabled CO₂ conversion, routes of CO₂ conversion, fuels generated from CO₂
136 conversion, application, technical issues and economic implications of transformation
137 of CO₂ into hydrocarbon fuels. The review also elaborates the research gaps that need
138 to be filled.

139 **2. Nanomaterials for CO₂ conversion**

140 Nanomaterials have gotten a lot of attention in the research world because of their
141 fascinating small size (1-100 nm), which is responsible for their improved functionality
142 (Afolabi et al., 2022; Alli et al., 2022, 2021). In this regard, the use of nanomaterials
143 for direct transformation of CO₂, to renewable organic fuels and other feedstocks has
144 become a promising solution to simultaneously mitigate the global energy crisis and
145 climatic change. Due to the thermodynamic stability, fully oxidized nature, and
146 inertness of CO₂, various nanoscale catalysts have been developed to activate CO₂
147 molecules into low (C₁) and high hydrocarbon (C₁-C₉) molecules. Figure 1 depicts
148 possible catalytic pathways for CO₂ transformation to fuels and chemical products.
149 They include thermocatalytic reduction of CO₂/H₂ to produce CH₄/CO, electrocatalytic
150 transformation of CO₂/H₂/electron to C₁-C₉ hydrocarbons, cycloaddition of CO₂ with
151 epoxide to form cyclic and polycarbonates, and the emerging photocatalytic reduction
152 of CO₂/H₂O to CH₄, CHOOH, CH₃OH, etc. The nature and kinds of nanomaterials for
153 conversion of CO₂ also play a vital role in product selectivity to get carbon-containing
154 fuels, in addition to process parameters such as solvent effects, reaction temperature,
155 H₂/CO₂ ratios, and partial pressure condition of CO₂. The nanomaterials for catalytic
156 conversion of CO₂ are range from plasmonic metal nanoparticles and metal oxides-
157 based composites to metal-free nanoporous materials including carbon nanostructures

158 such as grapheme oxide (GO) reduced grapheme oxide (rGO) and carbon nanotubes
 159 (CNT), silica, alumina, covalent organic polymers, etc.



160

161 Figure 1: Pathways for catalytic conversions of CO_2 to various feedstocks

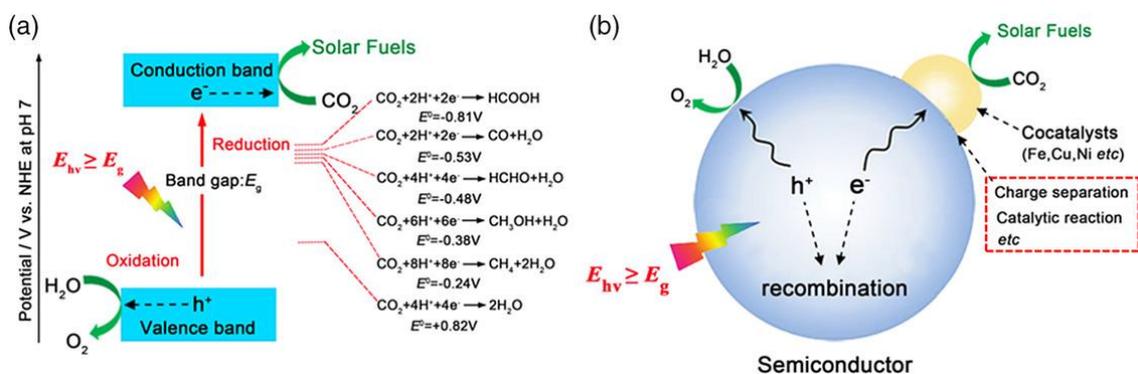
162 **3. Routes of CO_2 conversion**

163 **3.1 Photocatalytic transformation of CO_2**

164 The natural process of photosynthesis, in which plants change CO_2 and H_2O into
 165 oxygen and carbohydrates when exposed to sunlight, served as the inspiration for
 166 photocatalytic CO_2 reduction. This process transforms solar energy into chemical
 167 bonds, which are then stored (carbohydrates). It combines light and dark reactions with
 168 water oxidation and carbon dioxide reduction (or CO_2 fixation) reactions. The process
 169 of photocatalytic transformation of CO_2 into value added particularly using
 170 semiconductor or metal complex as catalyst can be divided into four steps: (i)
 171 absorption of light greater or equal to the band gap (ii) Separation of valence band (VB)
 172 and conduction band (CB) (iii) migration of electrons from the VB to CB and migration

173 of electrons to the surface of cocatalyst (iv) adsorption and activation of CO₂ by the
 174 photogenerated electrons (Kovačič et al., 2020)(Figure 2).

175 To understand the kinetic and thermodynamic point of view, the formal reduction
 176 potentials for the reactions connected to the photoreduction of CO₂ (at pH 7) is
 177 presented in Figure 12a. Due to their extremely high negative reduction potentials
 178 [E(CO₂/CO₂^{•-}) = -1.85 V vs NHE] in relation to the CB edges of many semiconductors,
 179 one-electron reduction processes of CO₂, such as the generation of CO₂^{•-}, are not
 180 practical (Lingampalli et al., 2017). A highly negative reduction potential results from
 181 the conversion of C's sp² to sp³ hybridization. Reduction potentials for HCOOH,
 182 HCHO, CH₃OH, and CH₄ production are minimal (-0.81, -0.48, -0.38, and -0.246 V)
 183 (Figure 12b) and positive relative to CB edges of various semiconductors. Proton
 184 coupled electron transfer (PCET), in which electron transfer to CO₂ is accompanied
 185 with proton transfer, is thus preferable (Kovačič et al., 2020; Lingampalli et al., 2017).
 186 A good number of works has been done recently to functionalize semiconductors and
 187 it's like as novel and effective photocatalysts. Various single and composites
 188 nanomaterial have been reported for photocatalytic transformation of CO₂. This section
 189 critically survey the scattered literatures



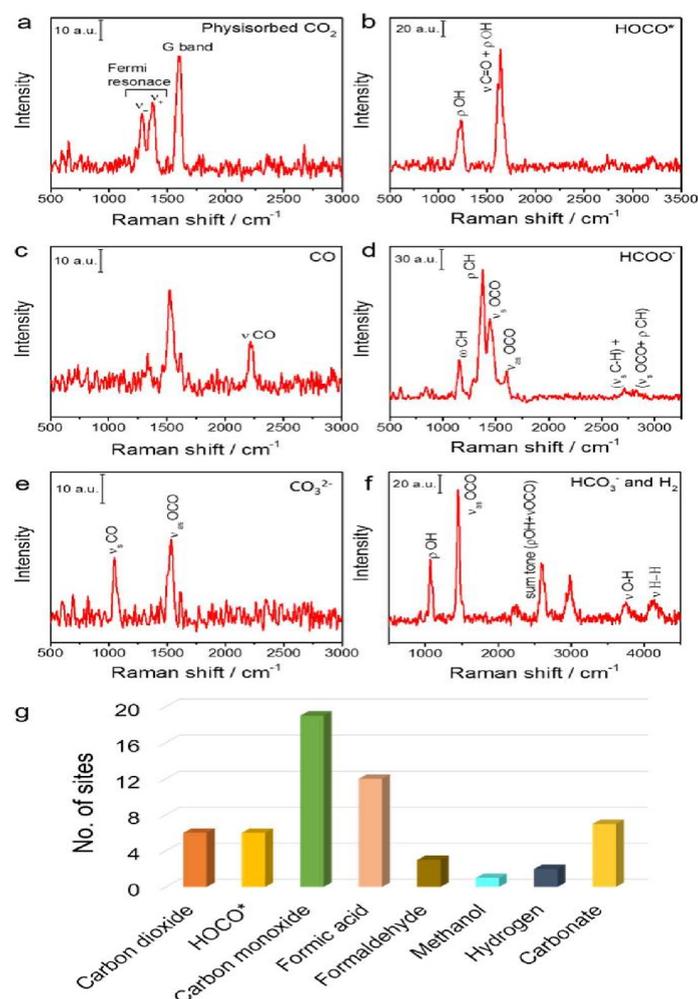
190
 191 Figure 2: (a) Energy diagram for CO₂ reduction and water oxidation on a
 192 semiconductor. b) A schematic representation of the overall photocatalytic reaction

193 process, demonstrating elements that may influence photocatalytic performance.
194 Reproduced with the permission from (Shen et al., 2020). Copy right 2020 Willey
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196 **3.1.1 Single metal nanoparticles**

197 Plasmonic metal nanoparticles (NPs) such as Au, Ag, and Cu have a large optical
198 extinction cross section and the ability to absorb significant visible light which accounts
199 for up to 40% of solar irradiation to catalyze a wide range of photochemical reactions.
200 As a result, , they offer several advantages over other conventional catalysts like Pt, Pd,
201 Ru, and Rh, whose localized surface plasmon resonances (LSPRs) fall in the UV region
202 of the solar spectrum. A single silver nanoparticles (AgNPs) photocatalyst was excited
203 in a microfluidic reaction cell filled with CO₂ led to CO₂ reduction reaction CO₂RR, to
204 CO and HCOOH. The synergy between photoexcited CO₂ and catalytic active sites,
205 which is not clearly understood at the molecular level, was evidenced by *in-situ*
206 surface-enhanced Raman spectroscopy (SERS) (Kumari et al., 2018). The SERS was
207 used to physi-sorb CO₂ on nanoparticles, LSPR-triggered CO₂ activation to HOCO*
208 (intermediate), followed by transformation of HOCO* to multiple products (H₂, CO,
209 HCOOH, HCHO and CH₃OH), (see Figure 3). The real-time monitoring of CO₂RR
210 activity by SERS shows that plasmonic AgNPs are selective for CO and HCOOH, with
211 CO being the predominant product. On polyvinylpyrrolidone (PVP)-capped plasmonic
212 AuNP-photocatalyst, photoexcited LSPR induced a multi-electron and multi-proton
213 reduction of CO₂ to C₁ (methane) and C₂ (ethane) hydrocarbons, without formation of
214 CO (Yu et al., 2018). The CO₂RR was conducted in isopropyl alcohol (IPA) saturated
215 CO₂-aqueous solution to prevent h⁺/e⁻ recombination during photoredox reaction, and
216 the CO₂RR selectively produced CH₄ (6.8 NP⁻¹) and C₂H₆ (5.6 NP⁻¹) after 10 h of light
217 irradiation. The results show that catalytic and selectivity of plasmonic gold

218 nanoparticles (AuNPs) for CO₂ transformation to C₁ and C₂ is modulated by laser
219 excitation wavelength (photon energy), and photon flux (light intensity). Thus, the CH₄
220 production rate increased with decreasing excitation wavelength and with overall 8e⁻
221 process ($8\text{H}^+ + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$), while C₂H₆ production was only observed at
222 lower excitation wavelength with 14e⁻ process ($14\text{H}^+ + 2\text{CO}_2 \rightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$). Zeng
223 *et al.* (Zeng et al., 2021) embedded uniformly distributed plasmonic CuNPs into a
224 triphenothiazine benzene ring (TPB) for photocatalytic CO₂ reduction to CO, H₂ and
225 CH₄. CO evolution rates over TPB-Cu increased as the wt% of Cu bonded to TBP units
226 increased, and CuNPs with 1wt% content yielded a CO evolution rate 3.2 times higher
227 than bare CuNPs. Interestingly, the evolution rates of H₂ and CH₄ on TPB-Cu remained
228 relatively constant, implying that incorporating plasmonic CuNPs into TPB increased
229 the directional selectivity for CO formation over H₂ and CH₄. Plasmonic copper NPs
230 conjugated with TBP could provide a large contact area for hot electron migration,
231 opening new doors for energy and carbon cycle processes.



232

233 Figure 3: Representative SERS spectra that capture specific adsorbates or products
 234 observed in photocatalytic CO₂ reduction on Ag NPs. Specific species captured include
 235 (a) physisorbed CO₂, (b) HOCO* reaction intermediate, (c) carbon monoxide or CO, (d)
 236 formate ion or HCOO⁻, (e) carbonate or CO₃²⁻, (f) bicarbonate or HCO₃⁻, adsorbed
 237 hydroxide or OH*, and H₂, and (g) Histogram of prevalence by the number of catalytic
 238 NPs on which each type of species was observed. Reproduced with permission from the
 239 American Chemical Society from ref. (Kumari et al., 2018).

240 3.1.2 Metal/metal oxide-based composites

241 In order to overcome the limitations of single-component plasmonic metal
 242 photocatalysts and to expand their light harvesting to UV region, researchers have

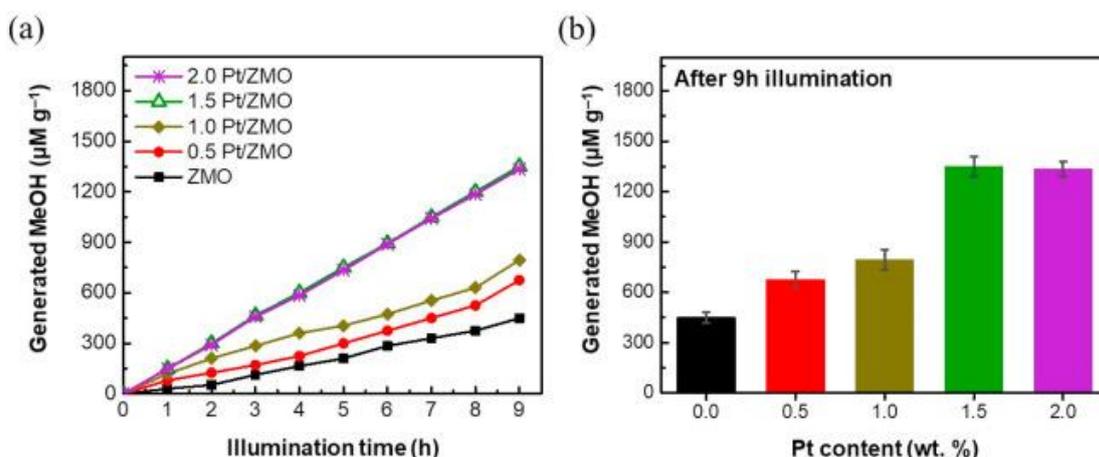
243 turned to multi-component semiconductors for a variety of applications. Decoration of
244 metal oxide semiconductors with transition or plasmonic metals has been a huge
245 success. Both plasmonic and transition metals on semiconductors can help harness UV
246 and visible light by reducing energy band gaps, which play key roles in CO₂ activation
247 and intermediates stabilization for CO₂RR.

248 For many years, the selective absolute conversion of CO₂ to CO has been a source of
249 contention. In 2020, Nguyen *et al.* (Nguyen et al., 2020) constructed air-stable Z-
250 scheme photocatalysts composed of Ag-decorated reduced titanium oxide/tungsten
251 hybrid nanoparticles (TiO₂/WO₃-AgHNPs) for CO₂ reduction to CO (100%, without
252 byproducts) and with an evolution rate of 1166.72 μmol g⁻¹ h⁻¹ after 7 h of light
253 illumination. On one hand, the plasmonic Ag (1wt% Ag) increased the photocatalytic
254 electron reaction rate up to 2333.44 μmol g⁻¹ h⁻¹, and facilitated intense absorption light
255 in the visible region of the catalysts due to its strong LSPR effect. The presence of Ti³⁺
256 states in the catalysts, on the other hand, facilitated the physisorption, stabilization, and
257 reorientation of the intermediates formed during CO₂ reduction. Other gas products
258 such as CH₄ and H₂ were produced in the absence of Ag deposition, suggesting the
259 importance of using plasmonic Ag to achieve the formation of only CO.

260 Zhang *et al.* (Zhang et al., 2021) reported p-type Cu₂O photocatalysts with phase
261 structures of 100 (100Cu₂O) and 111 (100Cu₂O) modified with Pd nanoparticles for
262 CO₂RR activities. The well-matched band alignments between Pd and 100Cu₂O
263 increased the work functions (Ws) of the 100Cu₂O-Pd composite, resulting in an
264 enhanced photocatalytic CO generation at a production rate of 0.13 μmol/g.h, which is
265 3.0 times higher than bare 100Cu₂O nanoparticles. Pd nanoparticles (in 100Cu₂O-Pd)
266 promoted efficient photoexcited electrons by acting as a photoinduced hole scavenger,
267 and also improved photostability of 100Cu₂O-Pd by reducing photocorrosion.

268 However, 111Cu₂O-Pd composites lacked electron-hole mobility due to mismatched
269 band structures between 111Cu₂O and Pd species, resulting in lower work function and
270 poor photocatalytic CO₂RR compared to 100Cu₂O-Pd composites, emphasizing the
271 importance of crystal surface structure and matched band structure construction for
272 selective CO₂RR to CO.

273 Wang and co-workers demonstrated LSPR photo-assisted electron migration from
274 plasmonic CuNPs to ZnO via metal-support interfaces in Cu/ZnO catalysts for CO₂
275 reduction to MeOH (Wang et al., 2019). In the photothermal process, the rate of MeOH
276 formation was 2.13 μmol/g. min, compared to 1.38 μmol/g. min recorded in pure
277 thermal process, and the apparent activation energy decreased from 82.4 to 49.4 kJ mol⁻¹.
278 The rate-determining step in the thermal process was the formation of reaction
279 intermediates (*HCOO, *HCOOH, and *H₂COOH species), followed by the
280 hydrogenation of *HCOOH to MeOH. Formation of MeOH in photothermal process
281 followed the same reaction pathway as thermal process, with the exception that induced
282 hot electrons on CuNPs accelerated the conversion of intermediates to product
283 (MeOH). Under visible light irradiation, the product selectivity over Cu/ZnO remained
284 relatively constant and the decreased activation energy had no effect. Small amounts of
285 Pt nanoparticles have also been used as co-catalyst on ZnMn₂O₄ nanorods as visible-
286 light-driven catalysts for promoting CO₂ reduction to produce methane, as was the case
287 in other studies (Alhaddad and Shawky, 2021) (see Figure 4a). The wt% of Pt species
288 on ZMO nanorods influenced the catalytic activity and selectivity of Pt/ZMO catalysts,
289 with 1.5% Pt/ZMO exhibiting the best photocatalytic performance for CO₂RR activity
290 (Figure 4b). Band connection and surficial interactions between Pt species and ZMO
291 nanorods with optimal Pt/ZMO at 1.5% Pt enhanced selective reduction of CO₂ to
292 MeOH with an evolution rate of 1,906 μmol/g within 9 h.



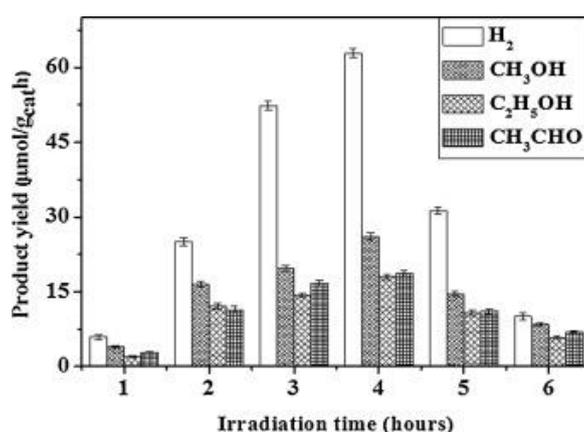
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294 Figure 4: (a) Photocatalytic generation of methanol over Pt/ZMO nanocomposites at
 295 different illumination time, and (b) impact of Pt content in Pt/ZMO composite for a
 296 dose of 1.0 g/L for each within 9 h of light illumination. Reproduced from (Alhaddad
 297 and Shawky, 2021) with permission.

298

299 V, Cr, and Co loaded on TiO_2 were studied for CO_2RR to produce H_2 , C_1 and C_{2+} .
 300 Higher photoconversion rates were observed compared to pristine TiO_2 , which were
 301 found to be sensitive to the metal concentrations and TiO_2 crystallite size modification
 302 (Ola and Maroto-Valer, 2015). After 4 h of illumination, 1wt% Co- TiO_2 demonstrated
 303 the highest photoconversion rates of $62.91 \mu\text{mol/g}_{\text{cath}}$ for H_2 and $26.12 \mu\text{mol/g}_{\text{cath}}$ for
 304 MeOH (Figure 5). Ni-modified CeO_2 , MgO , $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 NPs were studied for
 305 CO_2 methanation, and the effects of the solid supports were elucidated (Tada et al.,
 306 2012). CO_2 methanation pathways followed two steps: (i) reaction of CO_2 and H_2 at the
 307 meta/metal oxide interfaces to afford CO through reverse water gas shift reaction (CO_2
 308 + $\text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$), and (ii) prompt methanation of CO with H_2 ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 +$
 309 H_2O) at low temperature via the Fisher–Tropsch synthesis (FTs). CeO_2 has the highest
 310 number of CO_2 adsorption sites and exhibits the highest CO_2 methanation with near-
 311 unity CH_4 selectivity. Li and co-workers showed that partially oxidized metallic Fe NPs

312 (Fe and FeO_x) deposited on MgO-Al₂O₃ and then reduced under H₂ at different
 313 temperatures photothermally hydrogenated CO₂ into C₁ and C₂₊ hydrocarbons (Li et al.,
 314 2021). The Fe-500 sample (reduction performed at 500°C) showed the highest CO₂
 315 conversion and excellent selectivity for C₂₊ hydrocarbons with 0% CO. The FeO_x phase
 316 promotes CO₂ reduction to CO via RGSW reaction and modulates the electronic
 317 properties of Fe phase to suppress CH₂ and CH₃ hydrogenation, thus enhancing C₂₊
 318 hydrocarbon formation.



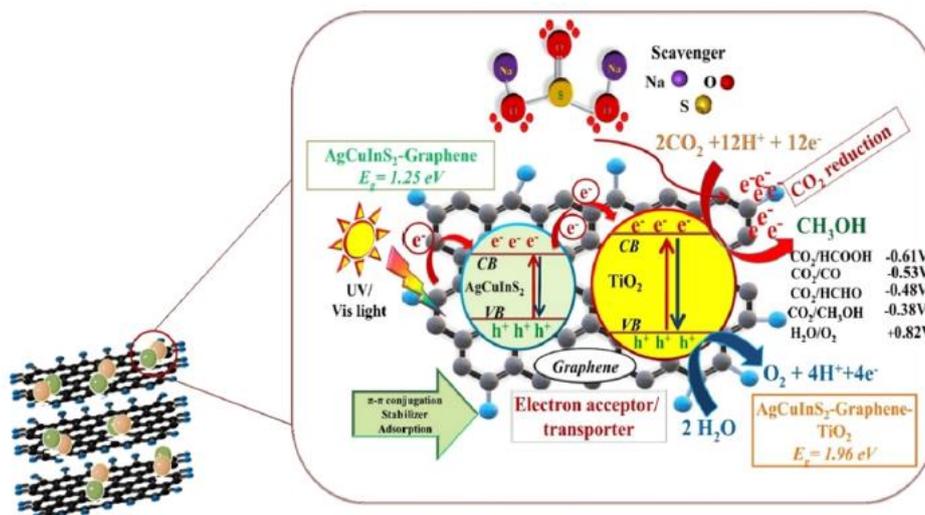
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320 Figure 5: Irradiation time profile of 1 wt%Co–TiO₂ for CO₂ reduction to fuels.
 321 Reproduced from (Ola and Maroto-Valer, 2015) with permission.

322

323 The conjoining of metal, e.g. Ag and narrow band semiconductor e.g. InS₂ has been
 324 reported to improve photocatalytic reduction of CO₂ activity. Recently, a quaternary
 325 nanocomposite (AgCuInS₂) deposited on a graphene-TiO₂ based material presented
 326 excellent photoreduction activity of carbon dioxide in H₂O with the formation of
 327 mostly methanol, formaldehyde and formic acid. AgCuInS₂ combined with TiO₂
 328 semiconductors (AgCuInS₂–TiO₂) absorb photon energy, which led to the excitation of
 329 electrons from valence band (VB) to conduction band (CB), creating electron–hole
 330 pair, and the graphene act as electron assimilates (Figure 6).

331



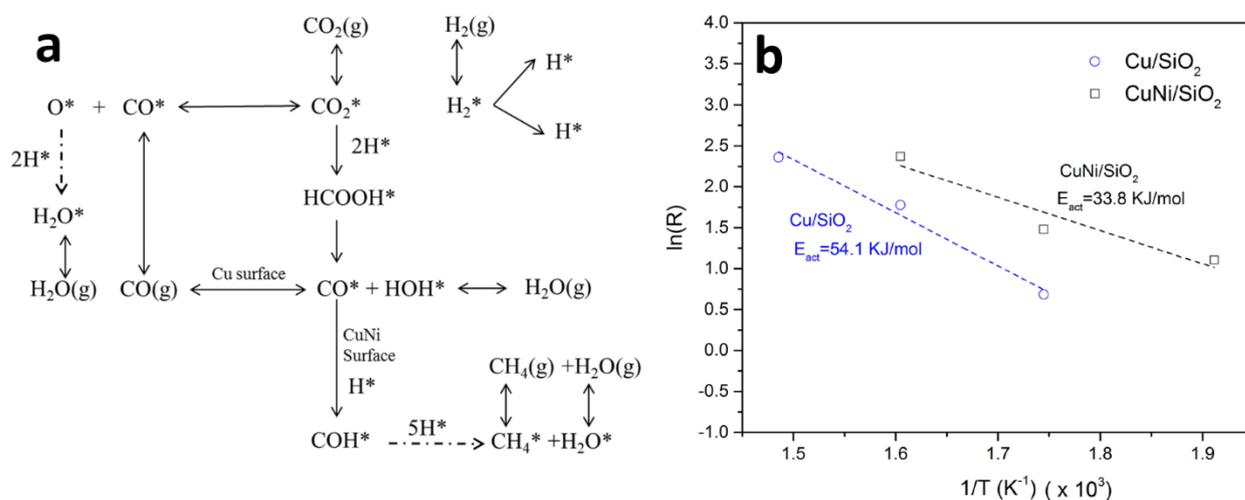
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333 Figure 6: Mechanism of photocatalytic CO₂ reduction. Re-used with permission from
334 (Otgonbayar et al., 2020). Copyright (2021) American Chemical Society.

335 3.1.3 Metal oxide/mesoporous oxides

336 Many metal-functionalized mesoporous aluminas and silicas have been studied as
337 catalysts for CO₂ hydrogenation to CO via RWGS or CO methanation by Fischer
338 Tropsch (FT) reactions. In terms of activity and selectivity, mesoporous materials with
339 high Brunauer-Emett-Teller (BET) surface areas are important features for CO₂
340 adsorption and conversion (Petrovic et al., 2021). The nature of metal species
341 immobilized on porous oxides also influences the CO₂RR selectivity for either CO or
342 CH₄. Deposition of Ni on CaO-Al₂O₃ showed CO₂ conversion with 81% selectivity to
343 CH₄; however, lower performance of the Ni-based catalyst in the subsequent
344 methanation reaction (due to partial oxidation of Ni fractions) suggests that a better
345 approach for CO₂RR on metal/mesoporous materials is required (Mutz et al., 2015).
346 Addition of La as a second metal to Ni/-Al₂O₃, enhanced direct CO₂ methanation (CO₂
347 + H₂ → CO + H₂O) via the Sabatier reaction, increasing the CO₂ conversion rate to
348 CH₄ from 42% to 80.3% (Rahmani et al., 2019). CO₂ methanation over mono and

349 bimetallic catalysts was temperature, feedstock (H_2/CO_2 ratio), and gas hourly space
 350 velocity (GHSV) sensitive. CO_2 was transformed into CO as a result of the RWGS
 351 reaction which occurred at higher GHSV values (between 6000-18,000 mL/(g_{cat}h)),
 352 350°C, and 3.5 H_2/CO_2 ratio, resulting in decreased CH_4 selectivity. In contrast, Bashiri
 353 and coworkers demonstrated that lowering the GHSV from 2000 to 1250 nml/min over
 354 a Ni-promoted iron catalyst on HZSM5- Al_2O_3 (Fe-Ni/HZSM5- Al_2O_3) increased CO_2
 355 methanation significantly (Bashiri et al., 2018). The results also show that adding
 356 HZSM5 to Al_2O_3 increases the rate of CO_2 conversion to light hydrocarbons, CO, and
 357 CH_4 by 15.53%, indicating that combined supports have the potential to improve CO_2
 358 conversion activity and selectivity.



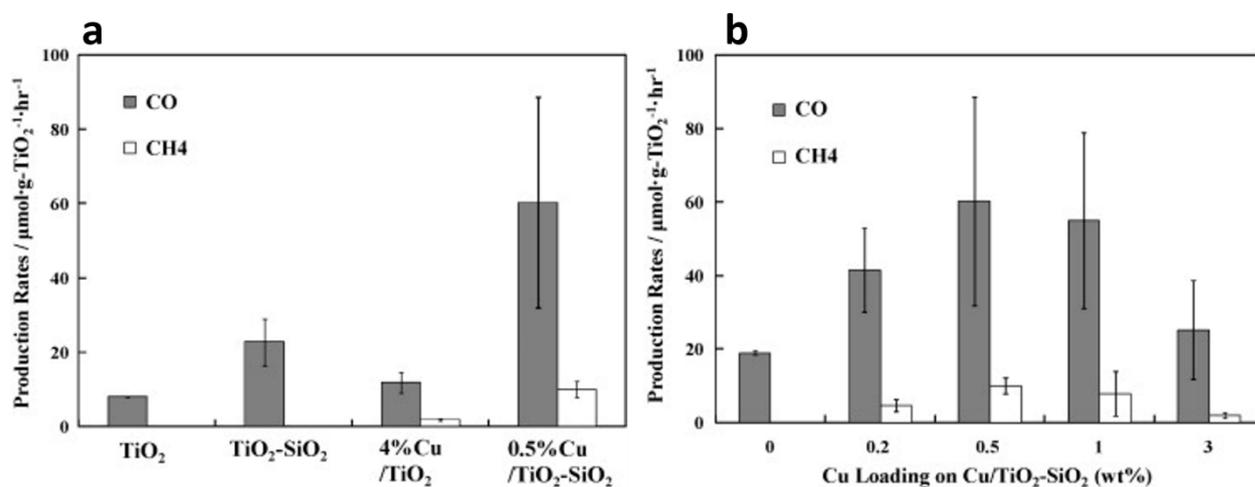
359
 360 Figure 7: (a) Proposed reaction pathways on Cu/fumed-SiO₂ and CuNi/fumed-SiO₂
 361 surface (b) Activation energy calculation for CO_2 conversion reaction over Cu/fumed-
 362 SiO₂ and CuNi/fumed-SiO₂. Reproduced from (Kumar et al., 2022) with permission.

363
 364 Mesoporous siliceous materials are valuable supports because of their large number of
 365 active sites for supporting various metal ions to catalyze CO_2RR to renewable
 366 feedstocks. Single Cu-based catalytic systems are not suitable for direct CO_2

367 hydrogenation to either CH₄ or CH₃OH because they lead preferentially to the
368 formation of CO via RWGS reaction. For example, CuNi/fumed-SiO₂ showed
369 enhanced activity and selectivity for CO, as well as a tendency for methanation to CH₄
370 via interaction of CO and neighboring H, whereas Cu/fumed-SiO₂ showed only
371 selectivity to CO due to decomposition of adsorbed formate intermediates to CO,
372 Figure 7a (Kumar et al., 2022). The incorporation of Ni increases the system's catalytic
373 active sites and lowers the activation barriers for CO₂RR to CO and CH₄, Figure 7b.
374 Mesoporous Cu/SiO₂ doped with Ga and/or Zn had greater catalytic activity for direct
375 CO₂ reduction to MeOH than undoped Cu/SiO₂ (Paris et al., 2020).

376 The strong promoting effects of dopants restricted the occurrence of RWGS reaction
377 for CO formation while increasing selectivity for MeOH one. Both dopants provide
378 more active sites on the catalysts, lowering the activation barrier of MeOH synthesis
379 compared to CO formation, so methanol formation was preferred over CO formation.
380 When mesoporous TiO₂/SiO₂ was irradiated with visible light without Cu species, CO
381 was the main product of photo-transformation of CO₂/H₂O (Li et al., 2010). Cu
382 deposition on TiO₂/SiO₂ improved photoreduction of CO₂ to CO, and CH₄ selectivity
383 increased as well, peaking at 0.5wt% optimum Cu specie on TiO₂/SiO₂ (Figure 8). XPS
384 allowed to identify the deposited Cu species as Cu₂O, which acts as a photoexcited
385 electron sink, limiting the recombination of photoinduced holes and excited electrons
386 and thus enhancing multi-electron photoredox reactions for CO₂ to CO and CH₄. Fu *et*
387 *al.* designed photocatalytic systems based on CoO and Co₃O₄ nanoparticles to convert
388 CO₂ to CO using bare CoONPs, CoO/s-SiO₂, CoO/s-SBA-15, and Co₃O₄/s-SBA-15 (Fu
389 et al., 2019). Under similar photoredox conditions, CoO/s-SBA-15 exhibited the best
390 activity for CO₂RR to CO with 85% selectivity at 14,147 μmol/hg after 2.5 h.
391 Interfacial interactions between porous silica -OH groups and reaction substrates

392 enhance sorption and photocatalytic CO₂ reduction to CO over CoO/s-SBA-15 catalyst
393 system.



394

395 Figure 8: (a) Peak production rates of CO and CH₄ on various TiO₂-containing
396 catalysts, and (b) Peak production rates of CO and CH₄ as a function of Cu loading in
397 Cu/TiO₂-SiO₂ catalysts. Reproduced from (Li et al., 2010) with permission.

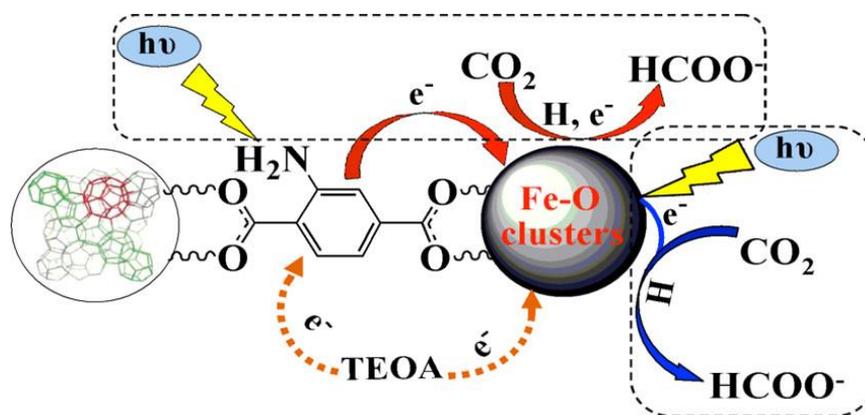
398 3.1.4 Inorganic/organic nanocomposites

399 3.1.4.1 Metal-organic frameworks (MOF) nanomaterials

400 MOFs are recognized as catalytic systems of choice for CO₂RR conversion to
401 renewable energy feedstocks due to the large panel of surface functionalities and
402 geometries, porosity as well as the possible customization these materials offer
403 specifically for CO₂ capture and utilizations (CCUs). Architectural flexibility and ease
404 of structural modification of MOFs through insertion of different metal ions (or metal
405 clusters) together with interconnection of multidentate organic linkers with different
406 functionalities are notable strategies to improve performance of MOF-based
407 photocatalysts for CO₂ reduction (Ejeromedoghene et al., 2022). Wang and coworkers
408 investigated the photocatalytic conversion of CO₂ to formate over a variety of amino-
409 functionalized and unfunctionalized Fe-based MOFs. They found that amine-

410 functionalized Fe-based MOFs outperformed their respective parent MOFs in this
411 transformation. NH₂-MIL-101(Fe), a framework composed of FeO clusters and 2-
412 aminoterephthalic acid (H₂ATA) ligands prepared in dimethylformamide (DMF),
413 exhibits the best catalytic activity, to generate HCOO⁻ at the evolution rate of 178
414 μmol/g (Wang et al., 2014). Mechanistic pathways for enhanced activities include
415 excitation of NH₂ functionality, electron transfer to the Fe center and direct excitation
416 of Fe-O cluster (Scheme 2). Wei *et al.* reported visible-light induced CO evolution
417 from CO₂RR over a series of UiO-based MOFs photocatalysts modified with different
418 functional groups (F, NH₂, OCH₃, CH₃) (Wei et al., 2019). They observed an influence
419 of the electron-withdrawing and electron-donating character of the introduced
420 functional groups, CO evolution following the order UiO-68-F < UiO-68-NH₂ < UiO-
421 68-CH₃ < UiO-68-OCH₃. The superior performance of UiO-68-OCH₃ was attributed to
422 the pronounced charge separation efficiency of OCH₃. Crake et al. investigated
423 applicability of titanium dioxide/carbon nitride (TiO₂/CNNS) nanosheet
424 nanocomposites in photoreduction of CO₂ (Crake et al., 2019). They found that
425 TiO₂/CNNS possessed improved CO₂ conversion and adsorption when compared to the
426 individual materials used to make the composites (> 10 times). In addition, it was
427 reported that the composite material with more {001} TiO₂ facets was the most
428 catalytically active and this is attributed to enhanced charge transfer at the TiO₂/CNNS
429 heterojunction interface. Previously, Crake et al (Crake et al. 2017) coupled NH₂-UiO-
430 66 onto pre-formed TiO₂ nanosheets via *in situ* process to develop TiO₂/NH₂-UiO-66
431 heterojunction with permanent pore sizes and exposed catalytic active sites for
432 enhance CO₂ uptake and photoreduction of adsorbed CO₂ to CO under UV-visible
433 light. The evolution rate of CO₂-to-CO conversion over the bound nanocomposite was
434 1.9 times more than that of pure TiO₂. Interestingly, the photoreduction efficiency of

435 mechanically blended TiO₂ and NH₂-UiO-66 is comparable to pure TiO₂, proving that
 436 *in situ* growth method was necessary for the enhanced catalytic activity. Transient
 437 absorption spectroscopy confirmed that the increased photoactivity of TiO₂/NH₂-UiO-
 438 66 was due to the efficient charge transfer at the interface of heterojunction.



439

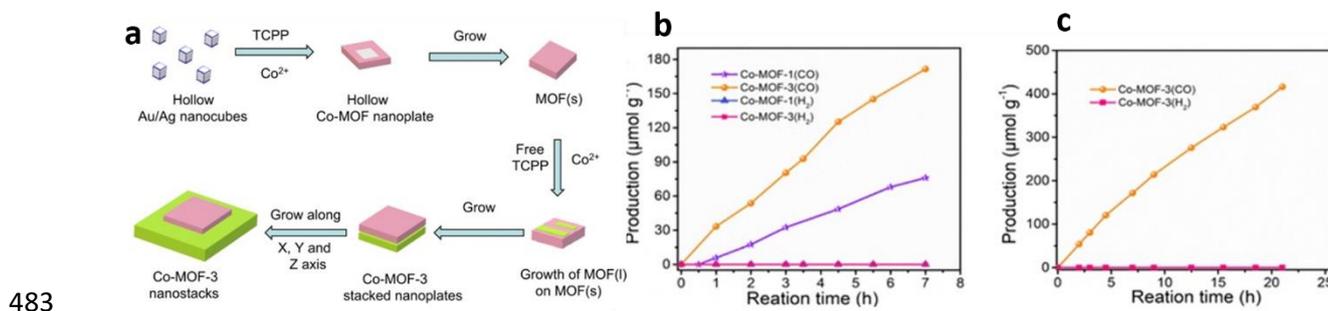
440 Scheme 2: Dual excitation pathways over amino-functionalized Fe-MOFs for
 441 photocatalytic reduction of CO₂ to formate. Reproduced from (Wang et al., 2014) with
 442 permission.

443 Besides the use of MOFs with multidentate linkers and different functional groups,
 444 multi-metallic MOFs can also offer improved stability and overall catalytic efficiency
 445 for CO₂ reduction in comparison to monometallic counterparts. Different MOFs with
 446 multi-metallic nodes have been explored for CO₂RR. For instance, bimetallic ZnCu
 447 MOF-74 outperformed monometallic Cu-MOF-74 when used as catalysts in methanol
 448 synthesis (Stolar et al., 2021). Selectivity for MeOH formation increased by 4.7 times
 449 upon incorporation of Zn into Cu-MOF-74 (c-ZnCu-MOF-74), and this value
 450 increased further to a factor of 8.3 upon amorphization of c-ZnCu-MOF-74. The
 451 findings highlight the significance of using heterometal nodes and amorphous MOF to
 452 get improved activity and selectivity. Fe-N-TiO₂/CPO-Cu MOF nanocomposites were
 453 fabricated where CPO-Cu-27MOF is supported on 0.12%Fe-0.5%N-codoped TiO₂

454 leading to effective photocatalytic reduction of CO₂ (khalilzadeh and Shariati, 2019).
455 Reduction efficiency of Fe-N-TiO₂/CPO-Cu can be tuned by varying the amount of
456 CPO-Cu-27 (CPO) in composites from 8 to 65wt.%, and the Fe-N-Ti@50CPO sample
457 with 50wt% CPO yields the highest conversion of CO₂ to methane. The performance
458 achieved is ca. 1.7 times higher than in the case of CO₂ methanation over Fe-NTiO₂.
459 Liu *et al.* reported visible-light-driven CO₂ to CO conversion on hollow transition
460 metal NPs-based MOFs (Liu et al., 2021). Their results show that Co-MOF-3 with two
461 stacked piezoelectric phononic crystal nanoplates had a 2.5-fold higher CO₂
462 photoreduction efficiency than Co-MOF-1 with single nanoplate (Figure 9). The Co-
463 MOF-3 homojunction system demonstrated a high CO₂ to CO conversion rate with
464 100% selectivity, outperforming most of the previously reported semiconductors for
465 this reaction.

466 Polyoxometalates-based MOFs (POMOF) composites have also been studied for
467 CO₂RR due to POM's unique ability to act as nodes or pillars, and more importantly, as
468 high-efficiency catalytic sites in the MOF cages to adsorb reactants and improve MOF
469 acidity, stability, and redox activity. Li et al. (Li et al., 2019) reported the use of a
470 reductive POM and a hydrophobic fluorine-containing ligand to fabricate a stable
471 POM-based MOF (NNU-29) composite as an effective CO₂ photoconversion catalytic
472 system. The presence of a hydrophobic ligand improves the chemical stability of NNU-
473 29 and reduces H₂ generation due to water attack to some extent, resulting in 98%
474 selectivity for CO₂ reduction to HCOOH in aqueous solution after 16h of light
475 irradiation. Wang *et al.* (Wang et al., 2021) recently proposed SO₃H-MIL-101-Cr
476 (SO₃H-MOF) supported silicomolybdic acid (SMA) as a host-guest composite for CO₂
477 photoreduction. Pristine POM and MOF have negligible CO₂-to-CO activity compared
478 to SO₃H-MOF. CO formation over POMOF composite, on other hand, achieved a

479 remarkable yield of 829.46 mol/g and selectivity of 93.2%. The superior reductive
 480 activity of POMOF was attributed to increased CO₂ affinity for silicomolybdic acid
 481 (SMA) and synergy between POF and MOF, resulting in enhanced charge carrier
 482 separation.



484 Figure 9: (a) Schematic view for the hollow Au/Ag directed formation of Co-MOF-3
 485 nanocomposites. (b) Evolution of CO and H₂ as a function of reaction time during the
 486 CO₂ reduction under visible-light irradiation for Co-MOF-1 and Co-MOF-3
 487 photocatalysts. (c) Stability of Co-MOF-3 during the continuous CO₂ reduction
 488 process. Reproduced with permission from ref. (Liu et al., 2021). Copyright 2021
 489 Nature.

490 3.1.4.2 Metal-free nanomaterials

491 The high cost of production of metal-based nanomaterials, their susceptibility to
 492 deactivation in catalytic systems, environmental concerns about toxicity (Fall et al.,
 493 2022; Keller et al., 2017), and more often than not, their moderate catalytic
 494 performance in terms of activity and selectivity, have limited their use in CCUs.
 495 Graphene oxides, fullerenes, and graphitic carbon nitrides have recently emerged as
 496 valuable metal-free platforms for CO₂RR preparation, chemical inertness, and natural
 497 abundance (Yang et al., 2022). These materials are frequently used as a standalone
 498 material or in combination with other non-metal semiconducting materials to improve
 499 their CO₂RR performance (Shen et al., 2020). Several reports have shown that GO can

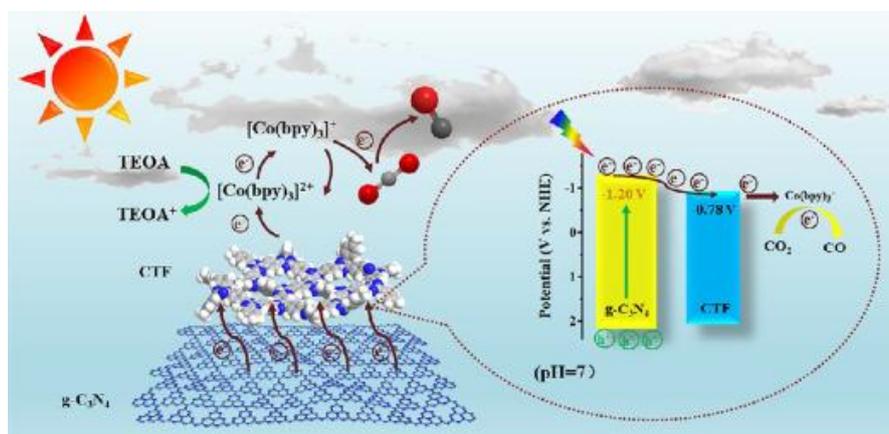
500 act by itself as a photocatalyst for CO₂ reduction either by adapting its method of
501 preparation or through UV-Vis light-induced activation of pristine GO (Kuang et al.,
502 2020). Hsu *et al.* (Hsu et al., 2013) studied the effect of volume of H₃PO₄ used as a
503 mild oxidizer to prevent overoxidation of pristine GO on the CO₂RR performance.
504 Their results show that modified GOs have increased visible light absorption and
505 improved CO₂ photoreduction to MeOH compared to pristine GO. The CO₂-to-MeOH
506 conversion rate of GO-3 with excess H₃PO₄ was found 6-fold higher than with pure
507 TiO₂. Kuang *et al.* (Kuang et al., 2020) reported on the photoreduction of CO₂ to CO
508 over GO activated either by UV or simulated sunlight. GO activated by simulated-
509 sunlight provided the highest CO₂ reduction efficiency, with a CO yield of 1.3-fold
510 higher than the UV-activated GO and nearly 3 times higher than with pristine GO. The
511 observed efficiency is due to light-induced increased defects and restoration of large π -
512 conjugative systems. Compared to GO, reduced-GO (rGO) are superior solid supports
513 for other semiconducting materials due to their high thermal and electrical conductivity.
514 Yang *et al.* supported quinacridone (QA) NPs on rGO nanosheets through H-bonding
515 and with different rGO contents and observed that this metal-free photocatalysts
516 allowed photoreduction of CO₂ to CO and CH₄ under UV light (Yang et al., 2019). The
517 sample containing 2% rGO had the highest CO₂ reduction efficiency and selectivity for
518 CO and CH₄ due to the synergistic effects of QA as a photosensitizer and rGO as an
519 electron acceptor to promote effective charge separation.

520 Based on the number of published articles on photocatalysis, graphitic carbon nitride
521 (gCN) materials is the highest promising among the reported carbon-based materials
522 for photoreduction of CO₂, due to its facile tunable synthetic routes, structural
523 maneuverability, and tailorable morphology. However, they are limited due to their
524 narrow visible light absorption window, low specific surface area, poor electrical

525 conductivity, and rapid recombination of photoexcited excitons (Shi et al., 2018). A
526 variety of strategies, including structural modification via elemental doping, the
527 attachment of a semiconducting motif, functional group modulation of gCN, and others,
528 can significantly improve the photocatalytic CO₂ reduction (Alaghmandfard and
529 Ghandi, 2022). Nonmetals like P, O, B, S, and N have become popular as interstitial or
530 substitutional dopants on gCN for CO₂ photoreduction and other photocatalytic
531 reactions.

532 Arumugam and coworkers synthesized a series of porous gCN doped with various
533 nonmetals (B, O, P, and S) for photoreduction of CO₂/H₂O to gaseous fuels
534 (Arumugam et al., 2022) among which S-doped gCN showed the highest CO₂-to-CH₄
535 conversion rate compared to others. Imaging studies showed that bare g-C₃N₄ has a
536 thin-layered structure with irregular porosity, whereas S-doped g-C₃N₄ has a denser
537 structure with a homogenous distribution of S atoms on the g-C₃N₄ matrix, suggesting
538 that S atom can act as an electron sink for improved activity. Doping of S atoms into g-
539 C₃N₄ did not enhance the surface area or modify the energy band gap of g-C₃N₄; rather,
540 the remarkable boost in photoreduction efficiency was due to charge separation and
541 migration processes. Mo et al. demonstrated that hydrothermal treatment of melamine
542 and hydroxylammonium chloride precursors structurally transformed bulk g-C₃N₄ from
543 an irregular morphology into a supramolecular hydrogen-bonded network intermediate;
544 and that subsequent heating of the intermediate under NH₃ atmosphere led to the
545 formation of porous TCN(NH₃) nanotubes with a 1D tubular structure. The structural
546 transition from bulk gCN to 1D tubular structure was confirmed using XRD, FTIR,
547 SEM, and TEM. The CO₂-to-CO conversion rate of porous TCN(NH₃) nanotubes was
548 17 and 15 times that of bulk g-C₃N₄ and TiO₂, respectively. Tubular structure of
549 TCN(NH₃) has permanent porosity and a large surface area, which enhances solar light

550 utilization and spatially resisted photoinduced charge recombination, resulting in a
 551 better photoreduction efficiency than bulk $g\text{-C}_3\text{N}_4$. Huang *et al.* (Huang et al., 2015)
 552 successfully photoreduced CO_2 to CH_4 and MeOH over bulk $g\text{-C}_3\text{N}_4$ and amine-
 553 functionalized $g\text{-C}_3\text{N}_4$, which was prepared by heating $g\text{-C}_3\text{N}_4$ in monoethanolamine
 554 (MEA) solution. Both pure and functionalized $g\text{-C}_3\text{N}_4$ have a 2D lamellar structure
 555 with equal porosity, indicating that the amine functionalization has no effect on $g\text{-C}_3\text{N}_4$
 556 morphology. The functionalized $g\text{-C}_3\text{N}_4$ heated in an oil bath for 5 hours had the
 557 highest CO_2 to fuel conversion rate. The CO_2 photoreduction efficiency over amine-
 558 functionalized $g\text{-C}_3\text{N}_4$ was significantly higher than pristine $g\text{-C}_3\text{N}_4$ due to the
 559 enhanced adsorption and destabilization of CO_2 by amine functional groups.



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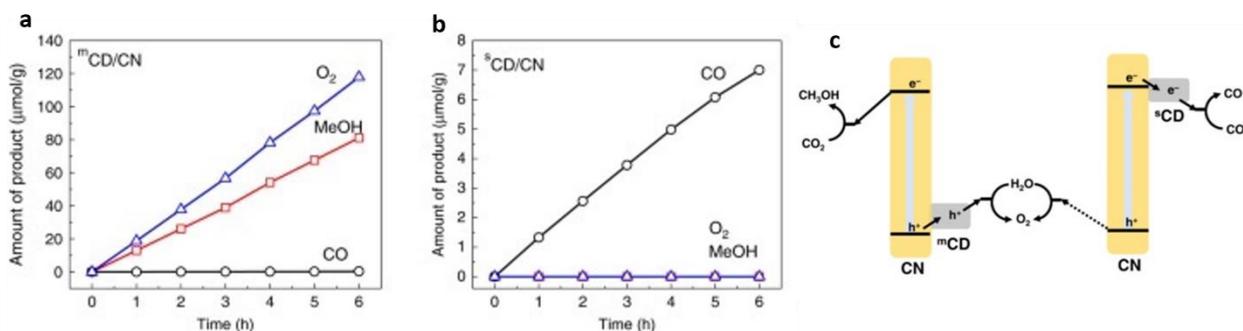
561 Figure 10: Schematic view and mechanism of CN/CTF heterostructure for
 562 photocatalytic CO_2 reduction. Reproduced with permission from ref. (He et al., 2022).

563

564 $g\text{CN}$ has also been decorated with COFs and carbon dots (CDs) to fabricate metal-free
 565 composites for improved visible-light-induced CO_2 reduction. He *et al.* (He et al.,
 566 2022) reported for the first-time $g\text{CN}/\text{covalent triazine framework}$ (2D/2D CN/CTF)
 567 heterostructures for CO_2 photoreduction. The TEM micrograph of CN/CTF reveals an
 568 overlaying lamellar structure of CN superimposed on an irregularly stratified

569 morphology of CTF, validating successful formulation of 2D/2D CN/CTF
570 heterostructure. The optimal CN/CTF heterostructure is up to 25.5 and 2.5-fold more
571 efficient in photoreduction of CO₂ to CO than CTF and CN, respectively. The enhanced
572 reduction efficiency of CN/CTF was attributed to a lower probability of hole-electron
573 recombination due to [Co(bpy)₃]²⁺, which acts as electron harvester to accelerate
574 charges separation, cleaving O=C=O to selectively produce CO (Figure 10). Wang *et*
575 *al.* (Wang et al., 2022) reported van der Waals interfacial bonding between N-deficient
576 gCN and Tp-Tta COF, demonstrating exceptional stability and selectivity for CO₂
577 photoreduction to CO. DFT calculations and EPR analysis confirmed the strong
578 electronic coupling between gCN and Tp-Tta COF, which was responsible for
579 improved photoreduction efficiency of the composite via large active sites for CO₂
580 capture and, an accelerated S-scheme charge separation system. Wang *et al.* (Wang et
581 al., 2020) described carbon nanodots (CDs) electrostatically bounded to the surface of
582 protonated gCN which demonstrated an excellent metal-free bifunctional photocatalysts
583 to promote selective reduction of CO₂ to nearly 100% methanol. Structural elucidation
584 reveals that the boundaries and edges of CN nanosheets, which possess a graphene-like
585 structure, were coherently decorated by graphitic structure of ^mCDs, indicating strong
586 electrostatic interactions between the two phases, which may have enhanced the
587 composite's charge transfer process. In contrast, the amorphous structure of ^sCD was
588 barely located in the phase structure of CN/^sCD composite following heterojunction
589 formation, indicating weak interaction between the two phases. ^mCD features near-
590 crystallized graphitic structures, whereas ^sCD is composed of amorphous carbons;
591 hence, the photocatalytic functions of ^mCD/CN and ^sCD/CN are notably distinct.
592 According to this study, ^mCD/CN photoreduces CO₂ to 6e⁻ product MeOH (Figure
593 11a), while ^sCD/CN favors formation of 2e⁻ product CO (Figure 11b). The authors

594 attributed the improved ^mCD/CN reduction efficiency to the hole-accepting role of
595 ^mCD, which led to electron accumulation on CN surface and facilitated a multi-electron
596 reduction process to produce MeOH with near-unity selectivity (Figure 11c).



597

598 Figure 11: Photocatalytic activity of (a) ^mCD/CN for methanol formation, and (b)
599 ^sCD/CN for CO formation measured under visible light ($\lambda > 420$ nm). (c) Schematic
600 diagram of photocatalytic CO₂ reduction by the ^mCD/CN and ^sCD/CN. Reproduced
601 with permission from ref (Wang et al., 2020). Copyright 2020 Nature.

602 Apart from all the aforementioned examples, this section also surveyed other
603 recent/relevant research works on photocatalytic transformation of CO₂ (see Table S1
604 in the supplementary information)

605

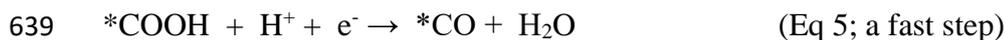
606 3.2. Electrochemical transformation of CO₂

607 The electrochemical transformation of CO₂ to value added fuels has received
608 considerable attention in recent years owing to its plethora benefits including energy
609 production, storage, and others. The conversion process is located at the interface
610 between the solid catalyst surface and the electrolyte, as is the case with all
611 electrochemical reactions. A compact layer of ions next to the electrode, followed by a
612 diffusion layer of solvated ions, can be used to describe the interface's structure (Rosen
613 and Hod, 2018). The more the potential an electroactive species has, the more the

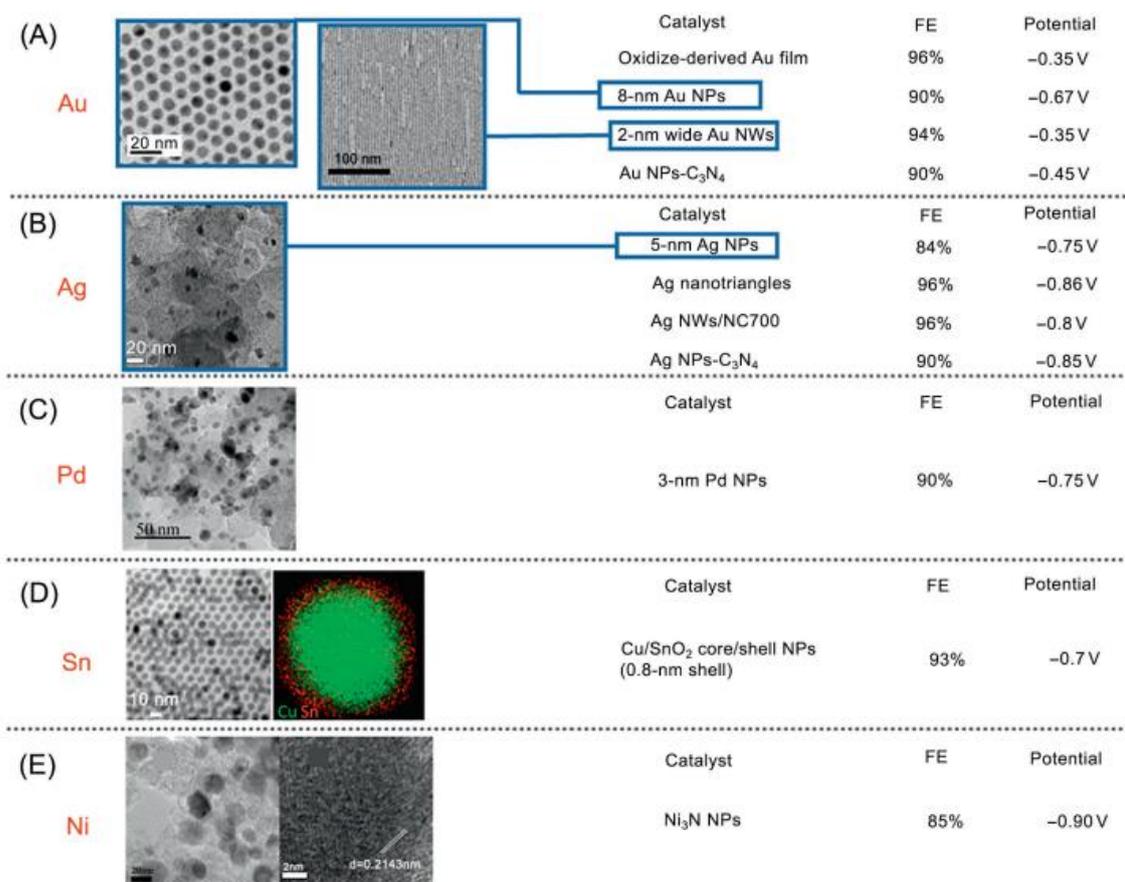
614 distance it can travel to the interface, and its relative orientation to the interface are all
615 influenced by the bilayer structure which is thus essential for the rate and efficiency of
616 the electrochemical CO₂RR. Electrochemical CO₂RR can produce useful chemicals and
617 fuels including formaldehyde, CO, formic acid, ethylene, ethanol, methane, and
618 methanol, depending on the electrical voltage supplied to the electrode (Chen et al.,
619 2020).

620 The methods most frequently used for electroreduction of CO₂ are cyclic voltammetry
621 (CV) and linear sweep voltammetry (LSV). The catalytic performance can also be
622 evaluated using chronoamperometry. These CO₂ conversion operations are typically
623 carried out at a specific reaction rate and ambient conditions of temperature and
624 pressure (Nielsen et al., 2018). A coupled proton electron transfer that results in the
625 protonation of the oxygen atom O (eq 1) or the carbon atom C (eq 2) triggers the
626 adsorption of CO₂ on the electrode surface (eq 4) (Nielsen et al., 2018; Zhu et al.,
627 2014). As such, this process requires the use of a large potential, which results in
628 competing reactions such as the hydrogen evolution reaction (HER). In lieu of the
629 above, integration of a catalyst in the system allows to reduce the overpotential and
630 activate CO₂ conversion. In general, a heterogeneous catalyst deposited on the
631 electrode surface or a homogeneous catalyst dissolved in solution are used in
632 electrocatalytic CO₂ transformation. These catalysts will allow for a faster electron
633 transfer coupled with protons, resulting in the observed products HCOOH (eq 2 and eq
634 3) or CO (eq 5 and eq 6) (Yin et al., 2019).





641 As shown in Figure 12, various studies using different metal electrodes modified with
 642 catalysts such as Sn, In, Au, Ag, Pd, Bi, Co, Mo, and others have been reported. As the
 643 other side reactions (i.e. HER) can be almost suppressed, these materials exhibit
 644 significant catalytic properties for the CO₂ transformation (Lu et al., 2019).
 645 Furthermore, they present an extremely low energy barrier for the formation of the
 646 intermediate, which must then be protonated at the carbon or oxygen atom before being
 647 converted to formate or carbon monoxide.



648

649 Figure 12: Overview of some typical Au, Ag, Pd, Sn, and Ni-based nanocatalysts for
650 electrochemical reduction of CO₂ to CO. All potentials are contrasted with an electrode
651 made of reversible hydrogen (RHE). NP stands for nanoparticle, whereas FE stands for
652 faradic efficiency. Reprinted with the permission from (Yin et al., 2019). Copyright
653 (2019) Elsevier.

654 Yang et al also investigated the CO₂RR on Ag, Pd, and Ag@Pd nanocubes. Pd
655 nanocubes led to CO with high selectivity as a result of Pd turning into Pd hydride
656 (PdH) during CO₂RR (Yang et al., 2022). In contrast, Ag@Pd makes the formation of
657 PdH more difficult due to inhibited production of CO from the intermediate *HOCO
658 which thus adjusts the reaction pathway towards HCOOH. The authors concluded that
659 Ag nanocubes have high selectivity for H₂ with no phase transition during CO₂RR.

660 Li et al. (Z. Li et al., 2022) studied electrochemical CO₂RR to formate, which not only
661 has the potential to reduce the issue of global warming brought on by CO₂, but also has
662 the potential to be exploited for energy storage as intermittent renewable energy. A
663 bimetallic BiSn nanomaterials were electrodeposited on copper mesh and tested as
664 electrocatalysts for the conversion of CO₂ to formate. The resulting electrodes
665 demonstrated excellent catalytic activity at 1.0 V vs. RHE, with a partial current density
666 of 34.0 mA/cm² and an astonishingly high faradaic efficiency of roughly 94.8%. The
667 production of formate at a remarkable rate of 634.3 mol/cm²h -significantly higher than
668 most rates previously reported- is noteworthy. The quick electron transfer of BiSn
669 nanomaterials also contributed in the creation of the CO₂⁻ intermediate. Additionally,
670 they produced a metastable metal oxide/metal interface that helped to stabilize the
671 CO₂⁻intermediate and suppress the HER side reaction. The pathway connected to the
672 OCHO• intermediate was improved because of the optimized electronic structure of

673 BiSn, promoting the conversion of CO₂ to formate. According to these results, Bi/Sn
674 bimetallic catalysts are a viable option for very effective CO₂ reduction.

675 In contrast, the conversion of CO₂ to CO and formate is less difficult than CO₂RR to C-
676 H hydrocarbons, which are more significant scientifically and technologically but are
677 more difficult to manage. Concerning the synthesis of ethylene, Cu and Cu₂O are
678 regarded as the most common and effective electrocatalysts for CO₂RR. Multi-carbon
679 oxygenates, such as ethanol (the primary product), acetate, and n-propanol, can also be
680 produced in an alkaline electrolyte at -0.25 to -0.5 V vs RHE with a total EF of 57 %
681 (Li et al., 2014).

682 In order to achieve a lofty ultra-high selectivity of 82.4% for ethylene in an H-cell
683 system with good catalytic stability and material durability of 100 h, Sultan et al.
684 (Sultan et al., 2022) presented a completely redesigned electrocatalyst consisting of
685 Al₂CuO₄ nanosheets uniformly coated with CuO nanoparticles (CuAl-1: CuO/Al₂ CuO
686 4 -23) by phase. They found that Cu (CuAl-1) permitted high surface CO intermediate
687 coverages and improved CO adsorption for C-C coupling to *OCCO, a generation of
688 CO intermediate, and Cu (CuAl-1) also enabled high surface coverages of CO
689 intermediates.

690 Cu catalysts for CO₂RR can produce a wide range of hydrocarbons at a high catalytic
691 activity. For selective CO₂RR, Yin et al. (Yin et al., 2019) used a catalyst based on
692 copper nitride (Cu₃N) nanocubes (NC). With a FE of 60%, a mass activity of 34 A/g, a
693 C₂H₄/CH₄ molar ratio over than 2000, and strong selectivity and stability of CO₂RR
694 towards ethylene at -1.6 V vs. RHE, their 25 nm Cu₃N NCs showed good performance.
695 This lacks of product selectivity is a significant barrier to the use of these catalysts for

696 selective CO₂RR, and more research on the application of these substitute catalysts is
697 required for increased hydrocarbon yield.

698 In a related piece of study, Liu and coworkers noted the formation of exceptional
699 oxygen-rich ultrathin CuO nanoplate arrays that spontaneously transform into Cu/Cu₂O
700 heterogeneous surfaces after CO₂RR (Liu et al., 2022). The electrocatalyst displayed a
701 high ethylene energy efficiency of 84.5%, steady electrolysis for 55h, and a total cell
702 ethylene energy efficiency of 27.6% at 200 mA.cm⁻² in a flow cell with a neutral KCl
703 electrolyte. A density functional theory (DFT) investigation of the mechanism,
704 highlighted that stable nanostructures, stable Cu/Cu₂O interfaces, and improved
705 adsorption of the intermediate *OCCOH can enhance selectivity and amount of C₂H₄
706 produced.

707 Wang et al. developed CuBi NPs that showed a CH₄ FE as high as 70.6% at 1.2 Vs
708 RHE. According to their study, adding Bi NPs to the matrix (CuBi NPs) significantly
709 boosted the FE when compared to regular Cu NPs by almost 25 times (Wang et al.,
710 2020). DFT studies showed that alloying Cu with Bi lowers the energy required for the
711 rate-determining phase of *COH production, which provides an additional explanation
712 for the enhanced performance.

713 In addition to the aforementioned systems, other metal-based nanomaterials have been
714 investigated towards the production of hydrocarbon via the electrochemical reduction
715 of CO₂, which are outlined in Table 1 below.

Table 1. Selected examples of electroactive metal nanoparticles for converting CO₂ into hydrocarbon products

Nanoparticles	FE (%)	Current Density (mA/cm ²)	overpotential vs RHE (V)	Products	Remarks	Reference
Dibenzylthiocarbamate functionalized AuNPs	100 ± 1	-	-0.8	CO	The hydrophobic nature of dibenzyl moieties permit CO ₂ to pass through	(L. Souza and H. B. Lima, 2021)
C ₃ N ₄ /Cu ₂ O-FeO nanocomposites	84.4	-	-0.24	CO	The interfacial interaction between g-C ₃ N ₄	(Woyessa et al., 2021)

					and $\text{Cu}_2\text{O-FeO}$ are responsible for the efficient CO_2 reduction to CO
Cu_xAu_y nanowire arrays	48	-	-0.5 to 0.7	EtOH	The selectivity (Zhu et al., 2019) of EtOH is attributed to the synergistic effect of morphology
Iron dispersed on graphene doped with nitrogen	80	-	-0.57	CO with small traces of CH_4	Fe-N_4 increased (Zhang et al., CO_2 activation 2018) resulting from the incorporation

					of trace Fe atoms to graphene matrices
ZnIn ₂ S ₄ /silver (gold)/tetra(4- carboxyphenyl) porphyrin iron(III) chloride hybrids	-	-	-	CO and H ₂	Au NPs favor H ₂ (P. Li et al., generation, 2022) whilst Ag NPs serve as a promoter for interfacial charge transfer from ZnIn ₂ S ₄ to the FeTCPP.
Cu nanocrystals	-	-1.74	-0.95	n-propanol	The increased (Ren et al., 2015) activity of the Cu

Composite of 64
 ZrO₂
 nanoparticles
 anchored on N-
 doped carbon
 sheets

2.6 -0.4 CO

nanocrystals
 toward the
 production of n-
 propanol was
 linked to the
 number of defect
 sites on their
 surface.

The dispersion (Miao et al.,
 of ZrO₂ NPs 2019)
 with oxygen
 vacancies on the
 N-C responsible
 for the improved
 electrochemical

					performance
Cu nanowires	60, 17.4, - 8 and 2		-1.1	H ₂ , ethylene, CO	Cu nanowire (Ma et al., and ethene, arrays can be 2016a) respectively tuned to systematically controlling hydrocarbon formation via the electrochemical reduction of CO ₂ .
Mesoporous carbon modified CNT anchored	98	60	-0.81	CO	The dispersive (Du et al., 2022) Ni nanoparticles and N-doping

by Ni NPs

active sites of mesoporous carbon is good for selective reduction of CO₂ to CO.

C-supported Bi 93 ± - -1.6 HCOO⁻
NPs 2.5%

The electrode (Ávila-Bolívar et al., 2019) deactivates after about 70 h (in 3-h electrolysis experiments at different potentials).

717 FE - Faradaic Efficiency; EtOH – Ethanol; FETCPP - Tetra(4-carboxyphenyl)porphyrin iron(III) chloride; HCOO⁻ - Formate ion; NPs –Nanoparticles; AuNPs –
718 Gold nanoparticles

719 In the quest for additional electro-active nanoparticles for CO₂ reduction, non-metal
720 NPs have been explored in order to speed up the reaction rate and increase the
721 selectivity for products. For instance, boron phosphide NPs were shown by Mou et al.
722 (Mou et al., 2019) to function remarkably as a non-metal electrocatalyst for the highly
723 selective electrochemical conversion of CO₂ to CH₃OH. In comparison to RHE in 0.1
724 m KHCO₃, this catalyst achieves a high FE of 92% for CH₃OH at 0.5 V. According to
725 DFT calculations, B and P synergistically facilitate the binding and activation of CO₂,
726 and the *CO + *OH to *CO + *H₂O pathway, with a free energy change of 1.36 eV, is
727 the rate-determining step for the CO₂RR. Liu et al. (Liu et al., 2022) reported B/N-
728 doped sp³/sp² hybridized nanocarbon, which consists of extremely small carbon NPs
729 with an sp³ carbon core surrounded by a sp² carbon shell, as an effective electrocatalyst
730 for CO₂ to ethanol reduction at relatively low overpotentials. They claim that CO₂
731 reduction occurs during the synthesis of ethanol and acetate at 0.5 0.6 V (vs. RHE),
732 with ethanol accounting for 51.6% - 56.0% of the total reduction. Due to the combined
733 effects of sp³/sp² carbon and B/N doping, there is a strong ethanol selectivity.

734 To perform electrocatalytic CO₂ reduction to liquid ethanol and acetone, Yuan and
735 colleagues presented their findings. Yuan and colleagues used five pyridine derivatives,
736 including pyridoxine, 4-hydroxypyridine, 4-aminopyridine, 8-hydroxyquinoline, and 5-
737 amino-1,10-phenanthroline, to functionalize graphene oxide (GRO) surfaces (Yuan et
738 al., 2018). Surprisingly, the greatest catalyst for electrochemical CO₂ conversion is
739 pyridoxine-modified GRO sheets with a pyridinic N concentration of 2.32% and an
740 overall FE of 45.8%. Furthermore, the CO₂ reduction potentials of the other four
741 pyridine derivatives functionalized GO varied with respect to ethanol and acetone. Li
742 and colleagues described non-metal nanoporous S-doped and S,N-codoped carbons as
743 catalysts for electrochemical transformation CO₂ (Li et al., 2016). The team found that

744 S,N-doped carbon has greater FE for conversion to CO and CH₄ compared to S-doped
745 counterpart. The former revealed a maximum FE of 11.3% and 0.18% for CO and CH₄
746 production, respectively. The S,N-nanoporous carbon was better at decreasing the
747 overpotential of the reduction process.

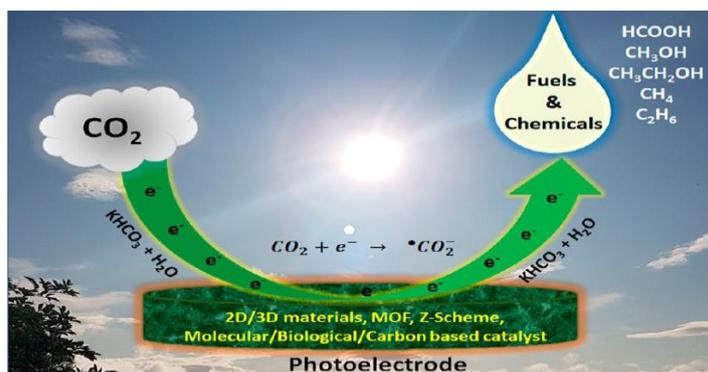
748 Two-dimensional (2D) boron nitride nanosheets or meshes (BNs) doped with beryllium
749 have been the subject of research by Azofra and coworkers (Azofra et al., 2016).
750 According to their mechanistic study, adding electron-deficient Be atoms to the 2D
751 network significantly lowered the energy barriers for CO₂ fixation and the initial steps
752 in hydrogenation. As a result of the exceptionally large hole created on the Be-doped
753 surface environment, CO₂ was spontaneously absorbed (in terms of the Gibbs free
754 binding energy).

755 Despite all the accomplishments in CO₂RR, it is worth to mention that high progress is
756 still needed in the design of catalysts based on metal and non-metal for achieving a
757 more performant CO₂ electrocatalytic transformation. The main challenge being the
758 energy requirement for reducing CO₂ (due to its stability), an electrochemical potential
759 [E°] of 1.9 V vs normal hydrogen electrode (NHE) at pH. Furthermore, due to the high
760 reactivity of the one-electron reduction product (CO₂^{•-}), regulating product selectivity is
761 difficult. When a multi-electron process is combined with proton-coupled electron
762 transfer, the potential for CO₂ reduction is greatly reduced, resulting in a variety of
763 products depending on the number of electrons involved (Maeda, 2019). Finally, the
764 quantum yield and current density reported thus far are extremely low, particularly for
765 C₂⁺ products, making commercial production extremely difficult. As a result, extensive
766 and intensive research is required to overcome all of the aforementioned challenges.

767 **3.3 Photo-electrochemical (PEC) reduction of CO₂**

768 Photoelectrochemical (PEC) conversion of CO₂ can be described as a procedure
769 mimicking the artificial photosynthesis technique. This method has been employed for
770 the conversion of CO₂ to formate, formaldehyde, formic acid, methane, methanol, and
771 ethanol (Kumaravel et al., 2020). This technique combines electrocatalytic and
772 photocatalytic systems in which photogenerated electrons are transferred to the
773 electrode surface under an applied electric field, thus reducing CO₂ in the process
774 (Nandal et al., 2022).

775 During the 80s, Fisher et al. (Fisher and Eisenberg, 2002) and Inoue et al. (Inoue et al.,
776 1979) studied the electrocatalytic reduction reactions that gave rise to studies of photo-
777 electrocatalytic reduction of CO₂ on selected semiconductors. However, an extensive
778 study using various metals and metal oxides requires large over potentials and suffers
779 from hydrogen evolution (Benson et al., 2009; Qiao et al., 2014; Shen et al., 2015).
780 Since then, it has become a promising technique for CO₂ conversion. In 2020, Arai et
781 al. (Arai et al., 2010) reported the PEC conversion of CO₂ into HCOOH using a p-InP-
782 Zn photocathode which has been modified with a Ru polymer. The conversion was
783 achieved in the presence of visible light/ solar energy. Similarly, Kumaravel and his
784 colleagues (Kumaravel et al., 2020) also synthesized a range of fuels and chemicals
785 (Formic acid, methanol, ethanol, methane and ethane) from CO₂. They employed a
786 catalyst-embedded microfluidic PEC reactor for the synthesis. The catalyst was
787 activated in the presence of visible light irradiation. The schematic of the conversion is
788 presented in Figure 13



789

790 Figure 13: PEC Conversion of CO_2 into value-added product using solar irradiation.

791 Adapted with permission from reference (Kumaravel et al., 2020). Copyright [2020],

792 [American Chemical Society].

793

794 According to a recent study by Karim et al. (Rezaul Karim et al., 2018), single electron

795 reduction of CO_2 to $\cdot CO_2^-$ occurs at -1.90 V vs NHE at $pH = 7$ in aqueous solution at 25

796 $^{\circ}C$ under 1 atm pressure. The $2e^-$ pathway of CO_2 reduction produces CO ($E = -0.53$ V

797 vs NHE) and formate ($E = -0.61$ V vs NHE) while the $6e^-$ pathway leads to the

798 production of methanol ($E = -0.38$ V vs NHE) (Qiao et al., 2014; Rezaul Karim et al.,

799 2018). The band varies depending on the type of metal coordination as shown in

800 **Figure 14.**

801 In the electrochemical process, ultraviolet radiation on the semiconductor photocatalyst

802 activates the metal center, thus forming an oxidation-reduction environment. During

803 this process, electrons get excited from the VB to CB, leaving behind positive holes

804 that oxidize water on the surface to form $OH\cdot$ radicals with strong oxidative

805 decomposing power. Excited electrons from the CB get accepted by CO_2 to form $\cdot CO_2^-$

806 radicals that react with the intermediate products of the oxidative reactions forming one

807 or more of the products in **Table 2** depending on the bandgap of the photocatalysts

808 (Ekambaram et al., 2007). Metal oxides present desirable bandgap and bandgap edge

809 positions, and their electronic structure plays a major role where the VB is fully filled
 810 by electrons and the CB is empty.

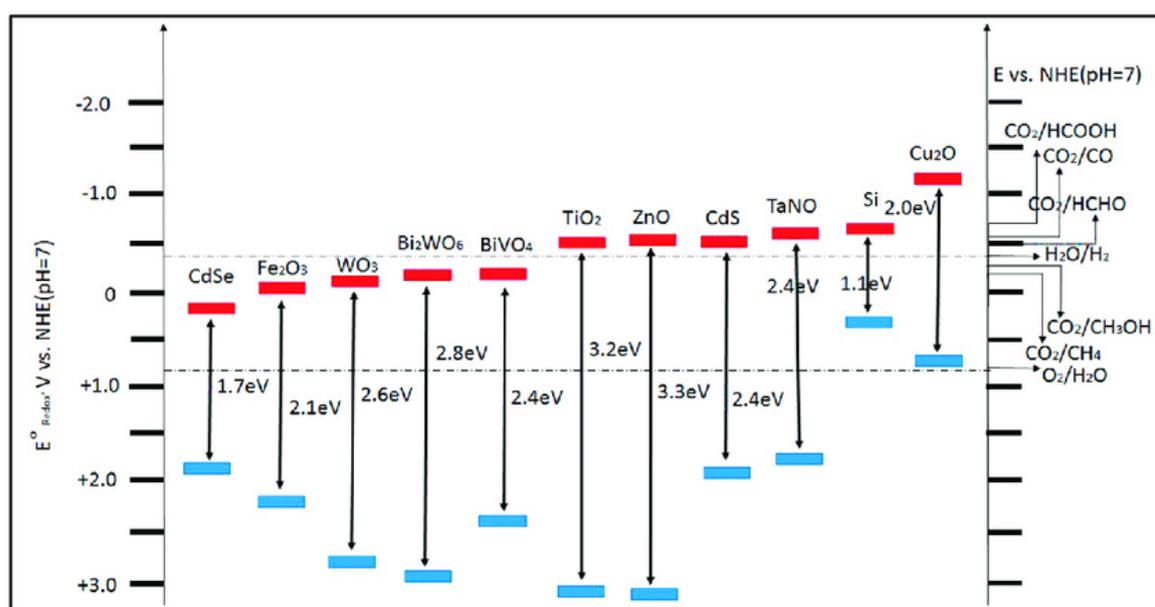
811 Table 2: The oxidation-reduction potential at pH=7 vs NHE and half-cell reactions
 812 (Ekambaram et al., 2007)

Reactants	Products	EMF
$\text{CO}_2 + 2\text{e}^- \rightarrow$	$\cdot\text{CO}_2$	-1.90
$\cdot\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow$	HCOOH	-0.61
$\cdot\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow$	CO + H ₂ O	-0.53
$\cdot\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow$	HCHO + H ₂ O	-0.48
$\cdot\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow$	CH ₃ OH + H ₂ O	-0.38
$\cdot\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow$	CH ₄ + 2H ₂ O	-0.24
$2\text{H}_2\text{O} + 4\text{H}^+ \rightarrow$	O ₂ + 4H ⁺	+0.81
$\text{H}^+ + 2\text{e}^- \rightarrow$	H ₂	-0.42

813

814 Therefore, the integration of electrocatalysis and photocatalysis generates a unique
 815 synergistic photo-electrochemical catalysis system (Huang et al., 2017; Rezaul Karim
 816 et al., 2018). The catalytic activity of a photocatalyst towards CO₂ reduction depends
 817 on its band gap and appropriate positioning of the conduction and valence bands
 818 (Handoko and Tang, 2013). Doping semiconductors have extensively been explored in
 819 the literature to enable visible-light-activated photocatalysis and the usage efficiency of
 820 solar light. Several published studies have used titanium for photocatalytic applications
 821 for organic compound decompositions due to its ability to oxidize organic and
 822 inorganic substances in water and air through a redox reaction (Xie et al., 2018). TiO₂
 823 and ZnO absorb ultraviolet light of the solar spectrum due to their large bandgap's

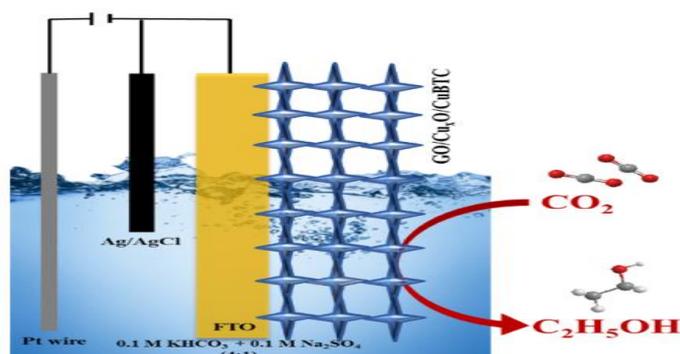
824 energy (~380 nm and ~360 nm respectively) (Liu et al., 2010). The bandgap (the
 825 distance between the valence band and conduction band) of each semiconductor
 826 determines are shown in Figure 14, it shows the relationship between the bandgap and
 827 EMF at pH 7. Several alternative semiconductors such as Fe₂O₃, ZnO, WO₃, SrTiO₃,
 828 NaTaO₃, CdS, Ag₃PO₄, BiPO₄ and g-C₃N₄ have been reported to have promising
 829 electro-photocatalytic performance (Kubacka et al., 2011; L. White et al., 2015; Liu et
 830 al., 2010; Wang et al., 2009).



831
 832 Figure 14: Band gap energy of various semiconductors (Wang et al., 2009). Copy right
 833 2019

834 More recently, Nandal et al. (Nandal et al., 2022) performed a selective conversion of
 835 CO₂ into ethanol via a PEC method (see **Figure 15**). The catalytic systems involve a
 836 mixture of Graphene oxide/Copper oxide and a copper-based MOF (GO/Cu_xO, Cu-
 837 MOF). The catalytic system was solar-driven and activated in the presence of sunlight.
 838 They reported an ethanol yield of 162 μM cm⁻¹. Most researchers believe that the PEC
 839 reduction technique is not only efficient, but it is also greener and sustainable. Other

840 PEC for CO₂ reduction surveyed in this section are listed in the supplementary file
841 (Table S2)



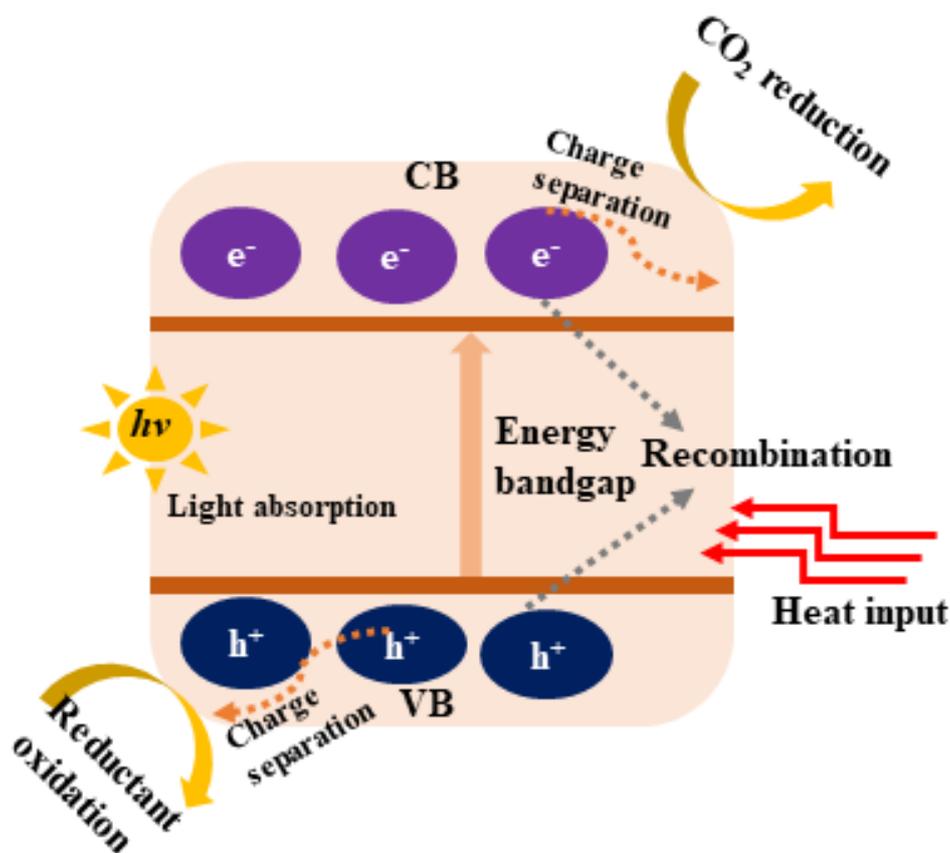
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843 Figure 15: PEC reduction of CO₂ to ethanol. Adapted with permission from reference
844 (Nandal et al., 2022). Copyright [2022], [Elsevier].

845 **3.4 Photothermal heterogeneous catalysts for the hydrogenation of CO₂**

846 The hydrogenation of CO₂ is gaining significant impetus in scientific investigations
847 considering the large amount of CO₂ generated by the industrial processes and the
848 associated environmental degradation. It facilitates the production of clean fuels and
849 hydrocarbons such as CO, CH₄, and C₂⁺ products (Fan and Tahir, 2022). The
850 hydrogenation reaction can proceed via thermal catalysis, photocatalysis, and
851 photothermal catalysis. While thermal and photocatalytic processes require the action
852 of heat and light energies respectively, the photothermal catalytic approach combines
853 both in a single reaction system. In photothermal catalytic systems, the CO₂
854 transformation reaction is driven by light energy into a thermally inspired catalytic
855 reaction system or utilizing the photoinduced thermal effect of a catalyst. The light
856 energy initiates a photoinduced redox reaction and a photoinduced thermally driven
857 reaction (Oladoye et al., 2021). For instance, the exposure of a transition metal oxide-
858 based catalyst to a sufficient amount of light energy causes an excitation of photons that
859 produces electron-hole pairs in the conduction band (CB) and valence band (VB)

860 (Figure 16). These highly energetic electrons enter the anti-bonding orbitals of the
861 reactants and activate the reactant molecules to stimulate a redox reaction. In other
862 instances, the absorbed photon could be converted into heat energy (Liu et al., 2022).
863 At an activated temperature, the active sites on the surface of the photothermal catalytic
864 material could induce a thermally driven catalytic reaction. Several semiconducting
865 metal oxides with tunable porosity and defective active sites have been designed for the
866 hydrogenation of CO₂ into different hydrocarbon-based fuels (Table 3).



867

868

Figure 16: Scheme of the photothermal catalytic CO₂ reduction

869 Table 3: Examples of photothermal catalysts for the hydrogenation of CO₂ in fuels and hydrocarbons

Photothermal catalyst	Light source	Reaction conditions	Selective products	Conversion rate (mmol·g ⁻¹ ·h ⁻¹)	Comments	References
Pd/ZnO	Visible light	Low pressure (12 bar)	CH ₃ OH		Localized SPR of Pd contributed to the high yield of methanol	(Wu et al., 2019)
AuPt@UiO-66-NH ₂	300 W Xe lamp	150°C, 4 h	CO	1451	Synergetic effect of plasmonic Au, doped active Pt, and encapsulation structure leading to the production of metal@MOF gives good hydrogenation performance	(Wang et al., 2022)

120 μm - SiNCs@Co nanoarray	300 W Xe arc lamp	Pressure (1 bar), power intensity (2.5 W cm^{-2})	CO	1780	Strong light-absorption ability over the entire solar spectrum due to the combination of the light-trapping effect of the nanoarray structures and the SPR of Co NPs increases the conversion rate	(Shen et al., 2022)
Ni/TiO _{2-x} H _x	300 W Xe lamp	Gas flow rate at 500 mL min^{-1} and purged for 10 min	CH ₄		Abundant defects such as oxygen vacancies, active hydrogen species, and Ni active sites enhance the performance of the catalyst	(Y. Li et al., 2022)
Nb ₂ C-	300 W Xe	36-sun	CO	8.5 mol·g ⁻¹ ·h ⁻¹	Ni NPs greatly enhance the	(Wu et al.,

nanosheet-supported Ni NPs	arc lamp	illumination without external heating			activation of H ₂ and accelerate CO ₂ hydrogenation reactions; formation of Ni-H is vital for CO ₂ conversion	(2021)
Fe ₃ O ₄	Xenon light source (200–1000 nm)	4 h of irradiation	CO	11.3	Fe-carbide and other Fe-based catalysts show excellent light-to-heat conversion performance and good light-harvesting properties	(Song et al., 2020)
θ-Fe ₃ C			CH _x	10.9		
α-MoC and β-Mo ₂ C mixed phases	300 W xenon lamp	130 °C, 5 h	CO and CH ₄	25.8 mL·g ⁻¹ ·h ⁻¹	dissociation of light-promoted surface intermediate (formate species) was responsible for the enhanced activity of photothermal catalytic CO ₂	(Zhao et al., 2021)

					hydrogenation	
Pd ₂ Cu alloy dispersed TiO ₂	UV-Vis (350 to 750 nm)	150 °C	C ₂ H ₅ OH	4.1	Pd active sites utilize the electrons and hydrogenate the *CO to *HCO, which is a key step in the conversion process	(Elavarasan et al., 2022)
SNAs support on Co	300 W Xe arc lamp	Pressure (1 bar), power intensity (2.5 W cm ⁻²)	CO	0.433	Photoexcited electron-hole pairs in the SNAs might be involved in the catalytic process	(D. Zhang et al., 2021)
Co@AAO	Sunlight	Power intensity (2.5 W cm ⁻²)	CO	1666	A dual-pass AAO with a large channel size facilitates gas diffusion and thus boosts photothermal catalytic	(D. Lou et al., 2021)

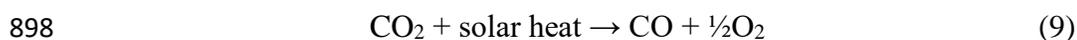
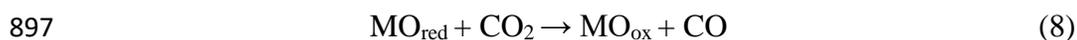
					performance	
Au/CeO ₂	Xe lamp	623 K	CO		Positive effect of light on CO ₂ transformation is associated with the hydrogen dissociation step.	(B. Lu et al., 2019)

870 SPR-Surface plasmon resonance; MOF-Metal organic frameworks; SiNCs-Silica nanocones, NPs-Nanoparticles, SNA-Silicon
871 nanowires arrays, AAO-Anodic aluminum oxide

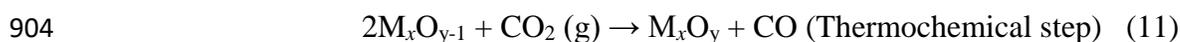
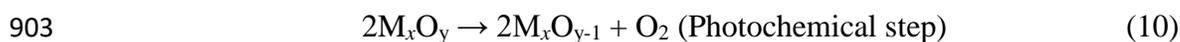
872 **3.5 Thermochemical transformation of CO₂**

873 The thermochemical transformation of CO₂ is an interesting strategy that has been gainfully
874 explored for the reduction, splitting, or reforming of CO₂ to fuels/products such as carbon
875 monoxide, methanol, methane, and dimethyl ether in the presence of suitable catalysts (Fuqiang
876 et al., 2017; Roy et al., 2018). Although, there are many high-temperature thermochemical
877 energy conversion processes for energy storage, energy conversion and water splitting reactions
878 (Ali et al., 2020; Cheng et al., 2021; Lorentzou et al., 2014; Wu et al., 2018), the solar-induced
879 thermochemical cyclic method is been emphasized as an outstanding approach for the efficient
880 conversion of CO₂ (**Table 4**). This approach has produced intriguing results from several the
881 experimental tests/designs conducted in different solar reactor models, which has given rise to
882 more intensified research and technology development in this field (Guene Lougou et al., 2020).
883 Many studies have shown that the solar thermochemical CO₂-transformation is a promising
884 solution for solar energy harvesting and storage using materials like Fe-Ni alloy embedded in a
885 perovskite (Hu et al., 2021), Ca- and Al-doped nSmMnO₃ perovskite (Gao et al., 2022), and
886 ZrO₂-supported NiFe₂O₄ (Shuai et al., 2021), to convert CO₂ into CO with a 99% conversion rate
887 of 381 mL g⁻¹ min⁻¹ at 850°C, high conversion of 595.56 mmol/g, and 37.89 mL of CO yield in
888 46 min, respectively. Meanwhile, Ni-doped CaCO₃ transformed 86.6% of CO₂ into syngas along
889 with CH₄ in a fixed bed photo-reactor (Teng et al., 2022). The solar thermochemical process
890 follows a two-step dissociation approach wherein the first step is an endothermic process that
891 involves the production of O₂ by partially reducing a perovskite or metal oxide (MO) to a non-
892 stoichiometric oxide with the assistance of high-temperature solar heat (Eq. 7). The second step
893 usually occurs at low temperature via an exothermic process. At this stage, the reduced

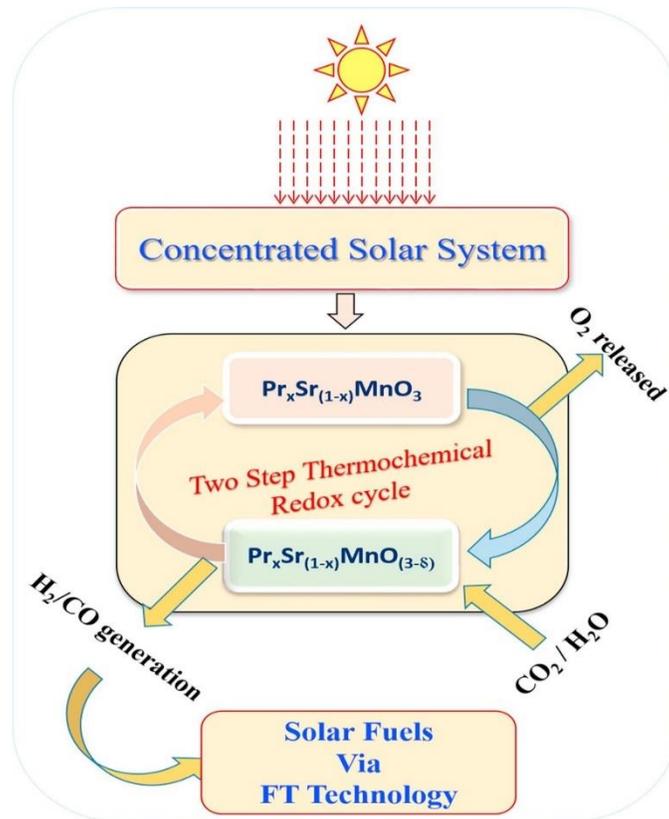
894 perovskite or MO is oxidized with H₂O and/or CO₂ giving rise to the formation of H₂ and/or CO
895 (Eq. 8-9), together with the stoichiometric oxide (Chen et al., 2022; Nair and Abanades, 2018).



899 In the same vein, the photo-thermochemical (PTC) model produces photoinduced oxygen
900 vacancies on the surface of the MO catalyst after exposure to UV-light energy (Eq. 10). Further,
901 the oxygen vacancies are used to reduce CO₂ at temperatures below 873 K, thereby producing
902 CO and O₂ (Eq. 5) (Xu et al., 2017, 2016).



905 By exploring the Fisher Tropsch (F-T) technology, solar-assisted MOs can also afford carbon-free
906 alternative fuels i.e. production of H₂ that can be used directly as a fuel or converted into other
907 value-added chemicals (**Figure 17**) (G. Takalkar and Bhosale, 2019). Besides, other
908 heterogeneous catalysts that change dynamically during the thermochemical reactions as well as
909 possessing catalytic active sites and definite reaction pathways have been identified for CO₂
910 transformation (Feng et al., 2021). For example, the loading of IrO_x onto LaFeO₃ almost double
911 the maximal CO release rate and increases the maximal O₂ evolution rate 0.5 times i.e. a 5-fold
912 CO production (Jiang et al., 2016); meanwhile, the sol-gel synthesized Co_xFe_{3-x}O achieved
913 higher CO generation rate via CO₂ splitting (Takalkar and Bhosale, 2019).



914

915 Figure 17: Solar-assisted thermochemical process for the production of hydrogen and syn gas by
 916 the F-T approach. Reproduced from (Takalkar and Bhosale, 2019). Copyright 2019 Elsevier Ltd

917 Table 4: Some investigations on solar-assisted thermochemical transformation of CO₂

Fabricated thermochemical material	Product(s) of the process	Condition	Conversion rate	References
NiFe ₂ O ₄ @SiC	CO	1073–1273 K	18.1 %, 410 μmol/g	(Jiang et al., 2022)
Ni-phyllsilicate @CeO ₂	H ₂ and CO	100 h of irradiation	90.4 %, 120.90 and 136.84 mmol	(Shi et al., 2023)

			$\text{g}_{\text{cat}} \text{min}^{-1}$	
$\text{CeO}_{2-\delta}$	H_2 and CO	1400 °C	5.1 mL/g	(Haeussler et al., 2020)
Zn/ZnO	Syngas	900-2300 K	31.5-52.1%	(Loutzenhiser and Steinfeld, 2011)
Ni-ferrite	CO or CO/ H_2	1100-1400 °C	0.07 mmol/g	(Lorentzou et al., 2014)
NiFe_2O_4 @ Alumina support	Fuels and chemicals	1300 K, 0.5 atm, and 0.4 m/s	98.22%	(Guene Lougou et al., 2020)
$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$	H_2 and CO	1000-1400 °C	137.5 $\mu\text{mol/g}$ (1.6-fold increase)	(Dey et al., 2015)
Ceria pellets	H_2	1400 °C	2.3 $\text{mL.g}^{-1}.\text{min}^{-1}$	(Abanades and Haeussler, 2021)
Porous ceria	CO	2.8–3.8 kW and 1400 to 1600 °C	4.56 \pm 0.12 mL.g^{-1}	(Furler et al., 2012)
$\text{LaCo}_{0.7}\text{Zr}_{0.3}\text{O}_3$	CO	1000 C to 1300 °C, flow	75%	(Wang et al., 2020)

		rate of 40 sccm		
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918

919 **3.6 Non-thermal plasma (NTP) catalysis**

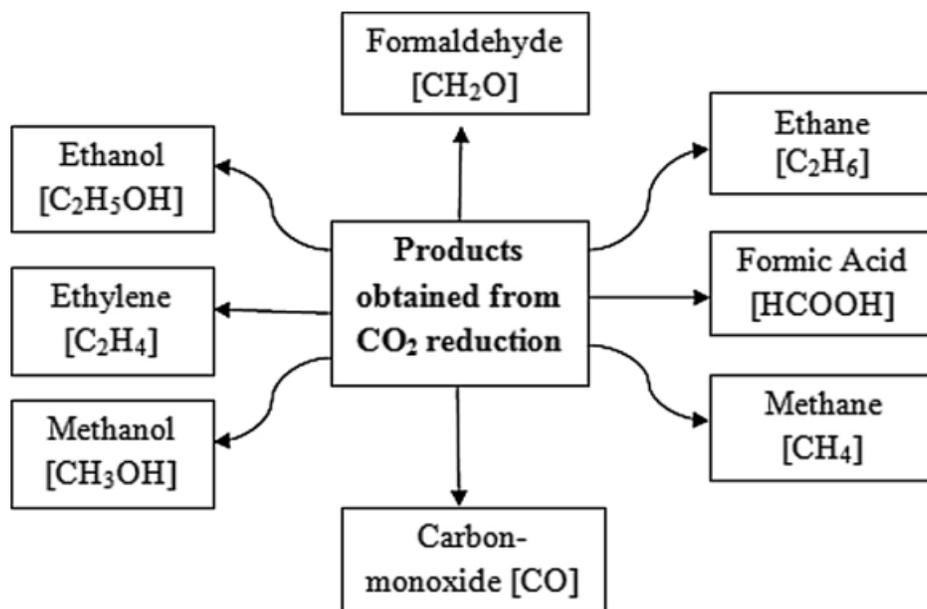
920 Non-thermal plasma (NTP) catalysis is an auspicious technology that is gaining significance in
921 C₁ chemistry. It has been postulated as an effective alternative to conventional thermal catalysis
922 due to the unique interplay between the plasma and heterogeneous catalyst. Thus, this approach
923 could overcome the kinetic limitation of conventional thermal catalysis without the need for any
924 external heat sources (Parastayev et al., 2018). Typically, this process employs an electric
925 discharge of partially ionized gas made up of electrons possessing average electron energy in the
926 range of 1-10 eV (Chen et al., 2020c). These electrons have the capacity to activate stable C₁
927 molecules as well as denature their bonding structures in the gaseous phase under moderate
928 conditions, thereby producing atoms, ions, and vibrationally-excited reactive species (Mehta et
929 al., 2019). The NTP catalytic approach has the potential of accelerating many energy-intensive
930 and kinetically and/or thermodynamically limited heterogeneous catalytic reactions such as CO₂
931 hydrogenation (Song et al., 2022), water–gas shift reaction (Xu et al., 2019), hydrocarbon
932 reformation (Wu et al., 2018) and CO₂ splitting (Chen et al., 2019), amongst others.

933 In Chen et al. (Chen et al., 2020a) Ni NPs supported on silicalite-1 zeolites with suitable active
934 sites and pore structures were comparably investigated in CO₂ hydrogenation under the thermal
935 and NTP conditions. The comparative investigation showed that the hierarchical meso-
936 microporous structures and the associated well-dispersion of Ni species were highly beneficial to
937 the catalysis under the NTP conditions, especially at relatively high voltages. Using a dielectric
938 barrier discharge (DBD) reactor at 150°C, Zeng and Tu (Zeng and Tu, 2017) showed that the
939 presence of Ni in the reactor and injection of argon (up to 60%) in the reaction promotes the

940 conversion of CO₂ to CO and CH₄ (selectively, 85%) and the energy efficiency of the plasma
941 process. In the reactor, Ar decelerates the breakdown voltage of the feed gas and accelerates
942 charge transfer through the reactor. Furthermore, the NTP-activated hydrogenation of CO₂ in the
943 presence of Ru/MgAl layered double hydroxide catalysts (having low activation energy)
944 provided ~84 % of CH₄ yield at relatively low temperatures (Xu et al., 2020). In another
945 approach, a MOF-supported Ni catalyst (15Ni/UiO-66) presented 99% selectively towards the
946 conversion of CO₂ to CH₄ under NTP conditions and the catalyst was still stable after 20h of
947 reaction (H. Chen et al., 2020b). The experimental investigations of Nizio et al. (Nizio et al.,
948 2016) revealed that ceria and zirconia-promoted Ni-containing hydrotalcite-derived catalysts
949 could yield high CH₄ under NTP conditions and temperatures < 330 °C.

950 **4. Fuels generated from CO₂ conversion**

951 The discovery and development of efficient technologies for the catalytic transformation of CO₂
952 is an exciting area of research (Ramírez-Valencia et al., 2021) as, in parallele of lowering the
953 atmospheric CO₂, this would allow the access to essential chemicals and fuels such as formic
954 acid (HCOOH), methanol (CH₃OH), carbon monoxide (CO), ethanol (CH₃CH₂OH) and methane
955 (CH₄), among others, that are presently produced from fossil resources. **Figure 18** describes the
956 potential products that could be derived from CO₂ conversion.



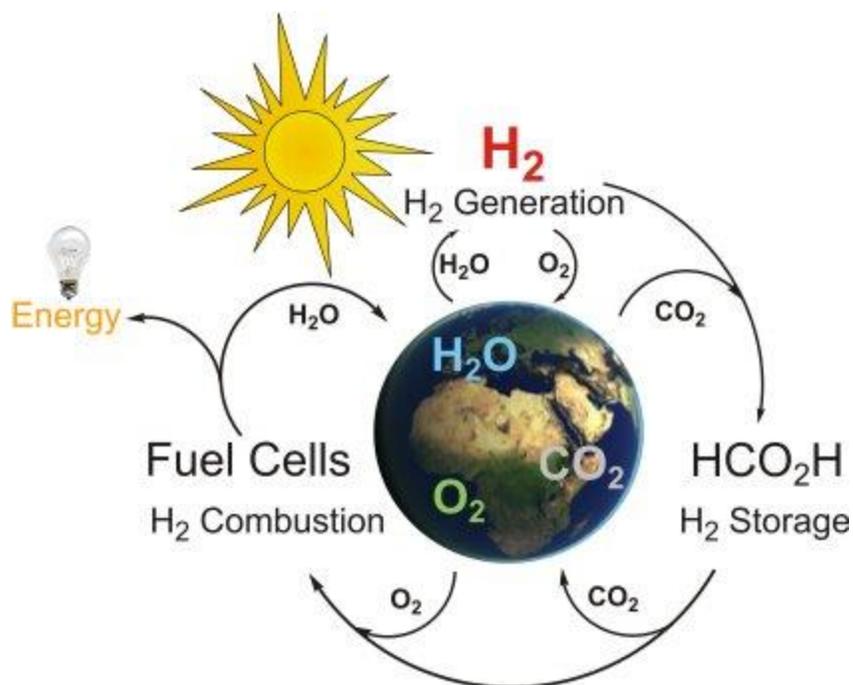
957

958 Figure 18: Potential products from CO₂ conversion (Ramírez-Valencia et al., 2021).

959

960 4.1 Formic acid

961 Among the myriad of products accessible from CO₂, formic acid is a valuable intermediate
 962 chemical and also used in the domain of energy for reversible hydrogen storage (**Figure 19**)
 963 (Moret et al., 2014). Formic acid is of great importance in textile industries, pharmaceuticals and
 964 food companies due to its acidic nature and reducing properties (Afshar, 2014). In particular,
 965 the leather and tanning industries are one of the largest global consumers of formic acid (Pérez-
 966 Fortes et al., 2016). Other critical applications of formic acid include preservatives and
 967 antibacterial agents in animal feeds (Anadón et al., 2006). Therefore, formic acid is a highly
 968 valued product with little or no alternative.



969

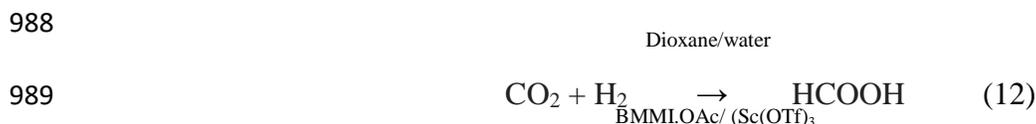
970 Figure 19: Reversible hydrogenation of CO₂ to formic acid (Li et al., 2002)

971 Several synthetic methods for the conversion of CO₂ to formic acid have been explored. This
 972 includes biochemical, photochemical, electrochemical, microwave-assisted, photosynthetic and
 973 catalytic reduction (Asiri and Lichtfouse, 2020; Hu et al., 2013; Lu et al., 2014; Scibioh and
 974 Viswanathan, 2004; Yadav et al., 2012). Catalytic conversion of CO₂ to formic acid was first
 975 reported by Inoue (Inoue et al., 1976) in 1976. Since then, CO₂ has become an attractive starting
 976 molecule for the synthesis of formic acid. Compared to other methodologies, the catalytic
 977 reduction method offers higher selectivity to targeted product, thus minimizing the risk of
 978 unwanted CO as a byproduct that may poison the fuel. However, the selectivity of the preferred
 979 product depends on the reduction method and the nature of the catalyst used.

980

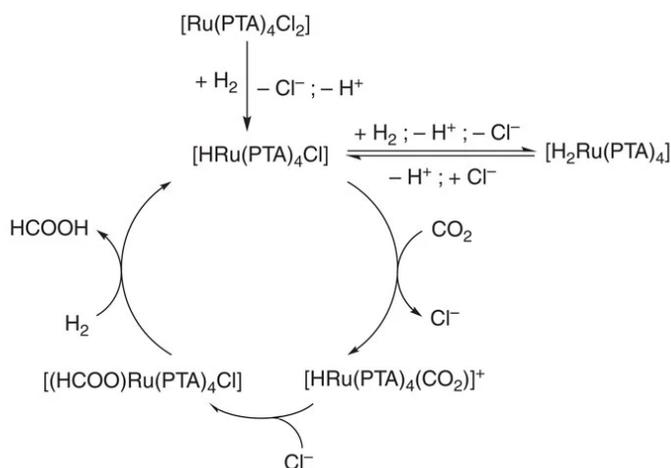
981 Weilhard *et al.* reported the synthesis of formic acid from CO₂ feedstock using an ionic liquid as
 982 an alternative to expensive precious metal-based catalytic systems (Weilhard et al., 2021). As

983 shown in Scheme 3, the synthetic strategy consists of a mixture of CO₂ and H₂ in 1:1 molar ratio.
 984 The catalytic system consists of a homogeneous mixture of 1-butyl-2,3-dimethylimidazolium
 985 acetate (BMMI.OAc) and Scandium(III) trifluoromethanesulfonate (Sc(OTf)₃). They reported a
 986 very high catalytic efficiency with turnover numbers (TON) and turnover frequency (TOF) of 8 x
 987 10⁵ and 2.1 x 10⁴ h⁻¹, respectively.



990

991 Moret *et al.* (Moret et al., 2014) applied a ruthenium-based homogeneous catalytic system to
 992 convert CO₂ feedstock into formic acid directly. The catalytic conversion was performed
 993 following the catalytic life cycle described in **Figure 20**. The reaction was performed at 40 °C
 994 using a mixture of water and dimethyl sulphoxide (DMSO) as the solvent.



995

996 **Figure 20:** Catalytic cycle and hydrogenation of CO₂ into formic acid over [HRu(PTA)₄Cl]

997 They reported that the catalytic system is highly sustainable than the existing routes. In addition,
 998 it is highly recyclable and gives a higher yield of the target product. More recently, Mubarak *et*

999 *al.* (Mubarak et al., 2022) published a greener approach via photocatalytic transformation of CO₂
1000 into formic acid. The catalytic procedure involves the breaking down of CO₂ into valuable
1001 chemicals in the presence of sunlight and Ag-doped TiO₂ NPs. This catalytic system is highly
1002 selective with HCOOH as the single product, formic acid being obtained at a yield of 193 μM
1003 cm⁻² h⁻¹.

1004 **4.2 Carbon monoxide**

1005 In the series of products derived from CO₂, carbon monoxide (CO) is one of the most critical
1006 chemicals and feedstock. It is a primary raw material along with H₂ gas for syngas production
1007 via Fischer-Tropsch synthesis to produce liquid fuels (Zeng et al., 2018). It is also valuable for
1008 the metallurgical industries (Liu et al., 2017). Most of the efforts concerning CO₂ reduction into
1009 CO efforts can be listed in two major categories, namely thermochemical reduction and
1010 electrochemical reduction (Porosoff et al., 2016). CO₂ being a very stable molecule, it requires a
1011 very high temperature (> 1200 °C) to decompose to CO (Equation 13). Therefore, this procedure
1012 is not thermodynamically favorable and must be catalytically driven.

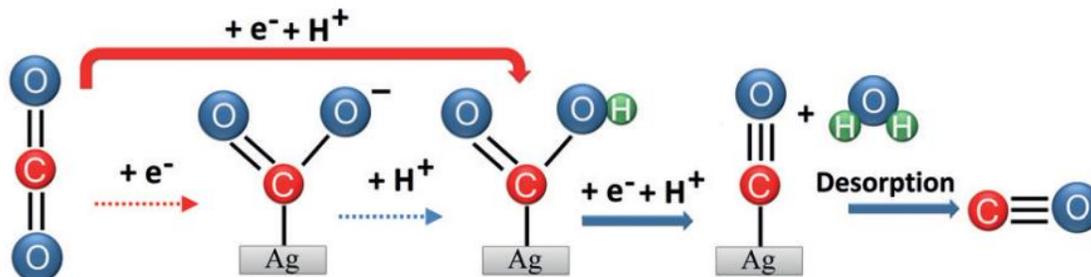


1014 Various catalytic materials have been employed to reduce the energy cost of the catalytic
1015 conversion of CO₂ to CO. For example, Au nanocatalysts have shown tremendous potential in
1016 converting CO₂ to CO with a remarkable selectivity (Qi et al., 2019). Qi *et al.* (Qi et al., 2021)
1017 reported a successful electrochemical conversion of CO₂ to CO over Au nanocatalyst. Wen *et al.*
1018 (Wen et al., 2018) used a nanoporous Au leaf electrocatalyst prepared by a de-alloying
1019 technique to reduce CO₂ to CO, achieving a very high catalytic efficiency to CO (90% FE).

1020 While gold-based catalysts are the most successful catalysts for the conversion of CO₂ to CO, the
1021 high cost of Au may prevent large-scale industrial applications (Ma et al., 2016b) which requires

1022 to find low-cost alternative catalysts. Metallic Ag is gaining considerable attention for CO₂
1023 conversion because of its significantly lower cost compared to Au and also high selectivity to
1024 CO (Ma et al., 2016b). This has been demonstrated by Ma *et al.* (Ma et al., 2016b) who
1025 developed a Ag-based electrocatalyst comprising oxide-derived nanostructure silver (OD-Ag)
1026 and polycrystalline Ag. The proposed reduction mechanism is described in Scheme 3. The
1027 obtained catalytic efficiency was 80% Faradic efficiency which is comparable to the results
1028 obtained with Au electrocatalysts.

1029



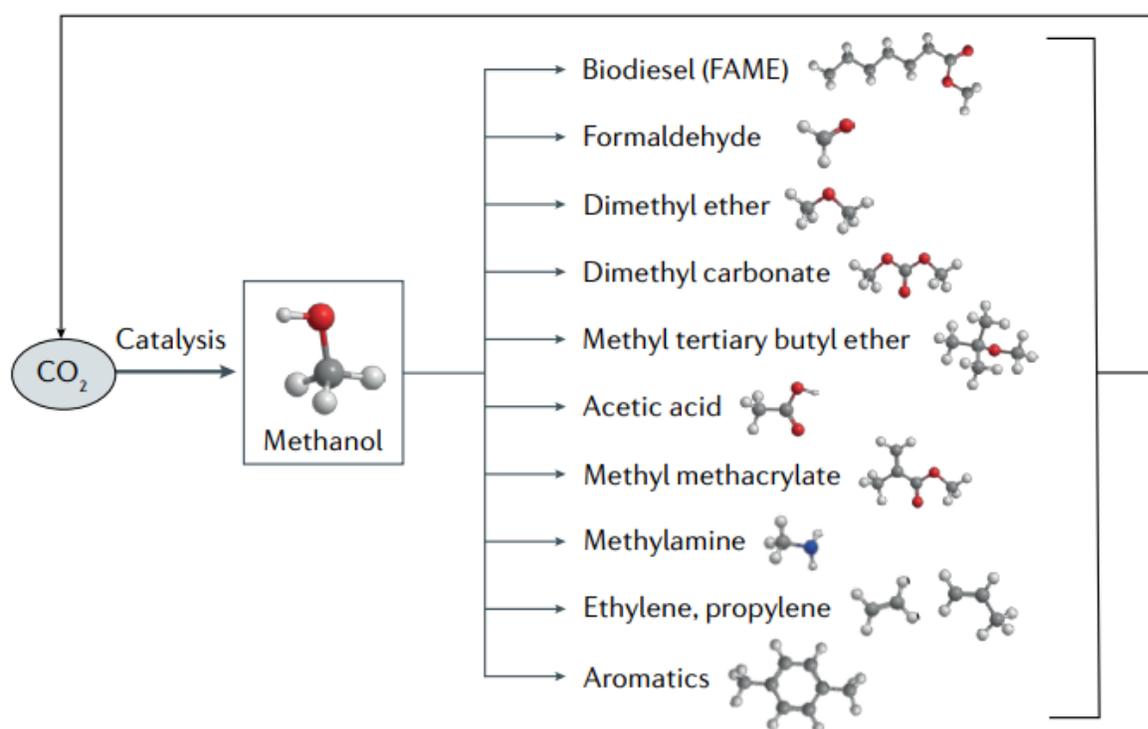
1030

1031 Scheme 3: Mechanism of the conversion of CO₂ to CO via electrochemical reduction proposed
1032 by (Ma et al., 2016b).

1033 Dong *et al.* (Dong et al., 2021) reported the use of low-cost ZnOHF nanorods as a substitute to
1034 expensive Au and Ag metals for the reduction of CO₂ to CO by electrochemical reduction. They
1035 obtained a CO Faraday efficiency of 76.4% with the CO current density of 57.53mA/Cm². It is
1036 worth mentioning that the catalytic efficiency of this Zn-based catalyst is not as high as Au and
1037 Ag-based ones, but the price is significantly lower which may open avenues for a large-scale
1038 electrochemical reduction of CO₂ to CO.

1039 4.3 Methanol

1040 The conversion of CO₂ to MeOH has been drawing tremendous attention lately because of the
1041 vast applications of methanol (Olah, 2013). Methanol is a multipurpose chemical feedstock
1042 (Offermanns et al., 2014) for producing various value-added products and fuel. The current
1043 production rate of methanol is 98 million metric tons per year (Kajaste et al., 2018). It is also an
1044 important hydrogen carrier. The various applications and Carbon cycle of methanol are described
1045 in **Figure 21**.



1046

1047 Figure 21: Main applications of methanol in industry

1048 Considering the vast application of methanol (Figure 16), conversion of CO₂ to MeOH is a
1049 crucial research area. The production of methanol has been dominated by the conversion of
1050 syngas (a mixture of CO and H₂) and CO₂ (Nieminen et al., 2019). From the mechanistic point of
1051 view, the synthetic pathway may occur through direct CO₂ hydrogenation (eq 14) or via reverse
1052 water gas shift (RWGS) (eq 15) followed by CO hydrogenation (eq 16) (Gaikwad et al., 2020).

1053 A challenge often characterized by this synthetic procedure is that it is performed at very high
1054 temperature and pressure (Bertau et al., 2014). In addition, it also suffers from poor selectivity
1055 and low yield (Jadhav et al., 2014).

1056 To improve this procedure, various homogeneous and heterogeneous catalytic hydrogenation
1057 reactions as well as thermocatalysis, photocatalysis, electrocatalysis, and enzymatic catalysis
1058 have been explored with promising results (Navarro-Jaén et al., 2021).



1062 Conventionally, methanol production from syngas is usually catalyzed by a Cu-based
1063 heterogeneous catalyst at 513-533K temperature and 50-100 bar pressure (Bart and Sneed,
1064 1987). It is worth mentioning that Cu alone exhibits a very low activity; to enhance the activity,
1065 the Cu catalyst is usually tethered on support or promoters such as Al₂O₃, ZnO, and ZrO₂. In
1066 most cases, the synergy between the Cu catalyst and the promoters only achieves a conversion of
1067 approximately 30% due to a fast deactivation of the Cu catalyst (Navarro-Jaén et al., 2021).
1068 Although the activity is low, Cu-based catalysts are very cheap thus justifying their
1069 predominance in methanol synthesis. However, the growing demand for methanol induced
1070 emergence of new ideas for converting CO₂ to methanol.

1071 For instance, Pd-based heterogeneous catalytic systems have been used to improve the synthesis
1072 of methanol. Díez-Ramírez *et al.* (Díez-Ramírez et al., 2016) reported the application of Pd/ZnO

1073 catalyst to convert CO₂ to methanol under atmospheric conditions, observing a low conversion
1074 rate due to the side reactions from coke formation and water from the (RWGS) reaction (eq 15).
1075 Various attempts have been made to suppress side reactions from the (RWGS) reaction.
1076 Fiordaliso *et al.* (Fiordaliso et al., 2015) reported the use of supported Pd-Ga bimetallic catalysts,
1077 specifically, GaPd₂/SiO₂ for converting CO₂ to methanol, at low CO₂ pressure, and with a MeOH
1078 production rate of 0.12 mol%. Although the catalytic activity of this GaPd₂/SiO₂ was better than
1079 in previous studies, the major drawback is the Pd cost, thus limiting practical applications.

1080 Ahmad *et al.* (Ahmad and Upadhyayula, 2019), developed an efficient, cheaper bimetallic
1081 catalyst Ga₃Ni₅ for CO₂ conversion and compared their results with those of Fiordaliso *et al.*
1082 (Fiordaliso et al., 2015). The activity of the Ga₃Ni₅ catalyst was found to be higher under the
1083 same experimental conditions, showing a MeOH conversion rate of 38.85 μmol g_{cat}⁻¹ min¹
1084 coupled to an impressive selectivity of 94 %.

1085 While Ga, Zn, Cu, Al, Pd, Ni, Pt-based catalysts have been widely tested for MeOH synthesis,
1086 To motivate a cost-effective catalyst, scientists are considering an alternative to Pt and noble
1087 metals. For instance, CeO₂-based catalyst is getting attention due to its abundant oxygen and
1088 reversible valence charges (Ce⁴⁺ and Ce³⁺) (F. Wang et al., 2016). This potential was
1089 demonstrated by Chang *et al.* (Chang et al., 2021), who applied a CeO₂-based catalyst Cu/ZnO–
1090 CeO₂ to convert CO₂ to methanol.

1091 Perovskites have been also identified as low-cost approach for CO₂ conversion to methanol. This
1092 is described by Zhan *et al.* (Zhan et al., 2014), who employed a perovskite-based catalyst to
1093 produce methanol from CO₂. They reported an excellent catalytic efficiency with impressive
1094 stability of the prepared catalyst.

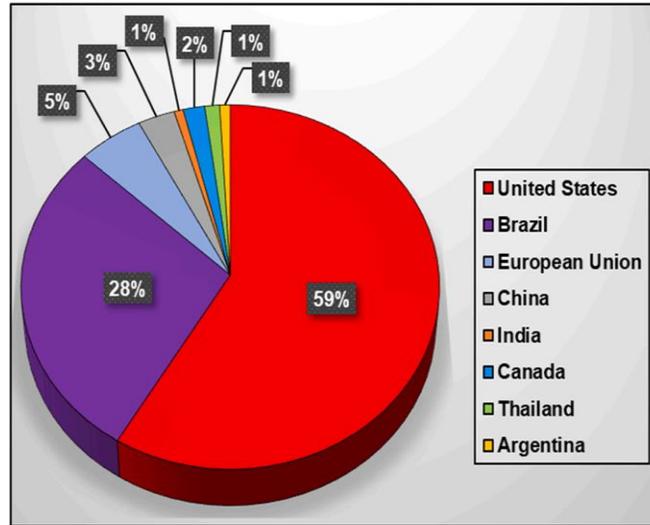
1095 Apart from heterogeneous-based catalytic systems, homogeneous catalysts have been also
1096 reported for methanol synthesis from CO₂. Kothandaraman *et al.* (Kothandaraman et al., 2016)
1097 developed a Ru-based homogeneous catalytic system that showed a very good yield (79 %) in
1098 methanol. In addition, this catalyst also shows excellent recyclability with over five runs without
1099 a significant loss in activity. Zhou *et al.* (Zhou et al., 2022) published the use of a ruthenium
1100 pincer complex [RuH₂(Me₂PCH₂SiMe₂)₂NH(CO)] which led to a good catalytic efficiency from
1101 the density functional theory (DFT) data.

1102 Application of enzymes to reduce CO₂ to methanol is also getting considerable attention. Zhang
1103 *et al.* (Z. Zhang et al., 2021) reported the enzymatic conversion of CO₂ to methanol in the
1104 presence of nicotinamide adenine dinucleotide (NADH). The enzyme was immobilized on
1105 porous a MOF (ZIF-8) to improve CO₂ concentration. The prepared NADH/ZIF-8 composite
1106 was placed in the bio-electrochemical cell. The methanol conversion rate was 822 μmol g⁻¹ h⁻¹,
1107 and the catalytic system was found stable and environmentally friendly.

1108 **4.4 Ethanol**

1109 Ethanol is a valuable chemical in our daily life. In contrast to methanol, ethanol has some distinct
1110 advantages, such as higher energy density, lower toxicity, and transportation safety (D. Wang et
1111 al., 2016). As a result of these advantages, it intervenes in a wide range of domestic and
1112 industrial applications, including chemical raw material for chemical synthesis, in disinfectants,
1113 pharmaceuticals and cosmetics, plasticizers, polishes and dyes (An et al., 2021). In addition to its
1114 domestic and industrial applications, ethanol is a necessary fuel and hydrogen carrier (Pang et
1115 al., 2019). The United States are the world largest ethanol producer, accounting for 59% of
1116 global production. This is followed by Brazil with 28% while the rest of the world accounts for
1117 13% (**Figure 22**).

1118



1119

1120 Figure 22: Ethanol production in various countries for the year 2020 (Cooper et al., 2021).

1121

1122 The high energy density and the compatibility of ethanol with existing and modern combustion
1123 engines make it a vital fuel. Ethanol is usually produced from the fermentation of starch and
1124 cellulose feedstock (Ali et al., 2022; Wang et al., 2021). With the population and increasing
1125 demand for food, the search for an alternative strategy for ethanol synthesis is highly urgent.
1126 That's why hydrogenation of CO₂ to ethanol has drawn a lot of attention.

1127 Several catalytic systems have been used for CO₂ conversion to ethanol, notably Pt, Co, Fe, and
1128 Cu systems (Zheng et al., 2019). Cu-based catalysts have been used for hydrogenating CO₂ to
1129 ethanol due to their success in converting CO₂ to methanol; however, the selectivity to ethanol is
1130 very low (Cao et al., 2016). Recently, it has been found out that ethanol selectivity can be
1131 improved by using Cu^I instead of Cu⁰. Despite this success, the Cu-catalyst suffers from long-
1132 term use due to instability under the reaction conditions and operating conditions.

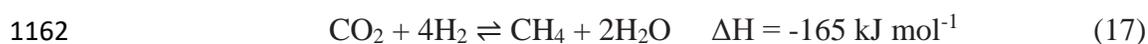
1133 Other catalytic systems have been tested to improve the selectivity and yield of ethanol from
1134 CO₂, including Pt-based catalysts and their alloys; while good yield was obtained with these

1135 catalysts, the high cost of the catalytic materials is an issue that limits their practical application
1136 (Choi and Liu, 2009). Lou *et al.* (Y. Lou et al., 2021) successfully applied a Pd/CeO₂ catalyst to
1137 convert CO₂ to ethanol. They reported a space yield time of 45.6 g_{ethanol} g_{Pd}⁻¹ h⁻¹. Together with
1138 an excellent selectivity of 99.2 %. Zhang *et al.* (F. Zhang et al., 2021) reported the application of
1139 supported sodium-modified Rh NPs in zeolite to hydrogenate CO₂ to ethanol that showed a CO₂
1140 conversion rate of 10 % and a selectivity of 24% to ethanol. Zheng *et al.* (Zheng et al., 2019)
1141 reported the conversion of CO₂ to ethanol using a LaCo_{1-x}Ga_xO₃ composite perovskite catalyst
1142 with a very good catalytic CO₂ conversion of 9.8% and a 88.1% selectivity to ethanol.
1143 Another challenge is catalyst separation from the product and recyclability; therefore, extensive
1144 research efforts are is devoted to develop effective and highly reusable catalysts in order to
1145 address this challenge.

1146 **4.5 Methane**

1147 Methane (CH₄) is a C₁ compound primarily used as fuel. Moreover, it is also used as a feedstock
1148 for chemical synthesis, especially as a synthetic natural gas and is also a major source of
1149 hydrogen storage (Koytsoumpa and Karellas, 2018). Therefore, the hydrogenation of CO₂ to
1150 methane is an effective strategy for CO₂ capture, utilization and conversion to valuable
1151 chemicals. Catalytic hydrogenation is the most widely studied route for CO₂ conversion to
1152 methane (Koytsoumpa and Karellas, 2018). This procedure is called methanation or Sabatier
1153 reaction (Lu et al., 2016) as it was first reported in 1902 by Sabatier *et al.* (Sabatier, 1902).
1154 According to the literature, two possible mechanisms have been proposed. The first mechanism
1155 is direct methanation (eq 17) which involves the reaction of CO₂ and H₂ with a nominal ratio of
1156 1:4, respectively, while the second mechanism is the reaction of CO and H₂ in a ratio of 1:3
1157 respectively (equation 2) (Dias and Perez-Lopez, 2021). As shown in equations 17 and 18, the

1158 conversion of CO₂ to methane is a highly exothermic reaction which can proceed at a relatively
1159 lower temperature. However, given the thermodynamic stability of CO₂ molecules due to the
1160 presence of delocalized π bonds, the conversion of CO₂ to methane remains a serious challenge
1161 at a lower temperature (Álvarez et al., 2017).



1164 To overcome this challenge and permit activation of CO₂ at lower temperatures, highly active
1165 catalytic materials with good selectivity to methane and low deactivation must be developed.
1166 CO₂ methanation has been performed with transition metals such as Co, Ni, Fe, Cu, Ru, Rh, and
1167 Pd (Y.-T. Li et al., 2022). However, due to the cost and limited availability, these noble metals
1168 are not widely employed for methane synthesis, especially on an industrial scale. Therefore, a
1169 new generation of low-cost and efficient catalysts have been investigated for methanation
1170 reaction. Among them, Ni, Fe, and Co-based catalysts have been widely studied because of their
1171 low cost and catalytic efficiency for CO₂ methanation. Ni-based catalytic materials are the most
1172 studied for CO₂ methanation due to their low cost and availability (Fukuhara et al., 2017). Dias
1173 *et al.* (Dias and Perez-Lopez, 2021) reported the conversion of CO₂ to Methanol using Ni/SiO₂
1174 catalyst promoted by Fe, Co, and Zn. They obtained a very high CO₂ conversion (73 %) and
1175 excellent selectivity (98.5 %) to methane.

1176 It is generally believed that catalytic behavior depends on several factors, such as surface
1177 properties, metal support interaction, etc. Researchers are currently developing further catalytic
1178 supports to enhance the performance of catalytically active metal species. This was recently
1179 demonstrated by Li *et al.* (Y.-T. Li et al., 2022) who used a metal-organic framework (MOF) as a
1180 support to enhance the catalytic activity of NiFe for the hydrogenation of CO₂ to methane. MOFs

1181 are highly porous coordination polymers that are characterized by high surface areas. As a result,
1182 they can enhance the catalytic activity in comparison to other traditional supports.

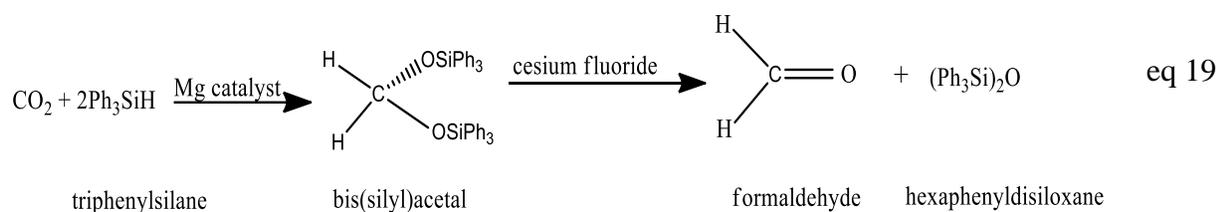
1183 Li *et al.* (Y.-T. Li et al., 2022) obtained a very high CO₂ conversion (72.3 %) and impressive
1184 selectivity (99.3 %) with the NiFe/MOF catalytic material. Similarly, Hu *et al.* (Hu et al., 2022)
1185 also established the role of metal-support interaction using Ni supported on CeO₂ nanofibers.
1186 The oxygen vacancy enhanced the catalytic efficiency of Ni in CeO₂. The prepared catalyst
1187 recorded 82.3 % conversion of CO₂ at low temperatures (250 °C - 300 °C). In addition, they also
1188 reported impressive stability of the catalyst up to 60h. This result can be attributed to synergistic
1189 effects between the Ni NPs and the CeO₂ nanofibers.

1190 **4.6 Formaldehyde**

1191 The ease of availability of CO₂ has provided an opportunity for energy production and
1192 commodity products for the economy. Among other compounds which could be generated from
1193 CO₂ is formaldehyde (FMD). Formaldehyde, with the chemical formula HCHO, is a substance
1194 that has gained wide usage by millions of people, directly or indirectly, across the globe due to
1195 its versatility (Rauch et al., 2019; Subasi 2020; Usanmaz et al., 2002). Generally, FMD is
1196 produced industrially via three stages. These include the production of synthesis gas (a mixture
1197 of water gas, carbon(iv) oxide and hydrocarbons) by steam reforming natural gas, synthesis of
1198 MeOH, and the generation of FMD through the partial oxidation of MeOH (Bahmanpour et al.,
1199 2015). All these methods are energy-intensive procedures (Heim et al., 2017; Nguyen et al.,
1200 2020). Moreover, during these processes, CO₂ was contained in most of the products formed
1201 (Lervold et al., 2021), leading to increased pollution.

1202

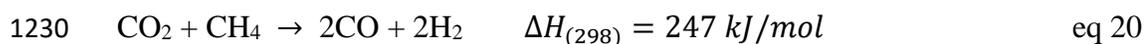
1203 In a bid to curb the emission of CO₂, scientists have developed methods that could possibly
 1204 convert CO₂ into useful products. Of these methods is the production of FMD (Friedlingstein
 1205 2015; Sümbelli et al., 2019). Although the generation of FMD from CO₂ is quite challenging,
 1206 frantic efforts are being made to overcome this fall-out as CO₂ is resistant to chemical changes
 1207 (Rauch et al., 2019). One of those efforts is the conversion of CO₂ at ambient temperature
 1208 yielding the formation of FMD. The CO₂ reacts with triphenylsilane in the presence of a
 1209 magnesium catalyst, resulting in an intermediate product formed, known as bis(silyl)acetal. This
 1210 product is then converted to FMD in the presence of cesium fluoride (Eq 19) (Rauch et al.,
 1211 2019).



1213 Another way that allows to convert CO₂ into FMD is the hydrogenation process, which different
 1214 researchers have debated to be dependent on the catalytic system (heterogeneous or
 1215 homogeneous) involved (Dang et al., 2019; Nguyen et al., 2020; Studt et al., 2015). The most
 1216 prevalent catalysts used for this reaction are heterogeneous Cu-based, such as Cu-ZnO-Al₂O₃
 1217 (Kobl et al., 2016) or Pt-promoted Cu/SiO₂ (Lee et al., 2001). This latter converts CO₂ to FMD at
 1218 150°C for 120 min at 600 kPa. However, Lee and co-partners indicated some issues encountered
 1219 with this catalyst (Lee et al., 2001). Moreso, a mesoporous graphitic carbon nitride (g-C₃N₄)
 1220 material with specific crystallinity and surface area, has been shown to have a significant effect
 1221 on the conversion of CO₂ to FMD. Since this discovery other photocatalytic mesoporous
 1222 nanomaterials have been explored for the photocatalytic reduction of CO₂ (Park et al., 2012; Xu
 1223 et al., 2013).

1224 **4.7 Hydrogen**

1225 Aside from FMD, a critical commodity product is hydrogen, being also a fuel, that could be
1226 generated from CO₂ via a process called carbon dioxide reforming. This process, represented on
1227 equation 20, consumes CO₂ and methane (CH₄), two greenhouse gases. This process requires
1228 high temperature, and as such, it is highly endothermic and also favored by low pressure (Wang
1229 et al., 1996).



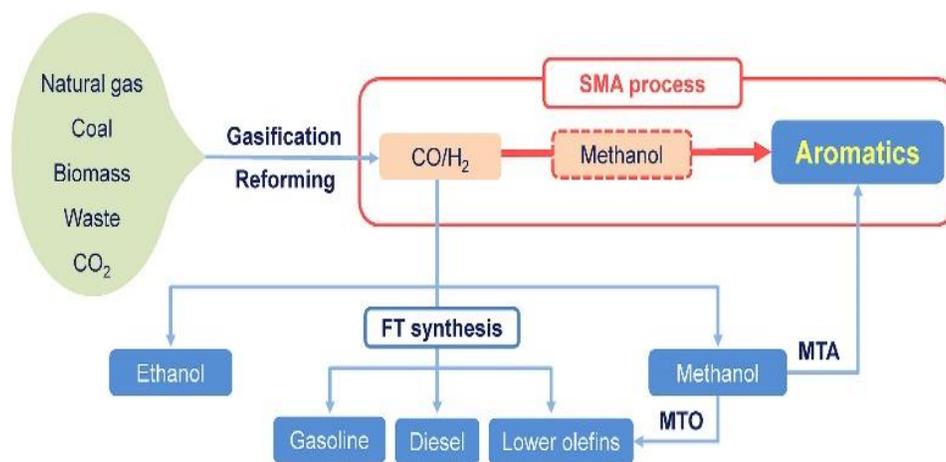
1231 Fan and coworkers reported this process has been catalyzed over a Ni-Co/MgO-ZrO₂
1232 nanomaterial, (Fan et al., 2011). The effect of Ni-based catalysts on the CO₂ reforming of
1233 methane had earlier been investigated by Takano et al., (1994). This process produces green
1234 hydrogen a quality of hydrogen which is otherwise generated via the electrolysis of water using a
1235 renewable energy source (Acar and Dincer 2022; Luo et al., 2022). This process could solve the
1236 problem of CO₂ emission during hydrogen production from classical techniques (Madadi
1237 Avargani et al., 2022). However, there is a fall-out associated with the production of green
1238 hydrogen via the method mentioned above; it involves the release of carbon(ii)oxide as a by-
1239 product. Although CO has a significant value as a fuel and is crucial in manufacturing other
1240 chemicals, it has been known over the years for its highly hazardous nature (Prockop and
1241 Chichkova 2007; Rose et al., 2017; Wu and Juurlink 2014) and toxicity. Studies should focus
1242 more on the production of hydrogen from CO₂, as this process is not well explored. This will go
1243 a long way in tackling the issue of global warming.

1244 **4.8 Olefins and gasoline**

1245 The hydrogenation of CO₂ into high molecular weight hydrocarbons such as lower olefins and
1246 gasoline has become increasingly popular due to the necessity to use non-fossil carbon resources

1247 as alternative to fossil oil for a sustainable production of liquid fuels and chemicals (Jiao et al.,
 1248 2016; Yang et al., 2017; Zhong et al., 2016). This process requires input energy to form C-H
 1249 bonds and to break C=O bonds (Dang et al., 2019) and efficient catalysts.

1250 Processes based on different catalysts and producing unique products distribution have been
 1251 developed in the past decades. A commonly used process is Fischer-Tropsch synthesis (FTS) that
 1252 yields typically straight-chain hydrocarbons controlled by the Anderson–Schulz–Flory (ASF)
 1253 product distribution, which restricts to C₂-C₄ hydrocarbon fraction of about 56.7% selectivity for
 1254 desired lower olefins (C₂⁻ - C₄⁻) with 29.2% of undesired CH₄ selectivity (Scheme 4). If
 1255 selective formation of lower olefins and low CH₄ formation can be achieved by proper catalyst
 1256 modification and optimization of reaction conditions (Chen et al., 2015; Liu et al., 2015; Lu et
 1257 al., 2014; Zhong et al., 2016; Zhou et al., 2015) achieve high selectivity for lower olefins and
 1258 high stability, requires to develop new catalysts that operate away from Anderson–Schulz–Flory
 1259 (ASF) distribution (Numpilai et al., 2017; Visconti et al., 2017; Zhang et al., 2015).



1260

1261 Scheme 4. Typical Reaction processes related to reduction of Syngas to hydrocarbons through
 1262 Fischer-Tropsch synthesis and methanol-to-Olefins Technology. (Adapted without change from
 1263 (Cheng et al., 2017)

1264 In recent years, significant progress in the development of new catalysts that increase the
1265 selectivity of product formed has been made. For instance bifunctional catalysts such as
1266 oxide/zeolite have been shown to increase selectivity for lower olefins (C_2^- – C_4^-) with significant
1267 inhibition of CH_4 formation (Jiao et al., 2016; Li et al., 2019; Liu et al., 2017). Bifunctional
1268 catalysts typically consist of oxides and zeolites, which activate CO_2 and catalyze C-C coupling,
1269 respectively. In a recent work Gao et al. obtained 80% C_2^- – C_4^- selectivity with ~ 4% CH_4
1270 inhibition among all hydrocarbons using In-Zr composite based oxides and SAPO-34 zeolites
1271 (Gao et al., 2018; Dang et al., 2018). In addition, CO selectivity over the bifunctional catalysts
1272 could be jacked up to 85 % during CO_2 reduction to lower olefins at high temperature reversed
1273 water-gas shift (RWGS).

1274 Moreover, the CO selectivity could be reduced if In_2O_3 is further modified by Zr and Zn
1275 promoters (Gao et al., 2017). The reduction of CO_2 to hydrocarbons over bifunctional catalysts
1276 involves hydrogenation of CO_2 to CH_xO species or intermediates on the oxygenated sites of the
1277 oxide component as the first step, and the migration of the intermediates to the zeolite
1278 component where they are transformed into various hydrocarbons at the acid sites of the zeolite
1279 (Cheng et al., 2017; Gao et al., 2017). The transport of the CH_xO intermediates plays a crucial
1280 role in suppressing the undesired RWGS side reaction and achieving a high selectivity and it can
1281 be improved by acid treatment of the zeolite crystals. The performance of bifunctional catalysts
1282 with and without acid treatment for In_2O_3 -ZnZrO_x/SAPO-34 composite is summarized in **Table**
1283 **5**. The maximum of C_2^- – C_4^- selectivity is 85 % among all hydrocarbons with 1.6 % CH_4 .
1284 Moreover, the decrease of zeolite crystal size (Dang et al., 2019) and shortening of the diffusion
1285 path of the methanol intermediates should favor the formation of lower olefins over the
1286 composite catalyst (Jiao et al., 2018; Yang et al., 2017).

1287 Table 5: Performance of In₂O₃-ZnZrO_x and SAPO-34 as bifunctional catalysts prior to and after
 1288 treatment with nitric acid (Dang et al., 2019)

Entr y	Catalyst type	Selectivity		CO ₂ conversion (%)	Hydrocarbon distribution			
		HC	CO		C ₂ ⁼ - C ₄ ⁼	C ₂ ^o -C ₄ ^o	C ₅₊	CH ₄
1.	In ₂ O ₃ - ZnZrO _x /SAPO- 34-S-a	17.0	44.2	55.8	85.0	11.1	2.3	1.6
2.	In ₂ O ₃ - ZnZrO _x /SAPO- 34-S	17.9	45.0	55.0	79.6	13.9	5.2	1.3
3.	In ₂ O ₃ - ZnZrO _x /SAPO- 34-S-H-a	17.0	46.6	53.4	84.5	11.0	3.3	1.2
4.	In ₂ O ₃ - ZnZrO _x /SAPO- 34-H	17.4	45.9	54.1	79.0	16.5	3.3	1.2
5.	In ₂ O ₃ - ZnZrO _x /SAPO-	17.2	46.2	53.8	80.6	15.2	2.9	1.3

34-C-a

6.	In ₂ O ₃ -	18.1	47.5	52.5	76.8	19.2	2.7	1.3
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ZnZrO_x/SAPO-

34-C

1289 **5. Conclusions and future outlook**

1290 Information gathered from recent literature confirms that continuous efforts are being made to
1291 reduce CO₂ in the environment. However, most articles are focused on its conversion to
1292 hydrocarbons, mainly methane, and other organic compounds, such as ethanol, methanol, and
1293 methanoic acid. Only limited articles were published on CO₂ reduction to either FMD (mostly as
1294 intermediates) or hydrogen. Thus, more reaction pathways that yield these products should be
1295 investigated. There are some challenges involved in CO₂ conversion into useful products, which
1296 should be considered. These include but are not limited to the production of harmful gases like
1297 CO, technological feasibilities in terms of more research as regards more-efficient conversion
1298 techniques, instability and low selectivity of the conversion products, and insufficient basic
1299 understanding of the catalytic processes (Sharma et al., 2022). Having pointed out these fall-outs,
1300 it is worth mentioning that scientists and other stakeholders should consider the project of CO₂
1301 conversion as germane because it technically solves the problem of global warming and, in turn,
1302 impacts the economy of the worldwide system.

1303 The use of nanomaterials-based technologies for the transformation of CO₂ is a relatively new
1304 area that scientists have to continue to explore. Unarguably, the demonstrated suitability,
1305 selectivity and applicability of nanomaterials for producing hydrocarbons and valued-added
1306 chemicals (methanol, ethanol, formic acid, formaldehyde, etc) have made nanomaterials

1307 promising systems for the transformation of CO₂ into various fuels. The research findings so far
1308 are quite intriguing at the laboratory scale. However, the extension of these findings to industrial
1309 scale would be highly phenomenal. It is therefore recommended and/or suggested industrially
1310 suitable, and applicable catalyst (nanomaterials) be developed to selectively and efficiently
1311 transformed atmospheric CO₂ to value-added products.

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1326 **References**

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