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## Nanomaterials as catalysts for CO<sub>2</sub> transformation into value-added products: A review

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 CO<sub>2</sub> Transformation into Value-added Products: A**  
2 **Review**

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### 33 **Abstract**

34 Carbon dioxide (CO<sub>2</sub>) is the most important greenhouse gas (GHG), accounting for  
35 76% of all GHG emissions. The atmospheric CO<sub>2</sub> 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 21<sup>st</sup> century. In addition to reducing CO<sub>2</sub> emissions from anthropogenic  
38 activities, strategies to adequately address climate change must include CO<sub>2</sub> capture. To  
39 promote circular economy, captured CO<sub>2</sub> 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 CO<sub>2</sub> capturing and/or transformation. This  
43 work critically reviewed the application of nanomaterials for the transformation of CO<sub>2</sub>  
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 CO<sub>2</sub> 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 CO<sub>2</sub> to fuels.

52 **Keywords:** CO<sub>2</sub> based fuels, nanomaterials, global warming, catalysts

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78 5. Conclusions and future outlook

79

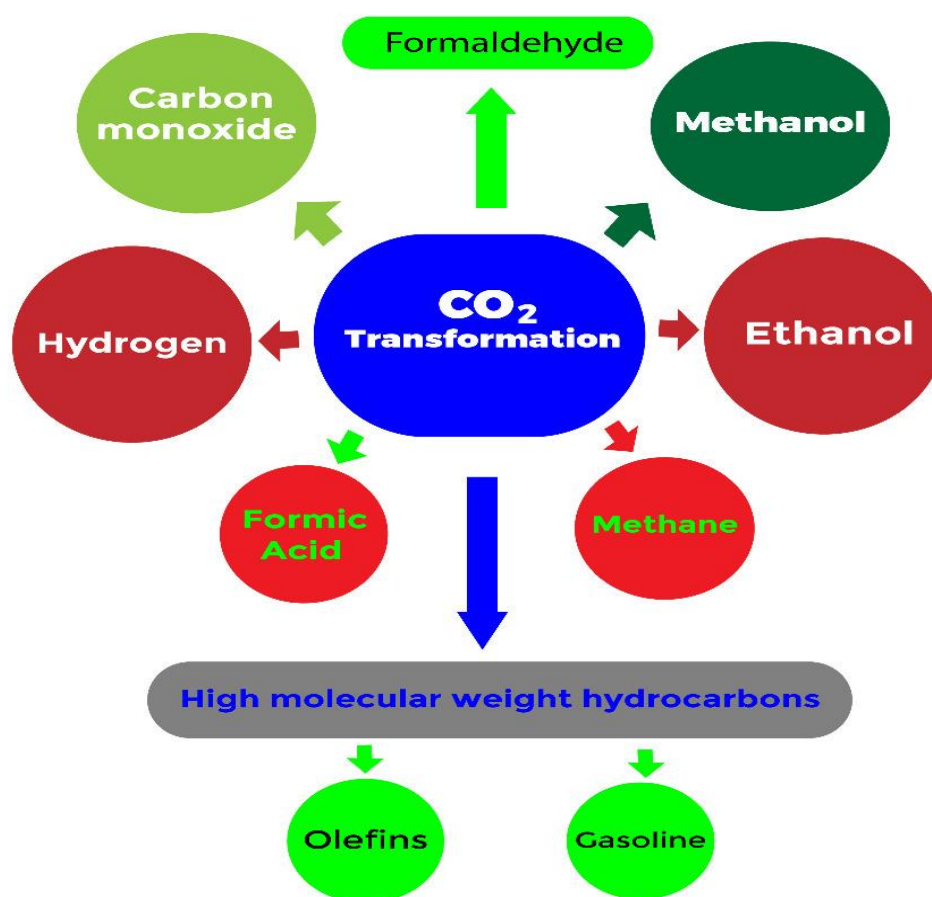
80 **1. Introduction**

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 CO<sub>2</sub> 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 CO<sub>2</sub> trend) and it is projected to  
93 reach 570 ppm by the end of the 21<sup>st</sup> century (Mustafa et al., 2020).

94 In order to ameliorate global warming and other climate change indicators, it is  
95 imperative that emission of CO<sub>2</sub> is controlled, and the excess atmospheric CO<sub>2</sub> is  
96 captured. Several strategies exist for achieving atmospheric CO<sub>2</sub> reduction. For  
97 instance, afforestation is effective for CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> conversion is also effective but is a herculean task due to the

103 characteristic thermodynamic stability of CO<sub>2</sub> molecule. The stability of CO<sub>2</sub> 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 CO<sub>2</sub> is extremely inactive and is kinetically  
106 inert owing to its occurrence at the highest oxidation state in CO<sub>2</sub> (Wang et al., 2022).  
107 As a result, the transformation of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. In terms of using  
115 catalysts for CO<sub>2</sub> 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 CO<sub>2</sub> reduction (Ateka et al., 2022). For  
118 example, in photo-catalyzed transformation using titanium dioxide (TiO<sub>2</sub>; a common  
119 photo-catalyst) as a catalyst, upon irradiation, a photo hole-electron pair is generated,  
120 which interacts with CO<sub>2</sub> and H<sub>2</sub>O 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 CO<sub>2</sub> transformation covered in this synthesis.



124

125                    Scheme 1: Products obtained from the transformation of CO<sub>2</sub>

126    A number of comprehensive, systematic and/or critical reviews on the transformation  
 127    of CO<sub>2</sub> 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 CO<sub>2</sub>, recent advances in technologies for CO<sub>2</sub> 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 CO<sub>2</sub> conversion

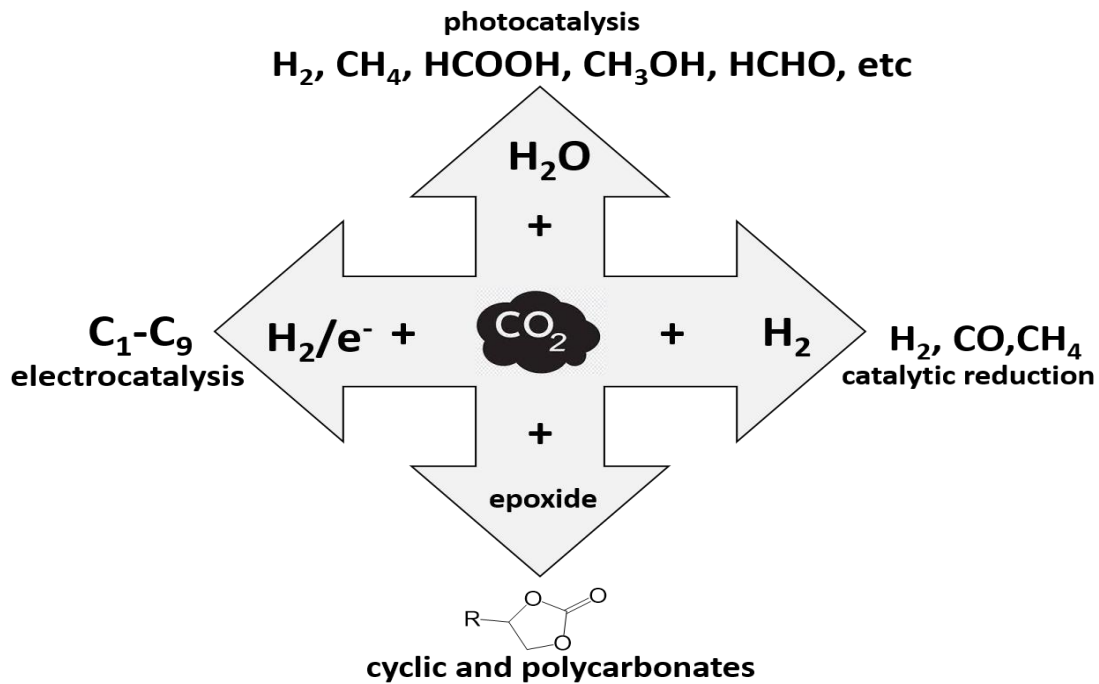
134 to valued-added products attempts to provide current and comprehensive understanding  
135 on nano-enabled CO<sub>2</sub> conversion, routes of CO<sub>2</sub> conversion, fuels generated from CO<sub>2</sub>  
136 conversion, application, technical issues and economic implications of transformation  
137 of CO<sub>2</sub> into hydrocarbon fuels. The review also elaborates the research gaps that need  
138 to be filled.

## 139 **2. Nanomaterials for CO<sub>2</sub> 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 CO<sub>2</sub>, 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 CO<sub>2</sub>, various nanoscale catalysts have been developed to activate CO<sub>2</sub>  
147 molecules into low (C<sub>1</sub>) and high hydrocarbon (C<sub>1</sub>-C<sub>9</sub>) molecules. Figure 1 depicts  
148 possible catalytic pathways for CO<sub>2</sub> transformation to fuels and chemical products.  
149 They include thermocatalytic reduction of CO<sub>2</sub>/H<sub>2</sub> to produce CH<sub>4</sub>/CO, electrocatalytic  
150 transformation of CO<sub>2</sub>/H<sub>2</sub>/electron to C<sub>1</sub>-C<sub>9</sub> hydrocarbons, cycloaddition of CO<sub>2</sub> with  
151 epoxide to form cyclic and polycarbonates, and the emerging photocatalytic reduction  
152 of CO<sub>2</sub>/H<sub>2</sub>O to CH<sub>4</sub>, CHOOH, CH<sub>3</sub>OH, etc. The nature and kinds of nanomaterials for  
153 conversion of CO<sub>2</sub> 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 H<sub>2</sub>/CO<sub>2</sub> ratios, and partial pressure condition of CO<sub>2</sub>. The nanomaterials for catalytic  
156 conversion of CO<sub>2</sub> 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  $\text{CO}_2$  to various feedstocks

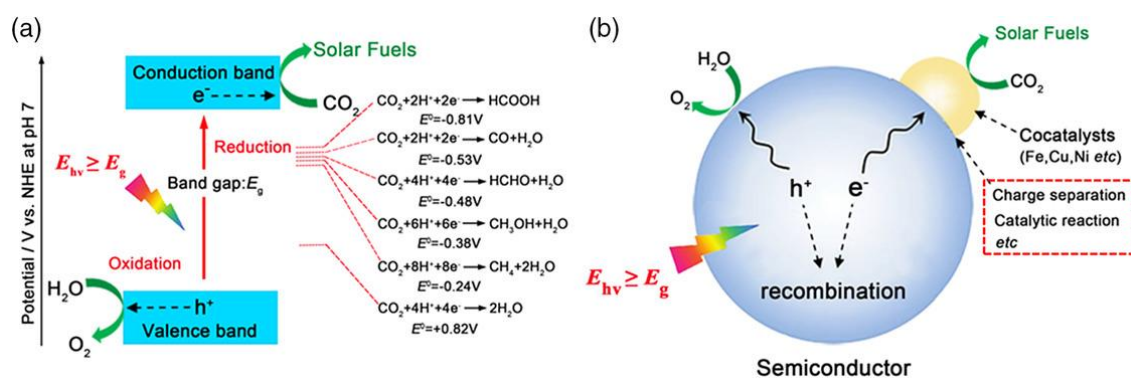
### 162 3. Routes of $\text{CO}_2$ conversion

#### 163 3.1 Photocatalytic transformation of $\text{CO}_2$

164 The natural process of photosynthesis, in which plants change  $\text{CO}_2$  and  $\text{H}_2\text{O}$  into  
 165 oxygen and carbohydrates when exposed to sunlight, served as the inspiration for  
 166 photocatalytic  $\text{CO}_2$  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  $\text{CO}_2$  fixation) reactions. The process  
 169 of photocatalytic transformation of  $\text{CO}_2$  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 CO<sub>2</sub> 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 CO<sub>2</sub> (at pH 7) is  
 177 presented in Figure 12a. Due to their extremely high negative reduction potentials  
 178 [E(CO<sub>2</sub>/CO<sub>2</sub><sup>•-</sup>) = -1.85 V vs NHE] in relation to the CB edges of many semiconductors,  
 179 one-electron reduction processes of CO<sub>2</sub>, such as the generation of CO<sub>2</sub><sup>•-</sup>, are not  
 180 practical (Lingampalli et al., 2017). A highly negative reduction potential results from  
 181 the conversion of C's sp<sup>2</sup> to sp<sup>3</sup> hybridization. Reduction potentials for HCOOH,  
 182 HCHO, CH<sub>3</sub>OH, and CH<sub>4</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. This section  
 189 critically survey the scattered literatures



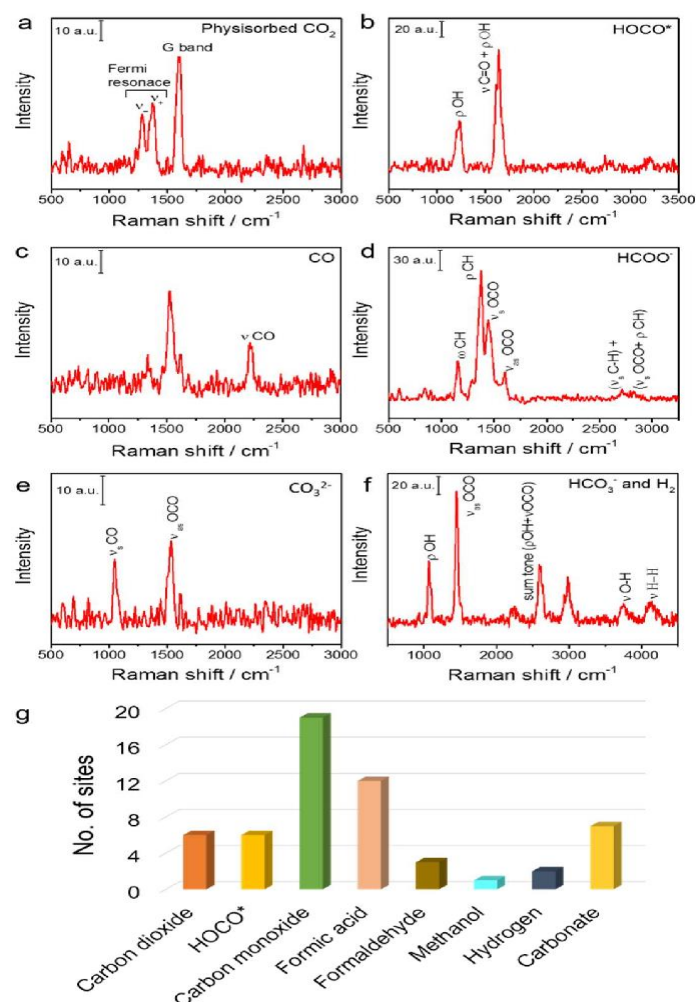
190  
 191 Figure 2: (a) Energy diagram for CO<sub>2</sub> reduction and water oxidation on a  
 192 semiconductor. b) A schematic representation of the overall photocatalytic reaction

193 process, demonstrating elements that may influence photocatalytic performance.  
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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 CO<sub>2</sub> led to CO<sub>2</sub> reduction reaction CO<sub>2</sub>RR, to  
204 CO and HCOOH. The synergy between photoexcited CO<sub>2</sub> 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 CO<sub>2</sub> on nanoparticles, LSPR-triggered CO<sub>2</sub> activation to HOCO\*  
208 (intermediate), followed by transformation of HOCO\* to multiple products (H<sub>2</sub>, CO,  
209 HCOOH, HCHO and CH<sub>3</sub>OH), (see Figure 3). The real-time monitoring of CO<sub>2</sub>RR  
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 CO<sub>2</sub> to C<sub>1</sub> (methane) and C<sub>2</sub> (ethane) hydrocarbons, without formation of  
214 CO (Yu et al., 2018). The CO<sub>2</sub>RR was conducted in isopropyl alcohol (IPA) saturated  
215 CO<sub>2</sub>-aqueous solution to prevent h<sup>+</sup>/e<sup>-</sup> recombination during photoredox reaction, and  
216 the CO<sub>2</sub>RR selectively produced CH<sub>4</sub> (6.8 NP<sup>-1</sup>) and C<sub>2</sub>H<sub>6</sub> (5.6 NP<sup>-1</sup>) after 10 h of light  
217 irradiation. The results show that catalytic and selectivity of plasmonic gold

218 nanoparticles (AuNPs) for CO<sub>2</sub> transformation to C<sub>1</sub> and C<sub>2</sub> is modulated by laser  
219 excitation wavelength (photon energy), and photon flux (light intensity). Thus, the CH<sub>4</sub>  
220 production rate increased with decreasing excitation wavelength and with overall 8e<sup>-</sup>  
221 process ( $8\text{H}^+ + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ ), while C<sub>2</sub>H<sub>6</sub> production was only observed at  
222 lower excitation wavelength with 14e<sup>-</sup> 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 CO<sub>2</sub> reduction to CO, H<sub>2</sub> and  
225 CH<sub>4</sub>. 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 H<sub>2</sub> and CH<sub>4</sub> on TPB-Cu remained  
228 relatively constant, implying that incorporating plasmonic CuNPs into TPB increased  
229 the directional selectivity for CO formation over H<sub>2</sub> and CH<sub>4</sub>. 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 CO<sub>2</sub> reduction on Ag NPs. Specific species captured include  
 235 (a) physisorbed CO<sub>2</sub>, (b) HOCO\* reaction intermediate, (c) carbon monoxide or CO, (d)  
 236 formate ion or HCOO<sup>-</sup>, (e) carbonate or CO<sub>3</sub><sup>2-</sup>, (f) bicarbonate or HCO<sub>3</sub><sup>-</sup>, adsorbed  
 237 hydroxide or OH\*, and H<sub>2</sub>, 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

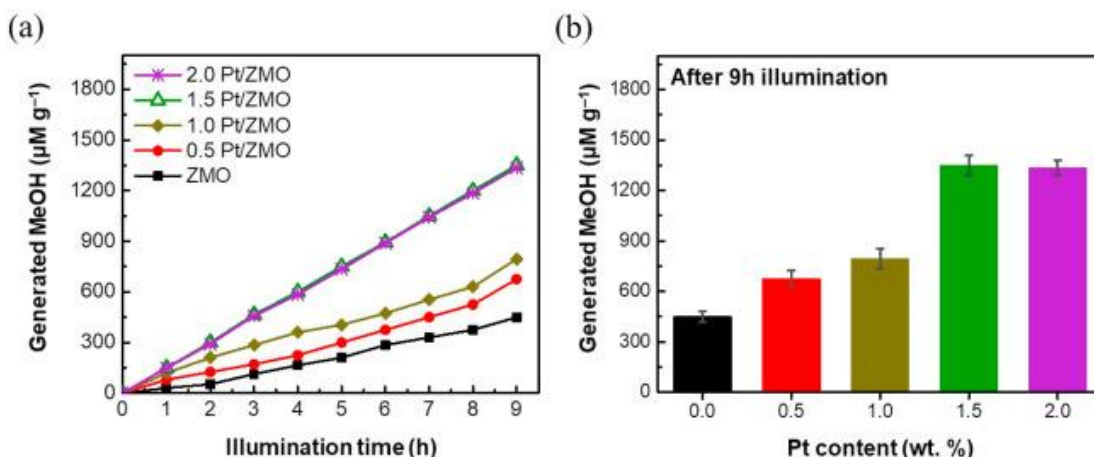
243 turned to multi-component semiconductors for a variety of applications. Decoration of  
244 metal oxide semiconductors with transition or plasmonic metals has been a huge  
245 success. Both plasmonic and transition metals on semiconductors can help harness UV  
246 and visible light by reducing energy band gaps, which play key roles in CO<sub>2</sub> activation  
247 and intermediates stabilization for CO<sub>2</sub>RR.

248 For many years, the selective absolute conversion of CO<sub>2</sub> 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 (TiO<sub>2</sub>/WO<sub>3</sub>-AgHNPs) for CO<sub>2</sub> reduction to CO (100%, without  
252 byproducts) and with an evolution rate of 1166.72 μmol g<sup>-1</sup> h<sup>-1</sup> 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<sup>-1</sup> h<sup>-1</sup>, and facilitated intense absorption light  
255 in the visible region of the catalysts due to its strong LSPR effect. The presence of Ti<sup>3+</sup>  
256 states in the catalysts, on the other hand, facilitated the physisorption, stabilization, and  
257 reorientation of the intermediates formed during CO<sub>2</sub> reduction. Other gas products  
258 such as CH<sub>4</sub> and H<sub>2</sub> 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 Cu<sub>2</sub>O photocatalysts with phase  
261 structures of 100 (100Cu<sub>2</sub>O) and 111 (100Cu<sub>2</sub>O) modified with Pd nanoparticles for  
262 CO<sub>2</sub>RR activities. The well-matched band alignments between Pd and 100Cu<sub>2</sub>O  
263 increased the work functions (Ws) of the 100Cu<sub>2</sub>O-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 100Cu<sub>2</sub>O nanoparticles. Pd nanoparticles (in 100Cu<sub>2</sub>O-Pd)  
266 promoted efficient photoexcited electrons by acting as a photoinduced hole scavenger,  
267 and also improved photostability of 100Cu<sub>2</sub>O-Pd by reducing photocorrosion.

268 However, 111Cu<sub>2</sub>O-Pd composites lacked electron-hole mobility due to mismatched  
269 band structures between 111Cu<sub>2</sub>O and Pd species, resulting in lower work function and  
270 poor photocatalytic CO<sub>2</sub>RR compared to 100Cu<sub>2</sub>O-Pd composites, emphasizing the  
271 importance of crystal surface structure and matched band structure construction for  
272 selective CO<sub>2</sub>RR 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 CO<sub>2</sub>  
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<sup>-1</sup>.  
278 The rate-determining step in the thermal process was the formation of reaction  
279 intermediates (\*HCOO, \*HCOOH, and \*H<sub>2</sub>COOH 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 ZnMn<sub>2</sub>O<sub>4</sub> nanorods as visible-  
286 light-driven catalysts for promoting CO<sub>2</sub> 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 CO<sub>2</sub>RR 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 CO<sub>2</sub> to  
292 MeOH with an evolution rate of 1,906 μmol/g within 9 h.



293

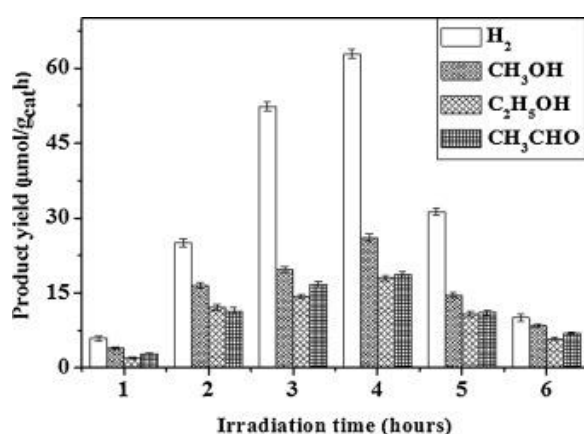
294 Figure 4: (a) Photocatalytic generation of methanol over Pt/ZMO nanocomposites at  
 295 different illumination time, and (b) impact of Pt content in Pt/ZMO composite for a  
 296 dose of 1.0 g/L for each within 9 h of light illumination. Reproduced from (Alhaddad  
 297 and Shawky, 2021) with permission.

298

299 V, Cr, and Co loaded on TiO<sub>2</sub> were studied for CO<sub>2</sub>RR to produce H<sub>2</sub>, C<sub>1</sub> and C<sub>2+</sub>.  
 300 Higher photoconversion rates were observed compared to pristine TiO<sub>2</sub>, which were  
 301 found to be sensitive to the metal concentrations and TiO<sub>2</sub> crystallite size modification  
 302 (Ola and Maroto-Valer, 2015). After 4 h of illumination, 1wt% Co-TiO<sub>2</sub> demonstrated  
 303 the highest photoconversion rates of 62.91 μmol/g<sub>cat</sub>h for H<sub>2</sub> and 26.12 μmol/g<sub>cat</sub>h for  
 304 MeOH (Figure 5). Ni-modified CeO<sub>2</sub>, MgO, α-Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> NPs were studied for  
 305 CO<sub>2</sub> methanation, and the effects of the solid supports were elucidated (Tada et al.,  
 306 2012). CO<sub>2</sub> methanation pathways followed two steps: (i) reaction of CO<sub>2</sub> and H<sub>2</sub> at the  
 307 meta/metal oxide interfaces to afford CO through reverse water gas shift reaction (CO<sub>2</sub>  
 308 + H<sub>2</sub> → CO + H<sub>2</sub>O), and (ii) prompt methanation of CO with H<sub>2</sub> (CO + 3H<sub>2</sub> → CH<sub>4</sub> +  
 309 H<sub>2</sub>O) at low temperature via the Fisher–Tropsch synthesis (FTs). CeO<sub>2</sub> has the highest  
 310 number of CO<sub>2</sub> adsorption sites and exhibits the highest CO<sub>2</sub> methanation with near-  
 311 unity CH<sub>4</sub> selectivity. Li and co-workers showed that partially oxidized metallic Fe NPs



312 (Fe and FeO<sub>x</sub>) deposited on MgO-Al<sub>2</sub>O<sub>3</sub> and then reduced under H<sub>2</sub> at different  
313 temperatures photothermally hydrogenated CO<sub>2</sub> into C<sub>1</sub> and C<sub>2+</sub> hydrocarbons (Li et al.,  
314 2021). The Fe-500 sample (reduction performed at 500°C) showed the highest CO<sub>2</sub>  
315 conversion and excellent selectivity for C<sub>2+</sub> hydrocarbons with 0% CO. The FeO<sub>x</sub> phase  
316 promotes CO<sub>2</sub> reduction to CO via RGSW reaction and modulates the electronic  
317 properties of Fe phase to suppress CH<sub>2</sub> and CH<sub>3</sub> hydrogenation, thus enhancing C<sub>2+</sub>  
318 hydrocarbon formation.



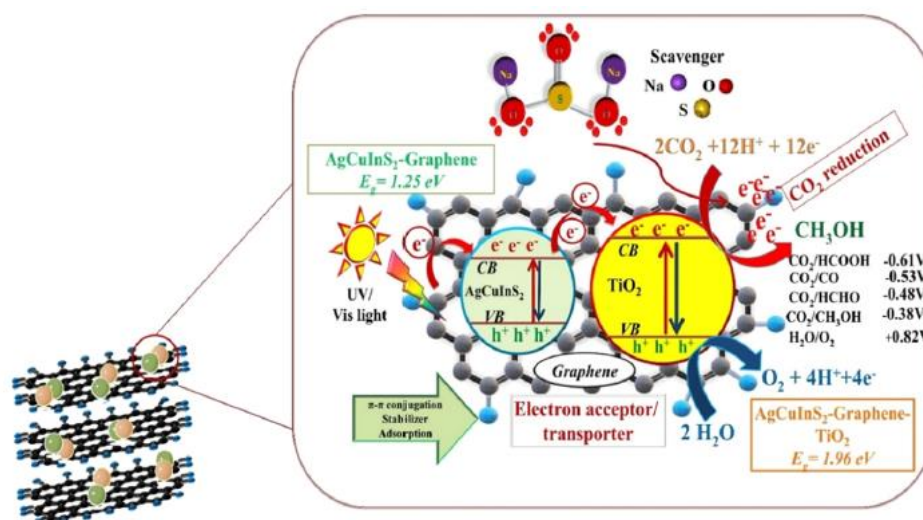
319

320 Figure 5: Irradiation time profile of 1 wt%Co–TiO<sub>2</sub> for CO<sub>2</sub> 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. InS<sub>2</sub> has been  
324 reported to improve photocatalytic reduction of CO<sub>2</sub> activity. Recently, a quaternary  
325 nanocomposite (AgCuInS<sub>2</sub>) deposited on a graphene-TiO<sub>2</sub> based material presented  
326 excellent photoreduction activity of carbon dioxide in H<sub>2</sub>O with the formation of  
327 mostly methanol, formaldehyde and formic acid. AgCuInS<sub>2</sub> combined with TiO<sub>2</sub>  
328 semiconductors (AgCuInS<sub>2</sub>–TiO<sub>2</sub>) 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



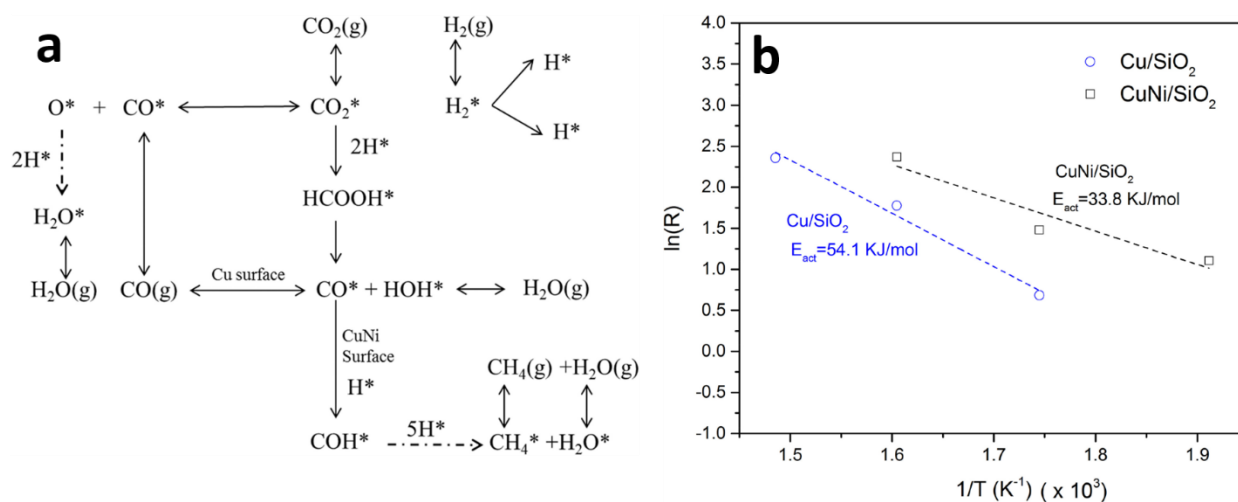
332

333 Figure 6: Mechanism of photocatalytic CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>  
340 adsorption and conversion (Petrovic et al., 2021). The nature of metal species  
341 immobilized on porous oxides also influences the CO<sub>2</sub>RR selectivity for either CO or  
342 CH<sub>4</sub>. Deposition of Ni on CaO-Al<sub>2</sub>O<sub>3</sub> showed CO<sub>2</sub> conversion with 81% selectivity to  
343 CH<sub>4</sub>; 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 CO<sub>2</sub>RR on metal/mesoporous materials is required (Mutz et al., 2015).  
346 Addition of La as a second metal to Ni/-Al<sub>2</sub>O<sub>3</sub>, enhanced direct CO<sub>2</sub> methanation (CO<sub>2</sub>  
347 + H<sub>2</sub> → CO + H<sub>2</sub>O) via the Sabatier reaction, increasing the CO<sub>2</sub> conversion rate to  
348 CH<sub>4</sub> from 42% to 80.3% (Rahmani et al., 2019). CO<sub>2</sub> 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<sub>cat</sub>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.



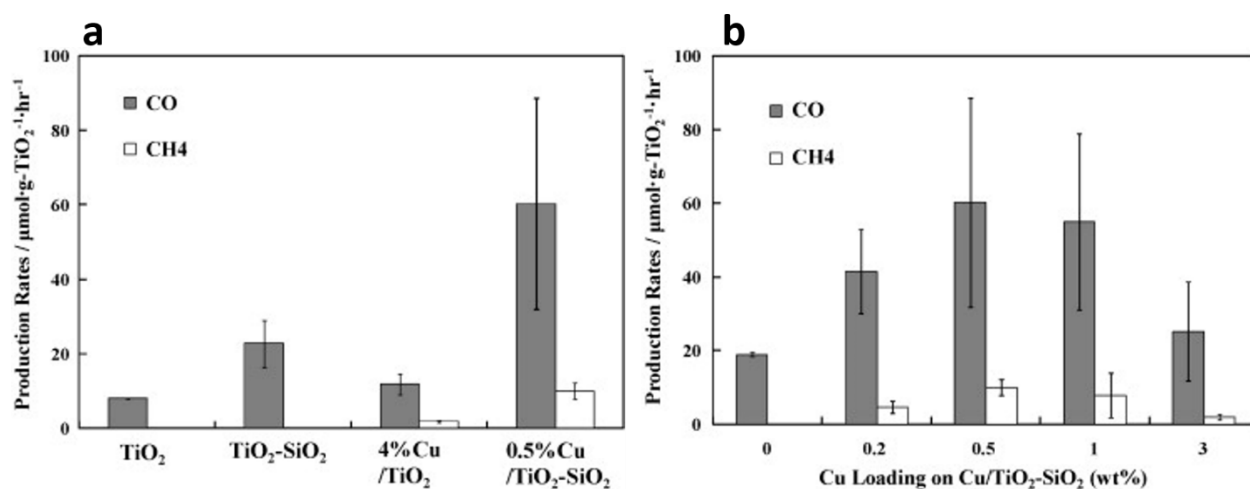
359  
 360 Figure 7: (a) Proposed reaction pathways on Cu/fumed-SiO<sub>2</sub> and CuNi/fumed-SiO<sub>2</sub>  
 361 surface (b) Activation energy calculation for  $CO_2$  conversion reaction over Cu/fumed-  
 362 SiO<sub>2</sub> and CuNi/fumed-SiO<sub>2</sub>. Reproduced from (Kumar et al., 2022) with 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 CH<sub>4</sub> or CH<sub>3</sub>OH because they lead preferentially to the  
368 formation of CO via RWGS reaction. For example, CuNi/fumed-SiO<sub>2</sub> showed  
369 enhanced activity and selectivity for CO, as well as a tendency for methanation to CH<sub>4</sub>  
370 via interaction of CO and neighboring H, whereas Cu/fumed-SiO<sub>2</sub> 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 CO<sub>2</sub>RR to CO and CH<sub>4</sub>, Figure 7b.  
374 Mesoporous Cu/SiO<sub>2</sub> doped with Ga and/or Zn had greater catalytic activity for direct  
375 CO<sub>2</sub> reduction to MeOH than undoped Cu/SiO<sub>2</sub> (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 TiO<sub>2</sub>/SiO<sub>2</sub> was irradiated with visible light without Cu species, CO  
381 was the main product of photo-transformation of CO<sub>2</sub>/H<sub>2</sub>O (Li et al., 2010). Cu  
382 deposition on TiO<sub>2</sub>/SiO<sub>2</sub> improved photoreduction of CO<sub>2</sub> to CO, and CH<sub>4</sub> selectivity  
383 increased as well, peaking at 0.5wt% optimum Cu specie on TiO<sub>2</sub>/SiO<sub>2</sub> (Figure 8). XPS  
384 allowed to identify the deposited Cu species as Cu<sub>2</sub>O, 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 CO<sub>2</sub> to CO and CH<sub>4</sub>. Fu *et*  
387 *al.* designed photocatalytic systems based on CoO and Co<sub>3</sub>O<sub>4</sub> nanoparticles to convert  
388 CO<sub>2</sub> to CO using bare CoONPs, CoO/s-SiO<sub>2</sub>, CoO/s-SBA-15, and Co<sub>3</sub>O<sub>4</sub>/s-SBA-15 (Fu  
389 et al., 2019). Under similar photoredox conditions, CoO/s-SBA-15 exhibited the best  
390 activity for CO<sub>2</sub>RR 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 CO<sub>2</sub> reduction to CO over CoO/s-SBA-15 catalyst  
393 system.



394

395 Figure 8: (a) Peak production rates of CO and CH<sub>4</sub> on various TiO<sub>2</sub>-containing  
396 catalysts, and (b) Peak production rates of CO and CH<sub>4</sub> as a function of Cu loading in  
397 Cu/TiO<sub>2</sub>-SiO<sub>2</sub> catalysts. Reproduced from (Li et al., 2010) with permission.

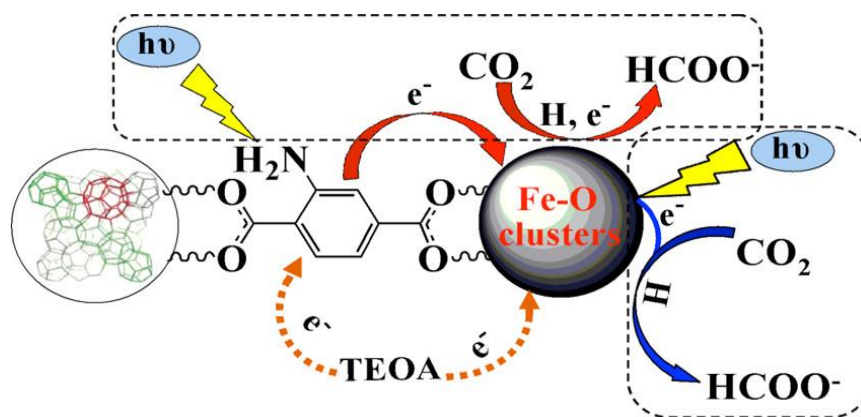
### 398 3.1.4 Inorganic/organic nanocomposites

#### 399 3.1.4.1 Metal-organic frameworks (MOF) nanomaterials

400 MOFs are recognized as catalytic systems of choice for CO<sub>2</sub>RR 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 CO<sub>2</sub> 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 CO<sub>2</sub> reduction (Ejeromedoghene et al., 2022). Wang and coworkers  
408 investigated the photocatalytic conversion of CO<sub>2</sub> 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. NH<sub>2</sub>-MIL-101(Fe), a framework composed of FeO clusters and 2-  
412 aminoterephthalic acid (H<sub>2</sub>ATA) ligands prepared in dimethylformamide (DMF),  
413 exhibits the best catalytic activity, to generate HCOO<sup>-</sup> at the evolution rate of 178  
414 μmol/g (Wang et al., 2014). Mechanistic pathways for enhanced activities include  
415 excitation of NH<sub>2</sub> 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 CO<sub>2</sub>RR over a series of UiO-based MOFs photocatalysts modified with different  
418 functional groups (F, NH<sub>2</sub>, OCH<sub>3</sub>, CH<sub>3</sub>) (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-NH<sub>2</sub> < UiO-  
421 68-CH<sub>3</sub> < UiO-68-OCH<sub>3</sub>. The superior performance of UiO-68-OCH<sub>3</sub> was attributed to  
422 the pronounced charge separation efficiency of OCH<sub>3</sub>. Crake et al. investigated  
423 applicability of titanium dioxide/carbon nitride (TiO<sub>2</sub>/CNNS) nanosheet  
424 nanocomposites in photoreduction of CO<sub>2</sub> (Crake et al., 2019). They found that  
425 TiO<sub>2</sub>/CNNS possessed improved CO<sub>2</sub> 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} TiO<sub>2</sub> facets was the most  
428 catalytically active and this is attributed to enhanced charge transfer at the TiO<sub>2</sub>/CNNS  
429 heterojunction interface. Previously, Crake et al (Crake et al. 2017) coupled NH<sub>2</sub>-UiO-  
430 66 onto pre-formed TiO<sub>2</sub> nanosheets via *in situ* process to develop TiO<sub>2</sub>/NH<sub>2</sub>-UiO-66  
431 heterojunction with permanent pore sizes and exposed catalytic active sites for  
432 enhance CO<sub>2</sub> uptake and photoreduction of adsorbed CO<sub>2</sub> to CO under UV-visible  
433 light. The evolution rate of CO<sub>2</sub>-to-CO conversion over the bound nanocomposite was  
434 1.9 times more than that of pure TiO<sub>2</sub>. Interestingly, the photoreduction efficiency of

435 mechanically blended TiO<sub>2</sub> and NH<sub>2</sub>-UiO-66 is comparable to pure TiO<sub>2</sub>, proving that  
 436 *in situ* growth method was necessary for the enhanced catalytic activity. Transient  
 437 absorption spectroscopy confirmed that the increased photoactivity of TiO<sub>2</sub>/NH<sub>2</sub>-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 CO<sub>2</sub> to formate. Reproduced from (Wang et al., 2014) with  
 442 permission.

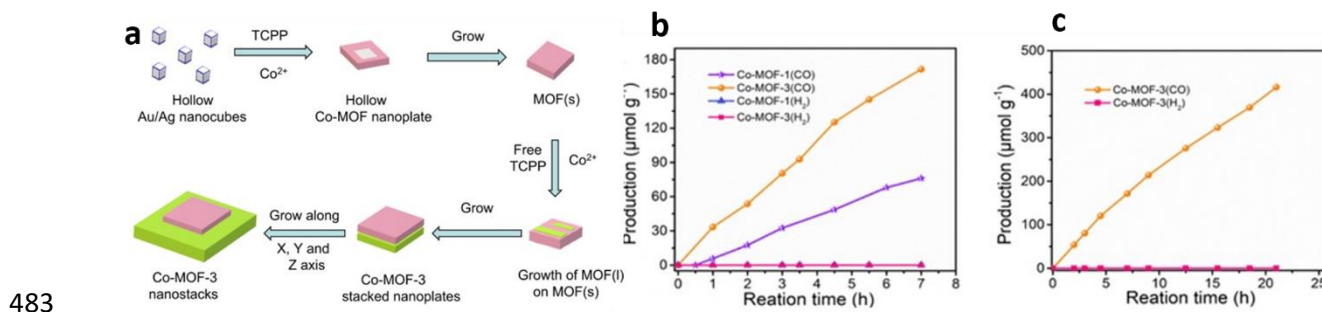
443 Besides the use of MOFs with multidentate linkers and different functional groups,  
 444 multi-metallic MOFs can also offer improved stability and overall catalytic efficiency  
 445 for CO<sub>2</sub> reduction in comparison to monometallic counterparts. Different MOFs with  
 446 multi-metallic nodes have been explored for CO<sub>2</sub>RR. 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-TiO<sub>2</sub>/CPO-Cu MOF nanocomposites were  
 453 fabricated where CPO-Cu-27MOF is supported on 0.12%Fe-0.5%N-codoped TiO<sub>2</sub>

454 leading to effective photocatalytic reduction of CO<sub>2</sub> (khalilzadeh and Shariati, 2019).  
455 Reduction efficiency of Fe-N-TiO<sub>2</sub>/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 CO<sub>2</sub> to methane. The performance  
458 achieved is ca. 1.7 times higher than in the case of CO<sub>2</sub> methanation over Fe-NTiO<sub>2</sub>.  
459 Liu *et al.* reported visible-light-driven CO<sub>2</sub> 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 CO<sub>2</sub>  
462 photoreduction efficiency than Co-MOF-1 with single nanoplate ( Figure 9). The Co-  
463 MOF-3 homojunction system demonstrated a high CO<sub>2</sub> 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 CO<sub>2</sub>RR 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 CO<sub>2</sub> photoconversion catalytic  
472 system. The presence of a hydrophobic ligand improves the chemical stability of NNU-  
473 29 and reduces H<sub>2</sub> generation due to water attack to some extent, resulting in 98%  
474 selectivity for CO<sub>2</sub> reduction to HCOOH in aqueous solution after 16h of light  
475 irradiation. Wang *et al.* (Wang et al., 2021) recently proposed SO<sub>3</sub>H-MIL-101-Cr  
476 (SO<sub>3</sub>H-MOF) supported silicomolybdic acid (SMA) as a host-guest composite for CO<sub>2</sub>  
477 photoreduction. Pristine POM and MOF have negligible CO<sub>2</sub>-to-CO activity compared  
478 to SO<sub>3</sub>H-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 CO<sub>2</sub> 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 H<sub>2</sub> as a function of reaction time during the  
 486 CO<sub>2</sub> reduction under visible-light irradiation for Co-MOF-1 and Co-MOF-3  
 487 photocatalysts. (c) Stability of Co-MOF-3 during the continuous CO<sub>2</sub> 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 CO<sub>2</sub>RR 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 CO<sub>2</sub>RR performance (Shen et al., 2020). Several reports have shown that GO can

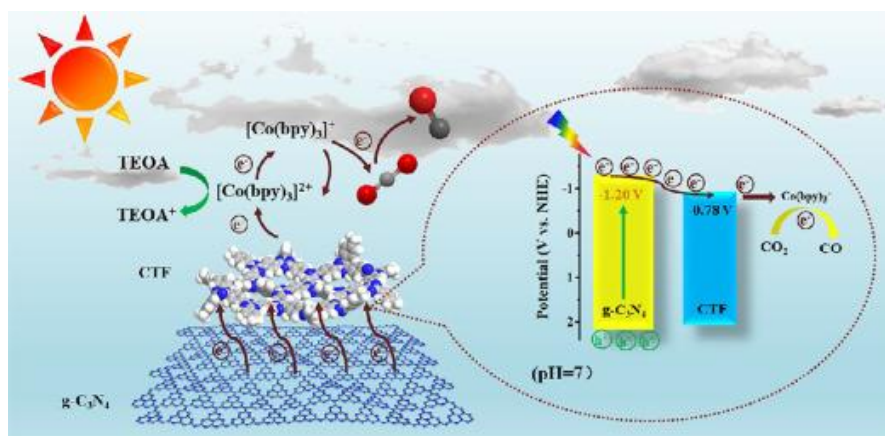
500 act by itself as a photocatalyst for CO<sub>2</sub> reduction either by adapting its method of  
501 preparation or through UV-Vis light-induced activation of pristine GO (Kuang et al.,  
502 2020). Hsu *et al.* (Hsu et al., 2013) studied the effect of volume of H<sub>3</sub>PO<sub>4</sub> used as a  
503 mild oxidizer to prevent overoxidation of pristine GO on the CO<sub>2</sub>RR performance.  
504 Their results show that modified GOs have increased visible light absorption and  
505 improved CO<sub>2</sub> photoreduction to MeOH compared to pristine GO. The CO<sub>2</sub>-to-MeOH  
506 conversion rate of GO-3 with excess H<sub>3</sub>PO<sub>4</sub> was found 6-fold higher than with pure  
507 TiO<sub>2</sub>. Kuang *et al.* (Kuang et al., 2020) reported on the photoreduction of CO<sub>2</sub> to CO  
508 over GO activated either by UV or simulated sunlight. GO activated by simulated-  
509 sunlight provided the highest CO<sub>2</sub> 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  $\pi$ -  
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 CO<sub>2</sub> to CO and CH<sub>4</sub> under UV light (Yang et al., 2019). The  
517 sample containing 2% rGO had the highest CO<sub>2</sub> reduction efficiency and selectivity for  
518 CO and CH<sub>4</sub> 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 CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>/H<sub>2</sub>O to gaseous fuels  
534 (Arumugam et al., 2022) among which S-doped gCN showed the highest CO<sub>2</sub>-to-CH<sub>4</sub>  
535 conversion rate compared to others. Imaging studies showed that bare g-C<sub>3</sub>N<sub>4</sub> has a  
536 thin-layered structure with irregular porosity, whereas S-doped g-C<sub>3</sub>N<sub>4</sub> has a denser  
537 structure with a homogenous distribution of S atoms on the g-C<sub>3</sub>N<sub>4</sub> matrix, suggesting  
538 that S atom can act as an electron sink for improved activity. Doping of S atoms into g-  
539 C<sub>3</sub>N<sub>4</sub> did not enhance the surface area or modify the energy band gap of g-C<sub>3</sub>N<sub>4</sub>; 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-C<sub>3</sub>N<sub>4</sub> from  
543 an irregular morphology into a supramolecular hydrogen-bonded network intermediate;  
544 and that subsequent heating of the intermediate under NH<sub>3</sub> atmosphere led to the  
545 formation of porous TCN(NH<sub>3</sub>) 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 CO<sub>2</sub>-to-CO conversion rate of porous TCN(NH<sub>3</sub>) nanotubes was  
548 17 and 15 times that of bulk g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub>, respectively. Tubular structure of  
549 TCN(NH<sub>3</sub>) 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  $\text{CO}_2$  to  $\text{CH}_4$  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  $\text{CO}_2$  to fuel conversion rate. The  $\text{CO}_2$  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  $\text{CO}_2$  by amine functional groups.



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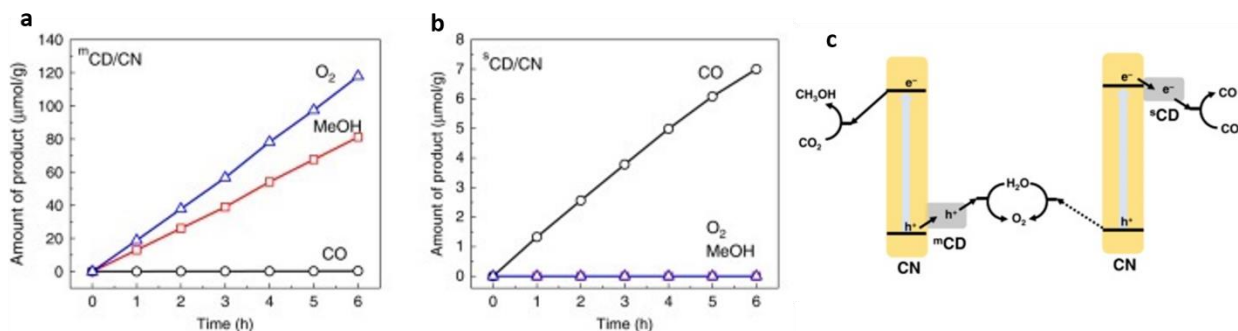
561 Figure 10: Schematic view and mechanism of CN/CTF heterostructure for  
 562 photocatalytic  $\text{CO}_2$  reduction. Reproduced with permission from ref. (He et al., 2022).

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  $\text{CO}_2$  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  $\text{CO}_2$  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 CO<sub>2</sub> 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)<sub>3</sub>]<sup>2+</sup>, 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 CO<sub>2</sub>  
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 CO<sub>2</sub>  
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 CO<sub>2</sub> 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 <sup>m</sup>CDs, 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 <sup>s</sup>CD was  
588 barely located in the phase structure of CN/<sup>s</sup>CD composite following heterojunction  
589 formation, indicating weak interaction between the two phases. <sup>m</sup>CD features near-  
590 crystallized graphitic structures, whereas <sup>s</sup>CD is composed of amorphous carbons;  
591 hence, the photocatalytic functions of <sup>m</sup>CD/CN and <sup>s</sup>CD/CN are notably distinct.  
592 According to this study, <sup>m</sup>CD/CN photoreduces CO<sub>2</sub> to 6e<sup>-</sup> product MeOH (Figure  
593 11a), while <sup>s</sup>CD/CN favors formation of 2e<sup>-</sup> product CO (Figure 11b). The authors

594 attributed the improved  $^m\text{CD}/\text{CN}$  reduction efficiency to the hole-accepting role of  
 595  $^m\text{CD}$ , 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)  $^m\text{CD}/\text{CN}$  for methanol formation, and (b)  
 599  $^s\text{CD}/\text{CN}$  for CO formation measured under visible light ( $\lambda > 420 \text{ nm}$ ). (c) Schematic  
 600 diagram of photocatalytic  $\text{CO}_2$  reduction by the  $^m\text{CD}/\text{CN}$  and  $^s\text{CD}/\text{CN}$ . 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  $\text{CO}_2$  (see Table S1  
 604 in the supplementary information)

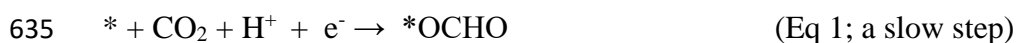
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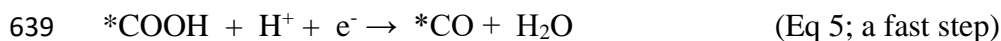
### 606 3.2. Electrochemical transformation of $\text{CO}_2$

607 The electrochemical transformation of  $\text{CO}_2$  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

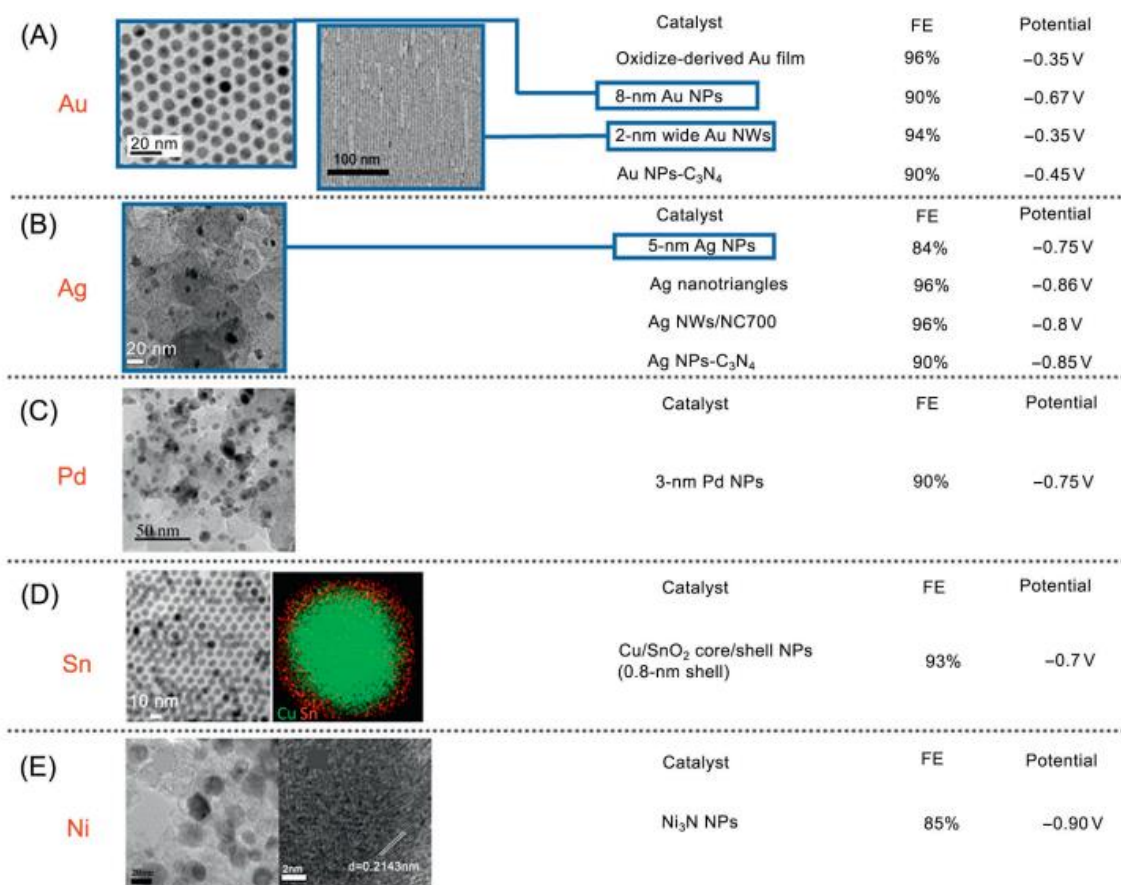
614 distance it can travel to the interface, and its relative orientation to the interface are all  
615 influenced by the bilayer structure which is thus essential for the rate and efficiency of  
616 the electrochemical CO<sub>2</sub>RR. Electrochemical CO<sub>2</sub>RR can produce useful chemicals 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 CO<sub>2</sub> are cyclic voltammetry  
621 (CV) and linear sweep voltammetry (LSV). The catalytic performance can also be  
622 evaluated using chronoamperometry. These CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> conversion. In general, a heterogeneous catalyst deposited on the  
631 electrode surface or a homogeneous catalyst dissolved in solution are used in  
632 electrocatalytic CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>RR 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 CO<sub>2</sub>RR (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 H<sub>2</sub> with no phase transition during CO<sub>2</sub>RR.

660 Li et al. (Z. Li et al., 2022) studied electrochemical CO<sub>2</sub>RR to formate, which not only  
661 has the potential to reduce the issue of global warming brought on by CO<sub>2</sub>, 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 CO<sub>2</sub> 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/cm<sup>2</sup> and an astonishingly high faradaic efficiency of roughly 94.8%. The  
667 production of formate at a remarkable rate of 634.3 mol/cm<sup>2</sup>h -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 CO<sub>2</sub>\* intermediate. Additionally,  
670 they produced a metastable metal oxide/metal interface that helped to stabilize the  
671 CO<sub>2</sub>\*-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 CO<sub>2</sub> to formate. According to these results, Bi/Sn  
674 bimetallic catalysts are a viable option for very effective CO<sub>2</sub> reduction.

675 In contrast, the conversion of CO<sub>2</sub> to CO and formate is less difficult than CO<sub>2</sub>RR 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 Cu<sub>2</sub>O are  
678 regarded as the most common and effective electrocatalysts for CO<sub>2</sub>RR. 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 Al<sub>2</sub>CuO<sub>4</sub> nanosheets uniformly coated with CuO nanoparticles (CuAl-1: CuO/Al<sub>2</sub> 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 CO<sub>2</sub>RR can produce a wide range of hydrocarbons at a high catalytic  
691 activity. For selective CO<sub>2</sub>RR, Yin et al. (Yin et al., 2019) used a catalyst based on  
692 copper nitride (Cu<sub>3</sub>N) nanocubes (NC). With a FE of 60%, a mass activity of 34 A/g, a  
693 C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> molar ratio over than 2000, and strong selectivity and stability of CO<sub>2</sub>RR  
694 towards ethylene at -1.6 V vs. RHE, their 25 nm Cu<sub>3</sub>N NCs showed good performance.  
695 This lacks of product selectivity is a significant barrier to the use of these catalysts for

696 selective CO<sub>2</sub>RR, 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/Cu<sub>2</sub>O  
700 heterogeneous surfaces after CO<sub>2</sub>RR (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<sup>-2</sup> 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/Cu<sub>2</sub>O interfaces, and improved  
705 adsorption of the intermediate \*OCCOH can enhance selectivity and amount of C<sub>2</sub>H<sub>4</sub>  
706 produced.

707 Wang et al. developed CuBi NPs that showed a CH<sub>4</sub> 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 CO<sub>2</sub>, which are outlined in Table 1 below.

Table 1. Selected examples of electroactive metal nanoparticles for converting CO<sub>2</sub> into hydrocarbon products

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

					and $\text{Cu}_2\text{O-FeO}$ are responsible for the efficient $\text{CO}_2$ reduction to $\text{CO}$
$\text{Cu}_x\text{Au}_y$ 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 $\text{CH}_4$	$\text{Fe-N}_4$ increased (Zhang et al., $\text{CO}_2$ activation 2018) resulting from the incorporation

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

Composite of 64  
 ZrO<sub>2</sub>  
 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 ZrO<sub>2</sub> 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 <sub>2</sub> , 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 <sub>2</sub> .
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 CO<sub>2</sub> to CO.

C-supported Bi 93 ± - -1.6 HCOO<sup>-</sup>  
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<sup>-</sup> - Formate ion; NPs –Nanoparticles; AuNPs –  
718 Gold nanoparticles

719 In the quest for additional electro-active nanoparticles for CO<sub>2</sub> 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 CO<sub>2</sub> to CH<sub>3</sub>OH. In comparison to RHE in 0.1  
724 m KHCO<sub>3</sub>, this catalyst achieves a high FE of 92% for CH<sub>3</sub>OH at 0.5 V. According to  
725 DFT calculations, B and P synergistically facilitate the binding and activation of CO<sub>2</sub>,  
726 and the \*CO + \*OH to \*CO + \*H<sub>2</sub>O pathway, with a free energy change of 1.36 eV, is  
727 the rate-determining step for the CO<sub>2</sub>RR. Liu et al. (Liu et al., 2022) reported B/N-  
728 doped sp<sup>3</sup>/sp<sup>2</sup> hybridized nanocarbon, which consists of extremely small carbon NPs  
729 with an sp<sup>3</sup> carbon core surrounded by a sp<sup>2</sup> carbon shell, as an effective electrocatalyst  
730 for CO<sub>2</sub> to ethanol reduction at relatively low overpotentials. They claim that CO<sub>2</sub>  
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 sp<sup>3</sup>/sp<sup>2</sup> carbon and B/N doping, there is a strong ethanol selectivity.

734 To perform electrocatalytic CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> (Li et al., 2016). The team found that

744 S,N-doped carbon has greater FE for conversion to CO and CH<sub>4</sub> compared to S-doped  
745 counterpart. The former revealed a maximum FE of 11.3% and 0.18% for CO and CH<sub>4</sub>  
746 production, respectively. The S,N-nanoporous carbon was better at decreasing the  
747 overpotential of the reduction process.

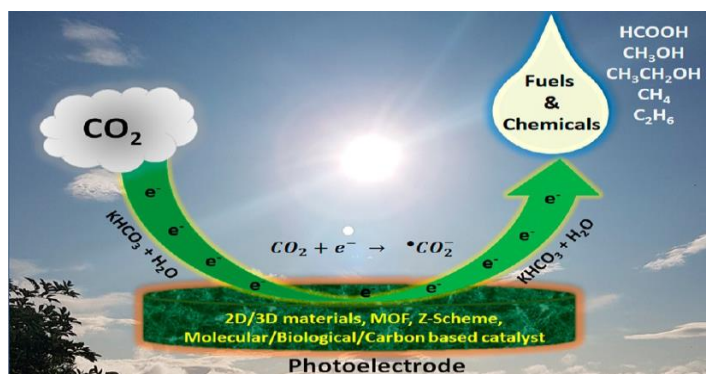
748 Two-dimensional (2D) boron nitride nanosheets or meshes (BNs) doped with beryllium  
749 have been the subject of research by Azofra and coworkers (Azofra et al., 2016).  
750 According to their mechanistic study, adding electron-deficient Be atoms to the 2D  
751 network significantly lowered the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

755 Despite all the accomplishments in CO<sub>2</sub>RR, 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 CO<sub>2</sub> electrocatalytic transformation. The main challenge being the  
758 energy requirement for reducing CO<sub>2</sub> (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 (CO<sub>2</sub><sup>•-</sup>), regulating product selectivity is  
761 difficult. When a multi-electron process is combined with proton-coupled electron  
762 transfer, the potential for CO<sub>2</sub> 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 C<sub>2</sub><sup>+</sup> 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 CO<sub>2</sub>**

768 Photoelectrochemical (PEC) conversion of CO<sub>2</sub> can be described as a procedure  
769 mimicking the artificial photosynthesis technique. This method has been employed for  
770 the conversion of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> conversion. In 2020, Arai et  
781 al. (Arai et al., 2010) reported the PEC conversion of CO<sub>2</sub> 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 CO<sub>2</sub>. 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.

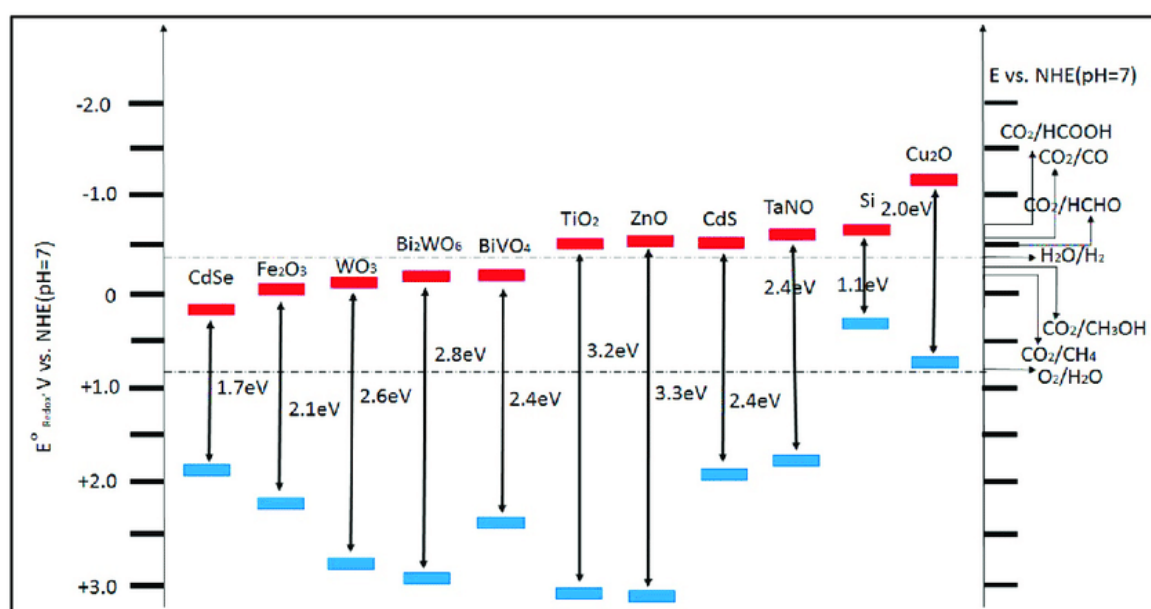
811 Table 2: The oxidation-reduction potential at pH=7 vs NHE and half-cell reactions  
812 (Ekambaram et al., 2007)

<b>Reactants</b>	<b>Products</b>	<b>EMF</b>
$\text{CO}_2 + 2\text{e}^- \rightarrow$	$\cdot\text{CO}_2$	-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 <sub>2</sub> O	-0.53
$\cdot\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow$	HCHO + H <sub>2</sub> O	-0.48
$\cdot\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow$	CH <sub>3</sub> OH + H <sub>2</sub> O	-0.38
$\cdot\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow$	CH <sub>4</sub> + 2H <sub>2</sub> O	-0.24
$2\text{H}_2\text{O} + 4\text{H}^+ \rightarrow$	O <sub>2</sub> + 4H <sup>+</sup>	+0.81
$\text{H}^+ + 2\text{e}^- \rightarrow$	H <sub>2</sub>	-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 CO<sub>2</sub> 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). TiO<sub>2</sub>  
823 and ZnO absorb ultraviolet light of the solar spectrum due to their large bandgap's

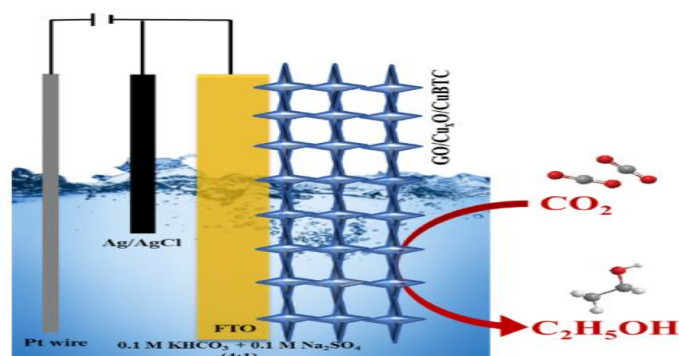
824 energy (~380 nm and ~360 nm respectively) (Liu et al., 2010). The bandgap (the  
 825 distance between the valence band and conduction band) of each semiconductor  
 826 determines are shown in Figure 14, it shows the relationship between the bandgap and  
 827 EMF at pH 7. Several alternative semiconductors such as Fe<sub>2</sub>O<sub>3</sub>, ZnO, WO<sub>3</sub>, SrTiO<sub>3</sub>,  
 828 NaTaO<sub>3</sub>, CdS, Ag<sub>3</sub>PO<sub>4</sub>, BiPO<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> 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 CO<sub>2</sub> 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<sub>x</sub>O, 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<sup>-1</sup>. Most researchers believe that the PEC  
 839 reduction technique is not only efficient, but it is also greener and sustainable. Other

840 PEC for CO<sub>2</sub> reduction surveyed in this section are listed in the supplementary file  
841 (Table S2)



842

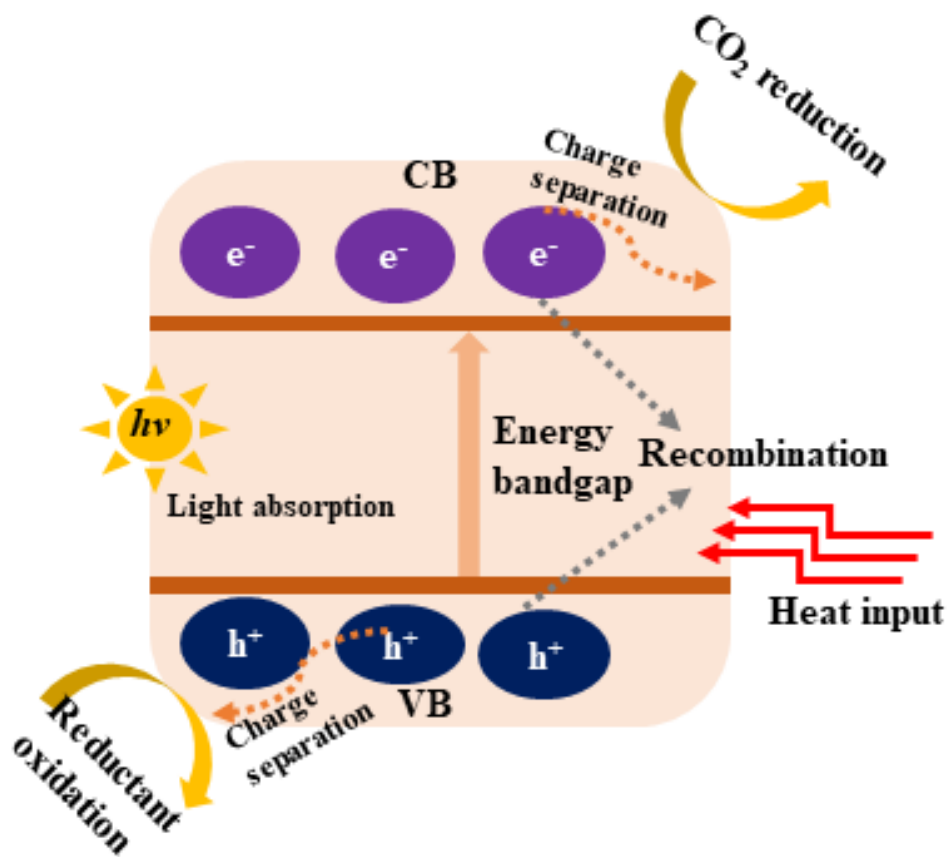
843 Figure 15: PEC reduction of CO<sub>2</sub> to ethanol. Adapted with permission from reference  
844 (Nandal et al., 2022). Copyright [2022], [Elsevier].

### 845 **3.4 Photothermal heterogeneous catalysts for the hydrogenation of CO<sub>2</sub>**

846 The hydrogenation of CO<sub>2</sub> is gaining significant impetus in scientific investigations  
847 considering the large amount of CO<sub>2</sub> generated by the industrial processes and the  
848 associated environmental degradation. It facilitates the production of clean fuels and  
849 hydrocarbons such as CO, CH<sub>4</sub>, and C<sub>2</sub><sup>+</sup> 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 CO<sub>2</sub>  
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 CO<sub>2</sub> into different hydrocarbon-based fuels (Table 3).



867

868

Figure 16: Scheme of the photothermal catalytic CO<sub>2</sub> reduction

869 Table 3: Examples of photothermal catalysts for the hydrogenation of CO<sub>2</sub> in fuels and hydrocarbons

Photothermal catalyst	Light source	Reaction conditions	Selective products	Conversion rate (mmol·g <sup>-1</sup> ·h <sup>-1</sup> )	Comments	References
Pd/ZnO	Visible light	Low pressure (12 bar)	CH <sub>3</sub> OH		Localized SPR of Pd contributed to the high yield of methanol	(Wu et al., 2019)
AuPt@UiO-66-NH <sub>2</sub>	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 $\mu\text{m}$ - SiNCs@Co nanoarray	300 W Xe arc lamp	Pressure (1 bar), power intensity (2.5 W $\text{cm}^{-2}$ )	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 <sub>2-x</sub> H <sub>x</sub>	300 W Xe lamp	Gas flow rate at 500 mL $\text{min}^{-1}$ and purged for 10 min	CH <sub>4</sub>		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 <sub>2</sub> C-	300 W Xe	36-sun	CO	8.5 mol·g <sup>-1</sup> ·h <sup>-1</sup>	Ni NPs greatly enhance the	(Wu et al.,

nanosheet-supported Ni NPs	arc lamp	illumination without external heating			activation of H <sub>2</sub> and accelerate CO <sub>2</sub> hydrogenation reactions; formation of Ni-H is vital for CO <sub>2</sub> conversion	(2021)
Fe <sub>3</sub> O <sub>4</sub>	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 <sub>3</sub> C			CH <sub>x</sub>	10.9		
α-MoC and β-Mo <sub>2</sub> C mixed phases	300 W xenon lamp	130 °C, 5 h	CO and CH <sub>4</sub>	25.8 mL·g <sup>-1</sup> ·h <sup>-1</sup>	dissociation of light-promoted surface intermediate (formate species) was responsible for the enhanced activity of photothermal catalytic CO <sub>2</sub>	(Zhao et al., 2021)

					hydrogenation	
Pd <sub>2</sub> Cu alloy dispersed TiO <sub>2</sub>	UV-Vis (350 to 750 nm)	150 °C	C <sub>2</sub> H <sub>5</sub> 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 <sup>-2</sup> )	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 <sup>-2</sup> )	CO	1666	A dual-pass AAO with a large channel size facilitates gas diffusion and thus boosts photothermal catalytic	(D. Lou et al., 2021)

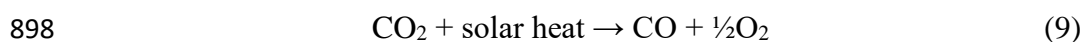
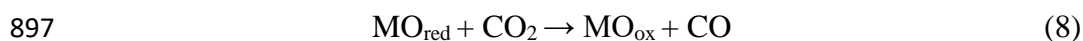
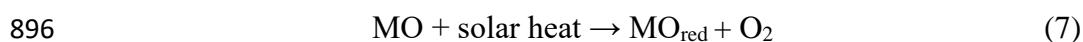
					performance	
Au/CeO <sub>2</sub>	Xe lamp	623 K	CO		Positive effect of light on CO <sub>2</sub> transformation is associated with the hydrogen dissociation step.	(B. Lu et al., 2019)

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

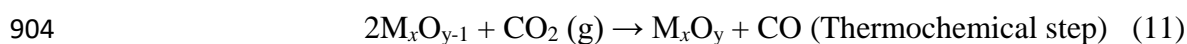
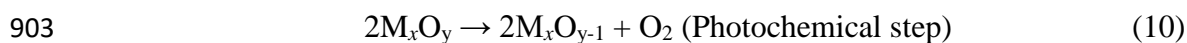
### 872 **3.5 Thermochemical transformation of CO<sub>2</sub>**

873 The thermochemical transformation of CO<sub>2</sub> is an interesting strategy that has been gainfully  
874 explored for the reduction, splitting, or reforming of CO<sub>2</sub> 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 CO<sub>2</sub> (**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 CO<sub>2</sub>-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 nSmMnO<sub>3</sub> perovskite (Gao et al., 2022), and  
886 ZrO<sub>2</sub>-supported NiFe<sub>2</sub>O<sub>4</sub> (Shuai et al., 2021), to convert CO<sub>2</sub> into CO with a 99% conversion rate  
887 of 381 mL g<sup>-1</sup> min<sup>-1</sup> 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 CaCO<sub>3</sub> transformed 86.6% of CO<sub>2</sub> into syngas along  
889 with CH<sub>4</sub> 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 O<sub>2</sub> 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 H<sub>2</sub>O and/or CO<sub>2</sub> giving rise to the formation of H<sub>2</sub> and/or CO  
895 (Eq. 8-9), together with the stoichiometric oxide (Chen et al., 2022; Nair and Abanades, 2018).

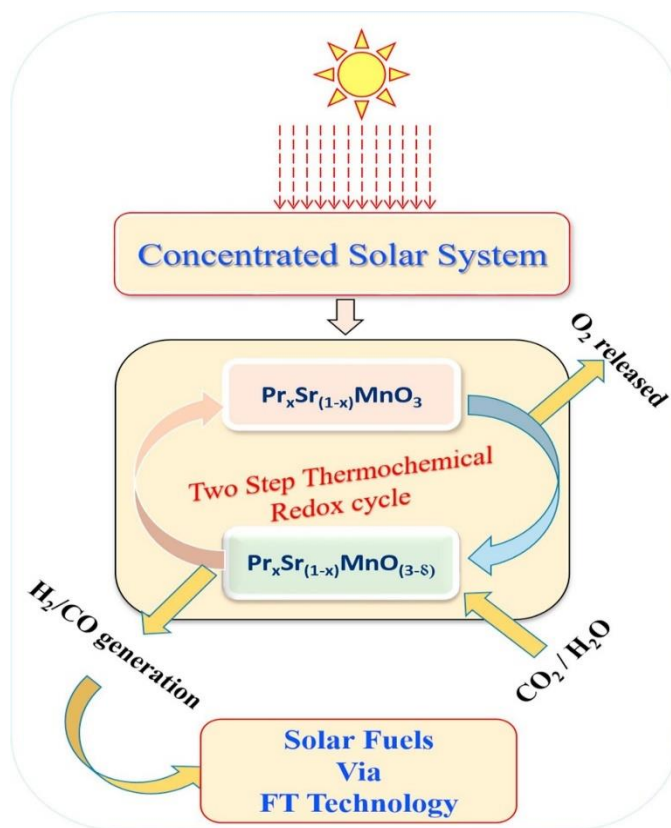


899 In the same vein, the photo-thermochemical (PTC) model produces photoinduced oxygen  
900 vacancies on the surface of the MO catalyst after exposure to UV-light energy (Eq. 10). Further,  
901 the oxygen vacancies are used to reduce CO<sub>2</sub> at temperatures below 873 K, thereby producing  
902 CO and O<sub>2</sub> (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 H<sub>2</sub> 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 CO<sub>2</sub>  
910 transformation (Feng et al., 2021). For example, the loading of IrO<sub>x</sub> onto LaFeO<sub>3</sub> almost double  
911 the maximal CO release rate and increases the maximal O<sub>2</sub> evolution rate 0.5 times i.e. a 5-fold  
912 CO production (Jiang et al., 2016); meanwhile, the sol-gel synthesized Co<sub>x</sub>Fe<sub>3-x</sub>O achieved  
913 higher CO generation rate via CO<sub>2</sub> 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 CO<sub>2</sub>

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

			$\text{g}_{\text{cat}} \text{min}^{-1}$	
$\text{CeO}_{2-\delta}$	$\text{H}_2$ 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 <sub>2</sub>	1100-1400 °C	0.07 mmol/g	(Lorentzou et al., 2014)
NiFe <sub>2</sub> O <sub>4</sub> @Alumina support	Fuels and chemicals	1300 K, 0.5 atm, and 0.4 m/s	98.22%	(Guene Lougou et al., 2020)
$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$	$\text{H}_2$ and CO	1000-1400 °C	137.5 $\mu\text{mol/g}$ (1.6-fold increase)	(Dey et al., 2015)
Ceria pellets	$\text{H}_2$	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 ± 0.12 $\text{mL.g}^{-1}$	(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**

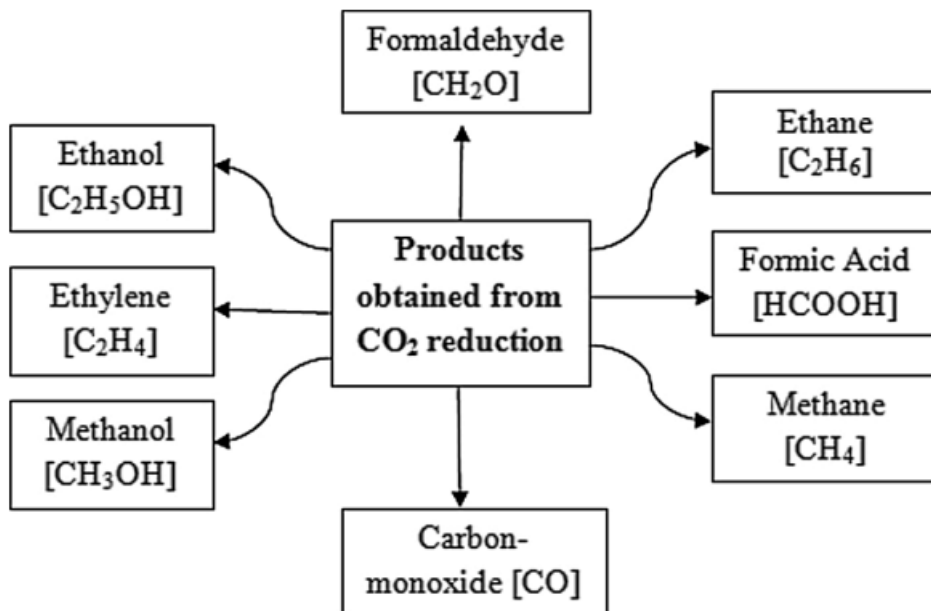
920 Non-thermal plasma (NTP) catalysis is an auspicious technology that is gaining significance in  
921 C<sub>1</sub> chemistry. It has been postulated as an effective alternative to conventional thermal catalysis  
922 due to the unique interplay between the plasma and heterogeneous catalyst. Thus, 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 C<sub>1</sub>  
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 CO<sub>2</sub>  
931 hydrogenation (Song et al., 2022), water–gas shift reaction (Xu et al., 2019), hydrocarbon  
932 reformation (Wu et al., 2018) and CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> to CO and CH<sub>4</sub> (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 CO<sub>2</sub> in the  
943 presence of Ru/MgAl layered double hydroxide catalysts (having low activation energy)  
944 provided ~84 % of CH<sub>4</sub> 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 CO<sub>2</sub> to CH<sub>4</sub> 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 CH<sub>4</sub> under NTP conditions and temperatures < 330 °C.

#### 950 **4. Fuels generated from CO<sub>2</sub> conversion**

951 The discovery and development of efficient technologies for the catalytic transformation of CO<sub>2</sub>  
952 is an exciting area of research (Ramírez-Valencia et al., 2021) as, in parallele of lowering the  
953 atmospheric CO<sub>2</sub>, this would allow the access to essential chemicals and fuels such as formic  
954 acid (HCOOH), methanol (CH<sub>3</sub>OH), carbon monoxide (CO), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and methane  
955 (CH<sub>4</sub>), among others, that are presently produced from fossil resources. **Figure 18** describes the  
956 potential products that could be derived from CO<sub>2</sub> conversion.



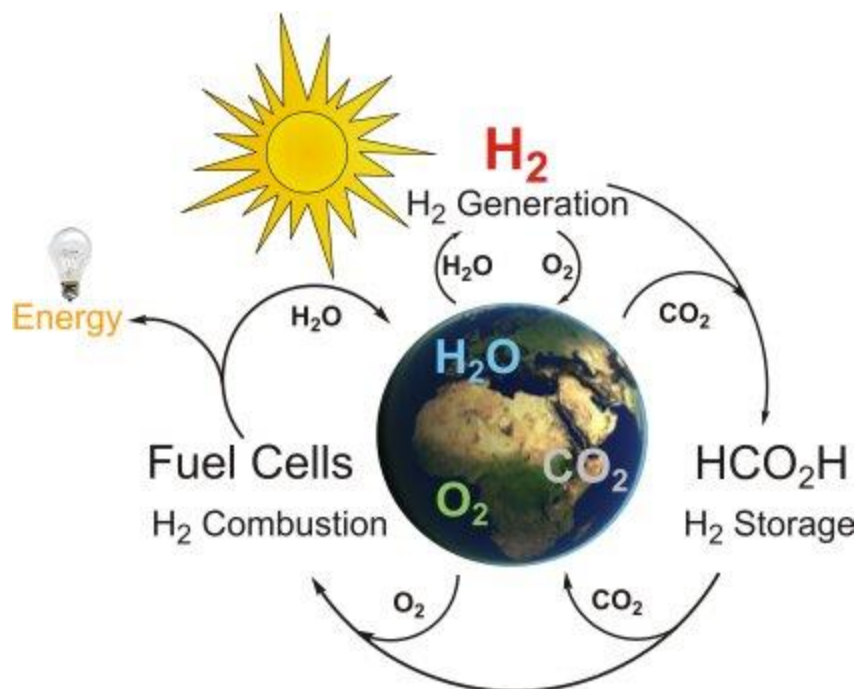
957

958 Figure 18: Potential products from CO<sub>2</sub> conversion (Ramírez-Valencia et al., 2021).

959

#### 960 4.1 Formic acid

961 Among the myriad of products accessible from CO<sub>2</sub>, 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

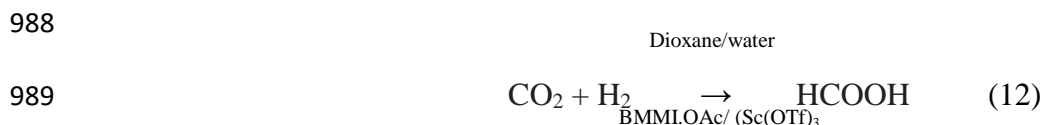
Figure 19: Reversible hydrogenation of CO<sub>2</sub> to formic acid (Li et al., 2002)

971 Several synthetic methods for the conversion of CO<sub>2</sub> 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 CO<sub>2</sub> to formic acid was first  
 975 reported by Inoue (Inoue et al., 1976) in 1976. Since then, CO<sub>2</sub> 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

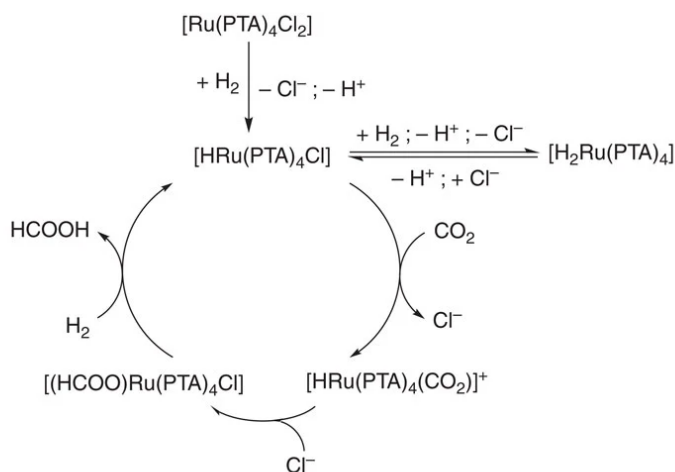
981 Weilhard *et al.* reported the synthesis of formic acid from CO<sub>2</sub> feedstock using an ionic liquid as  
 982 an alternative to expensive precious metal-based catalytic systems (Weilhard et al., 2021). As

983 shown in Scheme 3, the synthetic strategy consists of a mixture of CO<sub>2</sub> and H<sub>2</sub> 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)<sub>3</sub>). They reported a  
 986 very high catalytic efficiency with turnover numbers (TON) and turnover frequency (TOF) of 8 x  
 987 10<sup>5</sup> and 2.1 x 10<sup>4</sup> h<sup>-1</sup>, respectively.



990

991 Moret *et al.* (Moret et al., 2014) applied a ruthenium-based homogeneous catalytic system to  
 992 convert CO<sub>2</sub> 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 CO<sub>2</sub> into formic acid over [HRu(PTA)<sub>4</sub>Cl]

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 CO<sub>2</sub>  
1000 into formic acid. The catalytic procedure involves the breaking down of CO<sub>2</sub> into valuable  
1001 chemicals in the presence of sunlight and Ag-doped TiO<sub>2</sub> 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<sup>-2</sup> h<sup>-1</sup>.

## 1004 **4.2 Carbon monoxide**

1005 In the series of products derived from CO<sub>2</sub>, carbon monoxide (CO) is one of the most critical  
1006 chemicals and feedstock. It is a primary raw material along with H<sub>2</sub> 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 CO<sub>2</sub> reduction into  
1009 CO efforts can be listed in two major categories, namely thermochemical reduction and  
1010 electrochemical reduction (Porosoff et al., 2016). CO<sub>2</sub> 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.



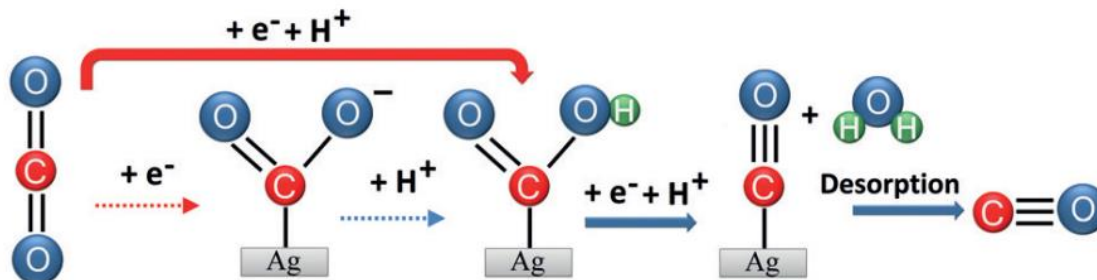
1014 Various catalytic materials have been employed to reduce the energy cost of the catalytic  
1015 conversion of CO<sub>2</sub> to CO. For example, Au nanocatalysts have shown tremendous potential in  
1016 converting CO<sub>2</sub> to CO with a remarkable selectivity (Qi et al., 2019). Qi *et al.* (Qi et al., 2021)  
1017 reported a successful electrochemical conversion of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>  
 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



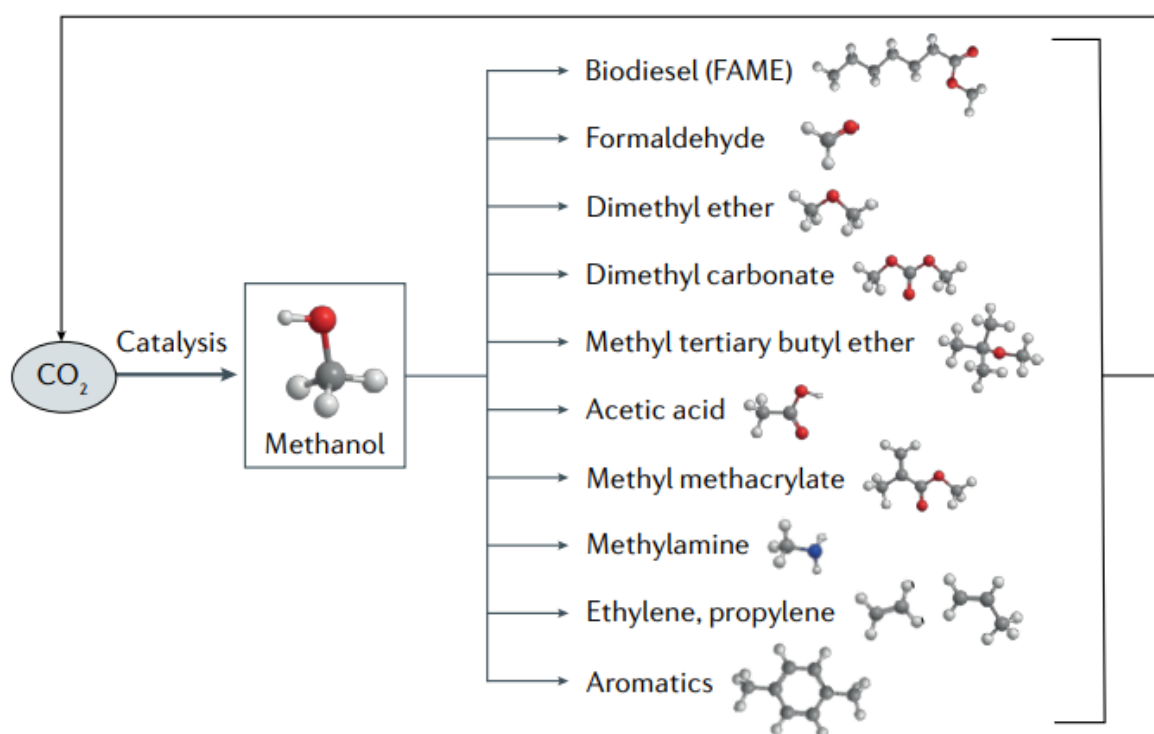
1030

1031 Scheme 3: Mechanism of the conversion of CO<sub>2</sub> 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 CO<sub>2</sub> to CO by electrochemical reduction. They  
 1035 obtained a CO Faraday efficiency of 76.4% with the CO current density of 57.53mA/Cm<sup>2</sup>. 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 CO<sub>2</sub> to CO.

### 1039 4.3 Methanol

1040 The conversion of CO<sub>2</sub> 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 CO<sub>2</sub> 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 H<sub>2</sub>) and CO<sub>2</sub> (Nieminen et al., 2019). From the mechanistic point of  
 1051 view, the synthetic pathway may occur through direct CO<sub>2</sub> 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 Al<sub>2</sub>O<sub>3</sub>, ZnO, and ZrO<sub>2</sub>. 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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, GaPd<sub>2</sub>/SiO<sub>2</sub> for converting CO<sub>2</sub> to methanol, at low CO<sub>2</sub> pressure, and with a MeOH  
1078 production rate of 0.12 mol%. Although the catalytic activity of this GaPd<sub>2</sub>/SiO<sub>2</sub> 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 Ga<sub>3</sub>Ni<sub>5</sub> for CO<sub>2</sub> conversion and compared their results with those of Fiordaliso *et al.*  
1082 (Fiordaliso et al., 2015). The activity of the Ga<sub>3</sub>Ni<sub>5</sub> catalyst was found to be higher under the  
1083 same experimental conditions, showing a MeOH conversion rate of 38.85 μmol g<sub>cat</sub><sup>-1</sup> min<sup>1</sup>  
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, CeO<sub>2</sub>-based catalyst is getting attention due to its abundant oxygen and  
1088 reversible valence charges (Ce<sup>4+</sup> and Ce<sup>3+</sup>) (F. Wang et al., 2016). This potential was  
1089 demonstrated by Chang *et al.* (Chang et al., 2021), who applied a CeO<sub>2</sub>-based catalyst Cu/ZnO–  
1090 CeO<sub>2</sub> to convert CO<sub>2</sub> to methanol.

1091 Perovskites have been also identified as low-cost approach for CO<sub>2</sub> 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 CO<sub>2</sub>. They reported an excellent catalytic efficiency with impressive  
1094 stability of the prepared catalyst.

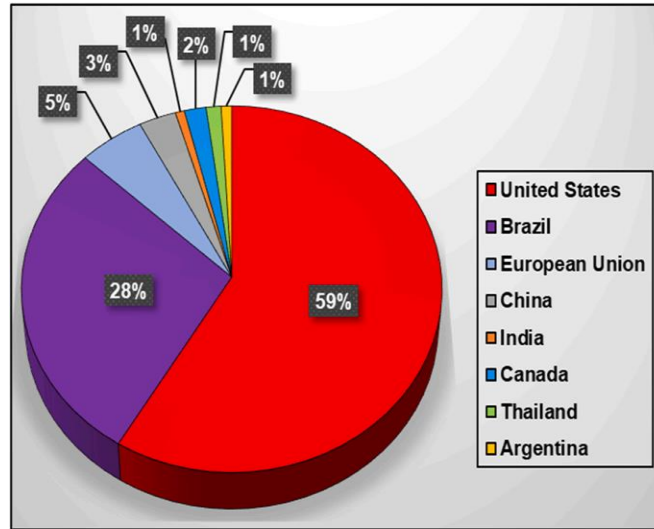
1095 Apart from heterogeneous-based catalytic systems, homogeneous catalysts have been also  
1096 reported for methanol synthesis from CO<sub>2</sub>. Kothandaraman *et al.* (Kothandaraman et al., 2016)  
1097 developed a Ru-based homogeneous catalytic system that showed a very good yield (79 %) in  
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 [RuH<sub>2</sub>(Me<sub>2</sub>PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>NH(CO)] which led to a good catalytic efficiency from  
1101 the density functional theory (DFT) data.

1102 Application of enzymes to reduce CO<sub>2</sub> to methanol is also getting considerable attention. Zhang  
1103 *et al.* (Z. Zhang et al., 2021) reported the enzymatic conversion of CO<sub>2</sub> to methanol in the  
1104 presence of nicotinamide adenine dinucleotide (NADH). The enzyme was immobilized on  
1105 porous a MOF (ZIF-8) to improve CO<sub>2</sub> concentration. The prepared NADH/ZIF-8 composite  
1106 was placed in the bio-electrochemical cell. The methanol conversion rate was 822 μmol g<sup>-1</sup> h<sup>-1</sup>,  
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 CO<sub>2</sub> to ethanol has drawn a lot of attention.

1127 Several catalytic systems have been used for CO<sub>2</sub> conversion to ethanol, notably Pt, Co, Fe, and  
1128 Cu systems (Zheng et al., 2019). Cu-based catalysts have been used for hydrogenating CO<sub>2</sub> to  
1129 ethanol due to their success in converting CO<sub>2</sub> 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<sup>I</sup> instead of Cu<sup>0</sup>. Despite this success, the Cu-catalyst suffers from long-  
1132 term use due to instability under the reaction conditions and operating conditions.

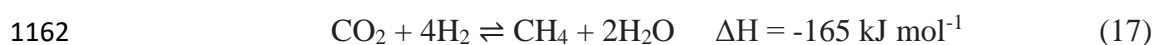
1133 Other catalytic systems have been tested to improve the selectivity and yield of ethanol from  
1134 CO<sub>2</sub>, including Pt-based catalysts and their alloys; while good yield was obtained with these

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/CeO<sub>2</sub> catalyst to  
1137 convert CO<sub>2</sub> to ethanol. They reported a space yield time of 45.6 g<sub>ethanol</sub> g<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup>. 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 CO<sub>2</sub> to ethanol that showed a CO<sub>2</sub>  
1140 conversion rate of 10 % and a selectivity of 24% to ethanol. Zheng *et al.* (Zheng et al., 2019)  
1141 reported the conversion of CO<sub>2</sub> to ethanol using a LaCo<sub>1-x</sub>Ga<sub>x</sub>O<sub>3</sub> composite perovskite catalyst  
1142 with a very good catalytic CO<sub>2</sub> 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 (CH<sub>4</sub>) is a C<sub>1</sub> 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 CO<sub>2</sub> to  
1150 methane is an effective strategy for CO<sub>2</sub> capture, utilization and conversion to valuable  
1151 chemicals. Catalytic hydrogenation is the most widely studied route for CO<sub>2</sub> 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 CO<sub>2</sub> and H<sub>2</sub> with a nominal ratio of  
1156 1:4, respectively, while the second mechanism is the reaction of CO and H<sub>2</sub> 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 CO<sub>2</sub> to methane is a highly exothermic reaction which can proceed at a relatively  
1159 lower temperature. However, given the thermodynamic stability of CO<sub>2</sub> molecules due to the  
1160 presence of delocalized  $\pi$  bonds, the conversion of CO<sub>2</sub> to methane remains a serious challenge  
1161 at a lower temperature (Álvarez et al., 2017).



1164 To overcome this challenge and permit activation of CO<sub>2</sub> at lower temperatures, highly active  
1165 catalytic materials with good selectivity to methane and low deactivation must be developed.  
1166 CO<sub>2</sub> 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 CO<sub>2</sub> methanation. Ni-based catalytic materials are the most  
1172 studied for CO<sub>2</sub> 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 CO<sub>2</sub> to Methanol using Ni/SiO<sub>2</sub>  
1174 catalyst promoted by Fe, Co, and Zn. They obtained a very high CO<sub>2</sub> 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 CO<sub>2</sub> 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.

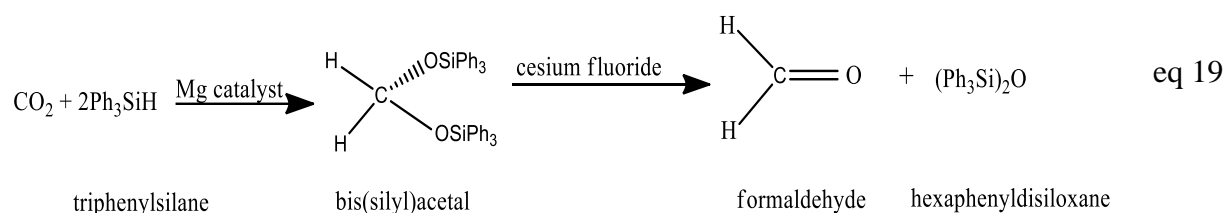
1183 Li *et al.* (Y.-T. Li et al., 2022) obtained a very high CO<sub>2</sub> conversion (72.3 %) and impressive  
1184 selectivity (99.3 %) with the NiFe/MOF catalytic material. Similarly, Hu *et al.* (Hu et al., 2022)  
1185 also established the role of metal-support interaction using Ni supported on CeO<sub>2</sub> nanofibers.  
1186 The oxygen vacancy enhanced the catalytic efficiency of Ni in CeO<sub>2</sub>. The prepared catalyst  
1187 recorded 82.3 % conversion of CO<sub>2</sub> 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 CeO<sub>2</sub> nanofibers.

#### 1190 **4.6 Formaldehyde**

1191 The ease of availability of CO<sub>2</sub> has provided an opportunity for energy production and  
1192 commodity products for the economy. Among other compounds which could be generated from  
1193 CO<sub>2</sub> 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, CO<sub>2</sub> was contained in most of the products formed  
1201 (Lervold et al., 2021), leading to increased pollution.

1202

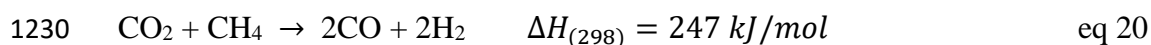
1203 In a bid to curb the emission of CO<sub>2</sub>, scientists have developed methods that could possibly  
 1204 convert CO<sub>2</sub> into useful products. Of these methods is the production of FMD (Friedlingstein  
 1205 2015; Sümbelli et al., 2019). Although the generation of FMD from CO<sub>2</sub> is quite challenging,  
 1206 frantic efforts are being made to overcome this fall-out as CO<sub>2</sub> is resistant to chemical changes  
 1207 (Rauch et al., 2019). One of those efforts is the conversion of CO<sub>2</sub> at ambient temperature  
 1208 yielding the formation of FMD. The CO<sub>2</sub> 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 CO<sub>2</sub> 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-Al<sub>2</sub>O<sub>3</sub>  
 1217 (Kobl et al., 2016) or Pt-promoted Cu/SiO<sub>2</sub> (Lee et al., 2001). This latter converts CO<sub>2</sub> 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-C<sub>3</sub>N<sub>4</sub>)  
 1220 material with specific crystallinity and surface area, has been shown to have a significant effect  
 1221 on the conversion of CO<sub>2</sub> to FMD. Since this discovery other photocatalytic mesoporous  
 1222 nanomaterials have been explored for the photocatalytic reduction of CO<sub>2</sub> (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 CO<sub>2</sub> via a process called carbon dioxide reforming. This process, represented on  
1227 equation 20, consumes CO<sub>2</sub> and methane (CH<sub>4</sub>), 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).



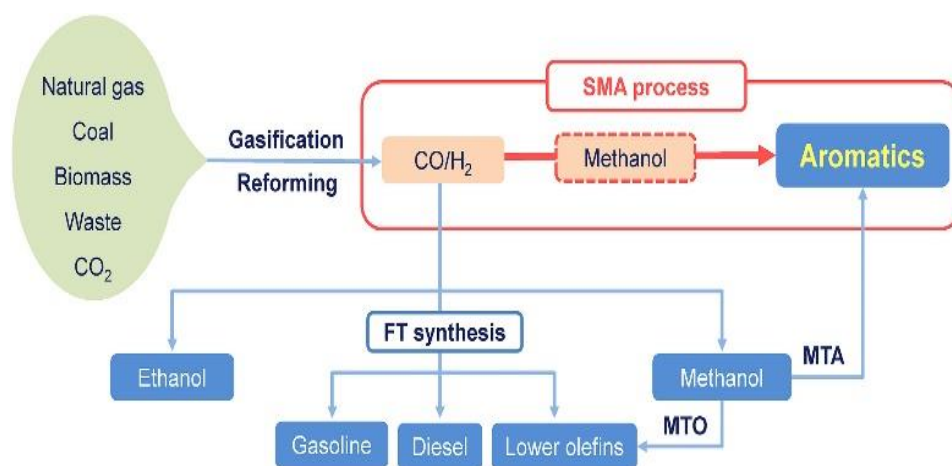
1231 Fan and coworkers reported this process has been catalyzed over a Ni-Co/MgO-ZrO<sub>2</sub>  
1232 nanomaterial, (Fan et al., 2011). The effect of Ni-based catalysts on the CO<sub>2</sub> reforming of  
1233 methane had earlier been investigated by Takano et al., (1994). This process produces green  
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 CO<sub>2</sub> 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 CO<sub>2</sub>, 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 CO<sub>2</sub> 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 C<sub>2</sub>-C<sub>4</sub> hydrocarbon fraction of about 56.7% selectivity for  
 1254 desired lower olefins (C<sub>2</sub><sup>-</sup> - C<sub>4</sub><sup>-</sup>) with 29.2% of undesired CH<sub>4</sub> selectivity (Scheme 4). If  
 1255 selective formation of lower olefins and low CH<sub>4</sub> 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 In<sub>2</sub>O<sub>3</sub>-ZnZrO<sub>x</sub> 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 <sub>2</sub> conversion (%)	Hydrocarbon distribution			
		HC	CO		C <sub>2</sub> <sup>=</sup> - C <sub>4</sub> <sup>=</sup>	C <sub>2</sub> <sup>o</sup> -C <sub>4</sub> <sup>o</sup>	C <sub>5+</sub>	CH <sub>4</sub>
1.	In <sub>2</sub> O <sub>3</sub> - ZnZrO <sub>x</sub> /SAPO- 34-S-a	17.0	44.2	55.8	85.0	11.1	2.3	1.6
2.	In <sub>2</sub> O <sub>3</sub> - ZnZrO <sub>x</sub> /SAPO- 34-S	17.9	45.0	55.0	79.6	13.9	5.2	1.3
3.	In <sub>2</sub> O <sub>3</sub> - ZnZrO <sub>x</sub> /SAPO- 34-S-H-a	17.0	46.6	53.4	84.5	11.0	3.3	1.2
4.	In <sub>2</sub> O <sub>3</sub> - ZnZrO <sub>x</sub> /SAPO- 34-H	17.4	45.9	54.1	79.0	16.5	3.3	1.2
5.	In <sub>2</sub> O <sub>3</sub> - ZnZrO <sub>x</sub> /SAPO-	17.2	46.2	53.8	80.6	15.2	2.9	1.3

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34-C-a

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6.	In <sub>2</sub> O <sub>3</sub> -	18.1	47.5	52.5	76.8	19.2	2.7	1.3
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ZnZrO<sub>x</sub>/SAPO-

34-C

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1289 **5. Conclusions and future outlook**

1290 Information gathered from recent literature confirms that continuous efforts are being made to  
1291 reduce CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>  
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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> to value-added products.

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1325

#### 1326 **References**



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