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# Carbon Dioxide Conversion to Methanol: Opportunities and Fundamental Challenges

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## Abstract

Greenhouse gases mitigation is one of most important challenges facing societies nowadays. Therefore, the way to reduce greenhouse gas emissions should be using carbon free sources that do not generate extra CO<sub>2</sub> to the atmosphere. However, there is a great potential in energy carriers and other materials from CO<sub>2</sub>, with many challenges to overcome. It has been suggested that the reduction of CO<sub>2</sub> and conversion to renewable fuels and valuable chemicals may be considered as a promising solution to reduce the greenhouse gas emissions. This chapter discusses the recent developments and remaining challenges of CO<sub>2</sub> utilization for the efficient production of methanol. This includes novel technologies, approaches, and current barriers for the conversion of CO<sub>2</sub> to methanol through heterogeneous catalysis, homogenous catalysis, electrochemical, photochemical, and photoelectrochemical conversion, which will contribute to the economic growth and mitigate the hazardous emissions for cleaner environment. A review of various state-of-the-art technologies for CO<sub>2</sub> conversion to methanol was carried out aiming to establish the advances in this area and present an overview of the recent research trend for future development of new ideas for CO<sub>2</sub> reduction into methanol in a large scale.

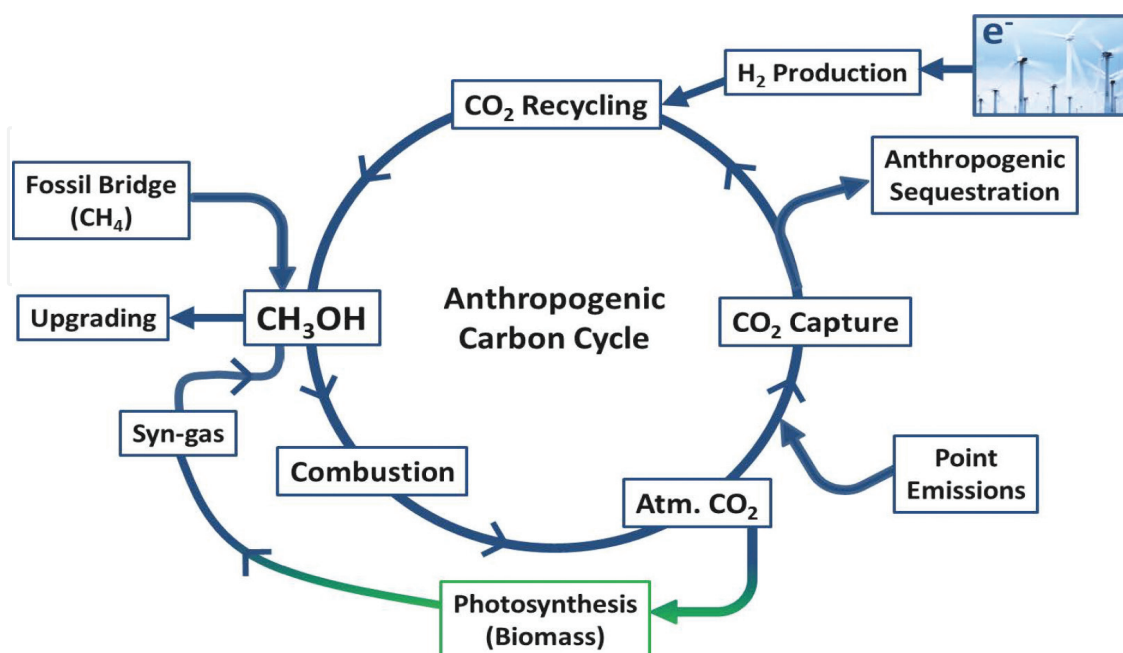
**Keywords:** CO<sub>2</sub> utilization, heterogeneous catalysis, homogeneous catalysis, electrochemical conversion, photochemical conversion, photoelectrochemical conversion

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## 1. Introduction

Nowadays, the demand for energy is rapidly increasing because of the economic growth worldwide. In order to meet this growing demand, an abundant amount of fossil fuel (oil, coal, and natural gas) is needed [1]. Fossil fuel combustion is often considered as one of the main threats to the environment because of the CO<sub>2</sub> release in the atmosphere. CO<sub>2</sub>, which is

considered as a primary greenhouse-gas (GHG), is periodically exchanged within land surface, ocean, and atmosphere where a variety of creatures, including animals, plants, and microorganisms absorb and produce it daily. However, the process of releasing and consuming  $\text{CO}_2$  trends has to be balanced by nature. Since 1750, when the industrial revolution began, so did climate change following the activities related to industries. In order to reduce the greenhouse gas emissions,  $\text{CO}_2$  sequestration and storage (CSS) processes gained a widespread attention. However, it will increase the amount of available captured  $\text{CO}_2$  as feedstock of zero cost. Therefore, utilizing  $\text{CO}_2$  and converting it into fuels and chemicals, which is called carbon capture and recycling (CCR) process, is an active option used worldwide to convert usable products into valuable products, and it is used to mitigate  $\text{CO}_2$  emissions which is more preferable compared to CSS option [2–5]. During the last years, conversion of  $\text{CO}_2$  into value-added chemicals (i.e., ethanol, methanol, and formic acid) using different ways has received a great attention from the researchers as it can be seen as a solution to reduce the global warming [6–8], energy crisis (i.e., fossil fuels depletion) [9–11], and the storage of energy [12] problems. Methanol is a renewable energy source that can be produced from any raw material containing carbon (mainly  $\text{CO}_2$ ), as well as it is a clean source of energy that can be used as transportation fuel. In general, for a fuel to satisfy the market demand, it must be sustainable material, clean, and able to be synthesized from available resources. Nowadays, as a matter of fact, most of the production companies around the world use methanol as a raw material to produce different products. Methanol is used in producing solvents like the acetic acid, which represents 10% of the global demand [13]. Methanol can also be used in direct methanol fuel cells (DMFC), which is used for the conversion of chemical energy in methanol directly to electrical power under ambient conditions [14]. Methanol is considered to be one of the most important organic feedstocks that can be used in the industries with an annual production of 65 million tons worldwide [15]. However, “Methanol Economy” term includes an anthropogenic carbon cycle for methanol production as shown in **Figure 1**, which can be used as a renewable fuel or to



**Figure 1.** Anthropogenic carbon cycle for methanol production [20].

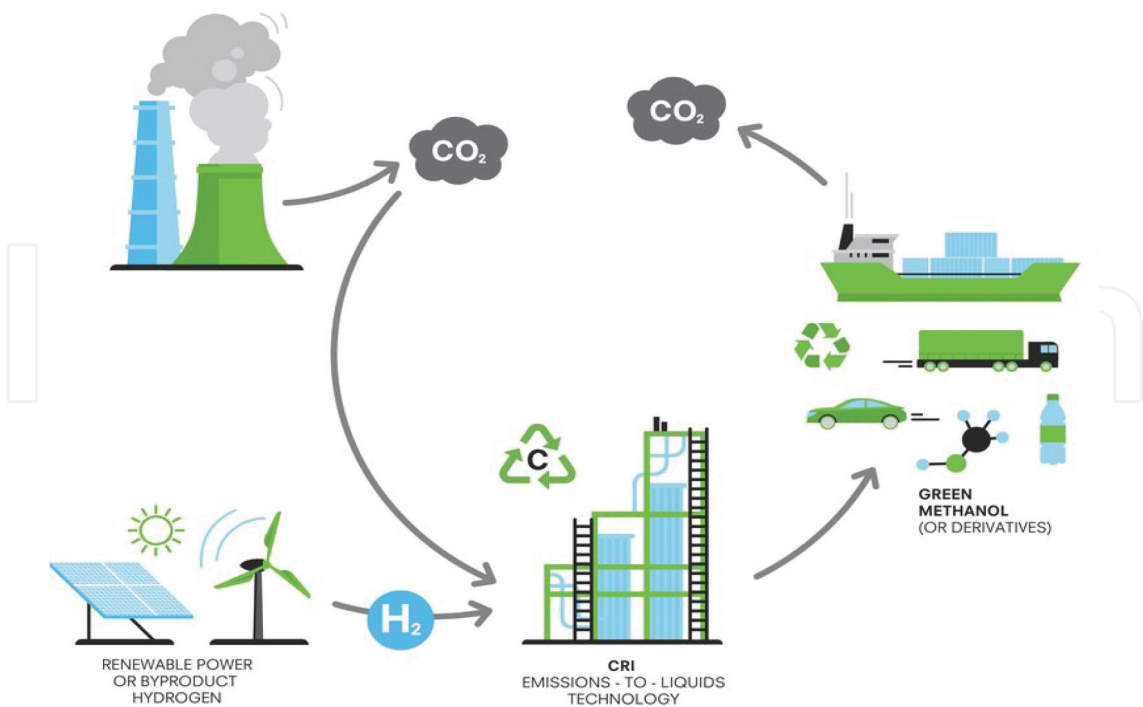


Figure 2. Green methanol production by Carbon Recycling International [18].

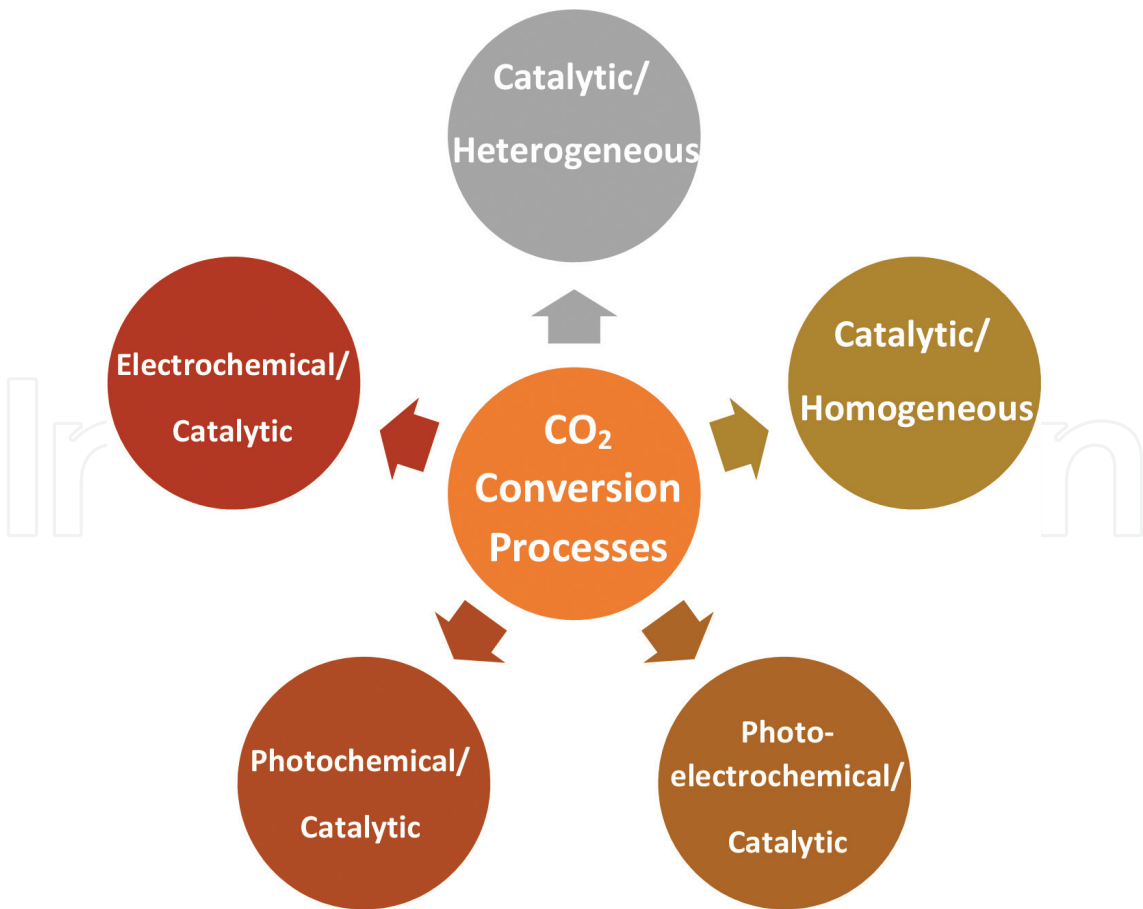


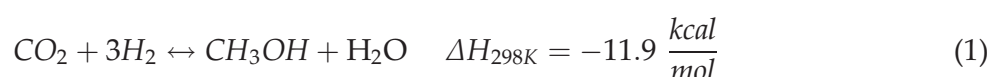
Figure 3. Outline of chemical conversion processes of CO<sub>2</sub>.

produce nearly all products that are derived from fossil fuels [16, 17]. Carbon Recycling International (CRI)'s George Olah plant is considered to be the world's largest CO<sub>2</sub> methanol plant. In 2015, Carbon Recycling International (CRI) scaled up the plant from a capacity of 1.3 million liters of methanol per year to more than 5 million liters a year. The plant now recycles 5.5 thousand tons of CO<sub>2</sub> a year. All energy used in the plant comes from the Icelandic grid that is generated from geothermal and hydro energy [18]. As shown in **Figure 2**, the plant uses electricity to make H<sub>2</sub> which reacts with CO<sub>2</sub> in a catalytic reaction for methanol production. The various pathways and processes for CO<sub>2</sub> conversion to methanol are described schematically in **Figure 3**. There are different CO<sub>2</sub> conversion routes such as the catalytic method which comes in the form of conventional, electrocatalytic, photocatalytic, and photoelectrocatalytic conversion [19].

## 2. Methods to convert CO<sub>2</sub> into methanol

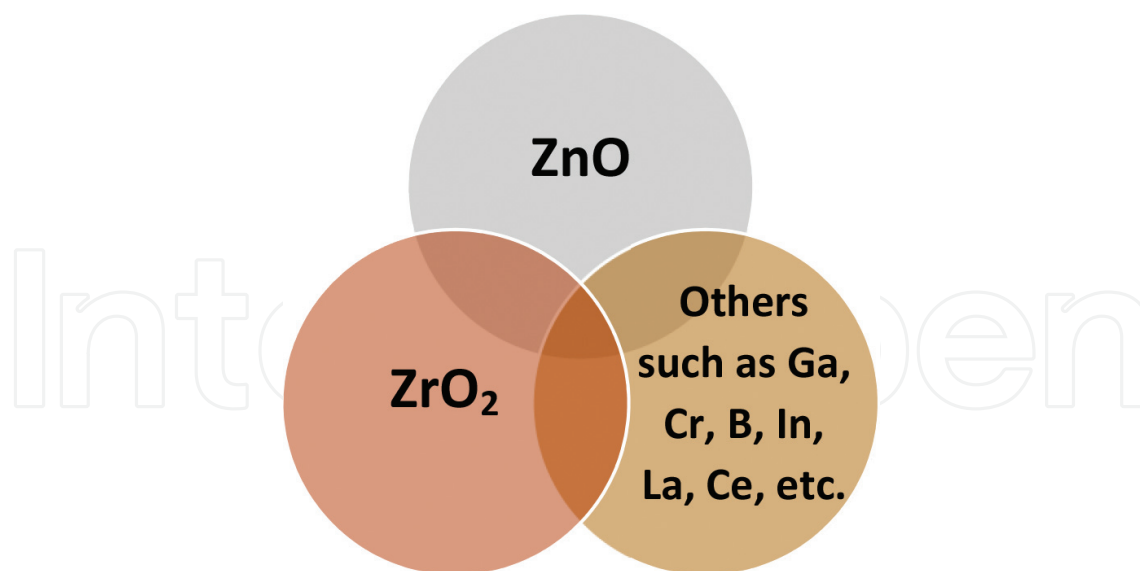
### 2.1. Chemical conversion

The catalytic hydrogenation of CO<sub>2</sub> with H<sub>2</sub> is considered to be the most straightforward way for methanol and DME production from CO<sub>2</sub>, as shown in Eq. (1). During the 1920s and 1930s, the earliest methanol production plants were operated in the USA, which were using CO<sub>2</sub> and H<sub>2</sub> to produce methanol. Both heterogeneous and homogeneous catalysts systems have been studied by many researchers for CO<sub>2</sub> hydrogenation process. However, heterogeneous catalysts have many advantages in terms of separation, stability, handling, cost, and recycling of the catalyst. Heterogeneous and homogeneous catalysts systems are discussed in the following sections [21–23].



#### 2.1.1. Heterogeneous catalytic conversion

Although homogeneous catalysis is also used for methanol production from CO<sub>2</sub>, heterogeneous catalysis is the preferred choice for chemical reaction engineers due to the advantages of heterogeneous catalysis. This includes easy separation of fluid from solid catalyst, convenient handling in different types of reactors (i.e., fixed-, fluidized- or moving-bed), and the used catalyst can be regenerated. Recently, a large number of experiments have been conducted for the development of stable and efficient heterogeneous catalysts for the reduction of CO<sub>2</sub> to produce methanol. However, many studies proved that the Cu based catalysts with different additives such as ZrO<sub>2</sub> and ZrO play an important role to improve the stability and activity of the heterogeneous catalyst (**Figure 4**). Therefore, some of the catalysts, that are shown in **Figure 4**, are already exist and used in demonstration and pilot plants. Some of the metals (i.e., Cu and Zn) and their oxides have been developed to be used as an efficient heterogeneous catalyst for the conversion of CO<sub>2</sub> to methanol [24, 25]. This type of catalyst is similar to Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> based catalysts that are used to produce methanol in the industry. However, it



**Figure 4.** Supports and additives used for Cu-based catalysts.

has been proved that the commercial methanol catalyst such as the heterogeneous mixture of zinc oxide, alumina, and copper (30, 10, and 60%, respectively) produces very little amount of methanol [26]. Various reviews discussed the different factors that may affect the methanol production from syngas such as catalyst preparation, catalyst design, reaction kinetics, reactor design, and catalyst deactivation [22, 27–30]. Therefore, the future research works should be focused on the methanol production from CO<sub>2</sub> and H<sub>2</sub> in which the amount of produced methanol by this way is higher compared to the syngas. In order to sustain high plant output, the catalyst should remain active to be used for several years. Moreover, improving the activity and stability of catalyst over time is very important in the economics of any methanol plant [31]. Recently, Lurgi, which is the leader in methanol synthesis process technology, has been collaborated with Süd-Chemie using a high activity catalyst (C79-05-GL, based on Cu/ZnO) to convert CO<sub>2</sub> and H<sub>2</sub> into methanol [24, 32]. The Lurgi methanol reactor is a tube-based converter which contains the catalysts in fixed tubes and uses a steam pressure control to achieve the controlled temperature reaction. This type of reactor is able to achieve low recycle ratios and high yield. Therefore, Lurgi has been developed to two-stage converter system which uses two combined Lurgi reactors for high methanol capacities. However, the space velocities and temperatures in the first converter will be higher than the single-stage converter in which it needs to achieve only partial conversion of synthesis gas to methanol. This makes the converter to be smaller and produces high-pressure steam due to the high temperatures which will help in saving the energy costs. The exit gas, from the first converter, contains methanol, and it will be directly sent to the second reaction stage that operates at a lower reaction rate [31]. Even if the operating temperature of the Lurgi system is around 260°C which is higher than that used for conventional catalysts to produce methanol, but the methanol selectivity of this system is excellent. However, the activity of this catalyst is decreased with the same rate as commercial catalyst's activity, which is currently used in the industries to produce methanol. There are different companies commercializing high stable catalysts for methanol production such as Mitsubishi Gas Chemical, Sinetix, and Haldor Topsøe. Arena et al. [33]

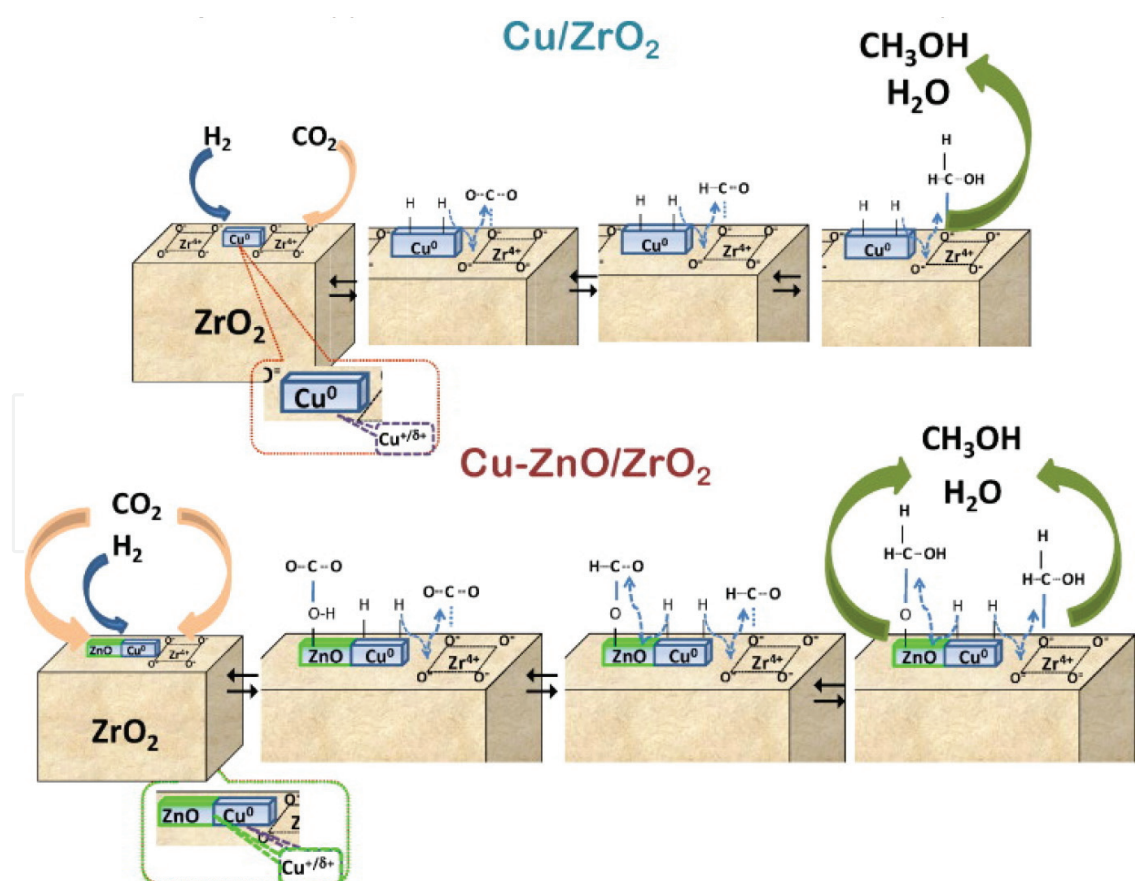


studied the solid-state interactions, functionality, and adsorption sites of Cu–ZnO/ZrO<sub>2</sub> catalysts and its ability for the conversion of CO<sub>2</sub> to methanol. Characterization data indicated that the strong Cu–ZnO interaction effectively promotes the dispersion and reactivity of metal copper to oxygen. The metal/oxide interface in Cu–ZnO/ZrO<sub>2</sub> catalysts plays an important role in hydrogenation of CO<sub>2</sub> to methanol. As shown in **Figure 5**, the dual-site nature of the reaction path explains the formal structure-insensitive character of CO<sub>2</sub> conversion over Cu–ZnO/ZrO<sub>2</sub> catalysts.

## 2.1.2. Homogenous catalytic conversion

### 2.1.2.1. Homogeneous catalysts for CO<sub>2</sub> Hydrogenation to produce methanol

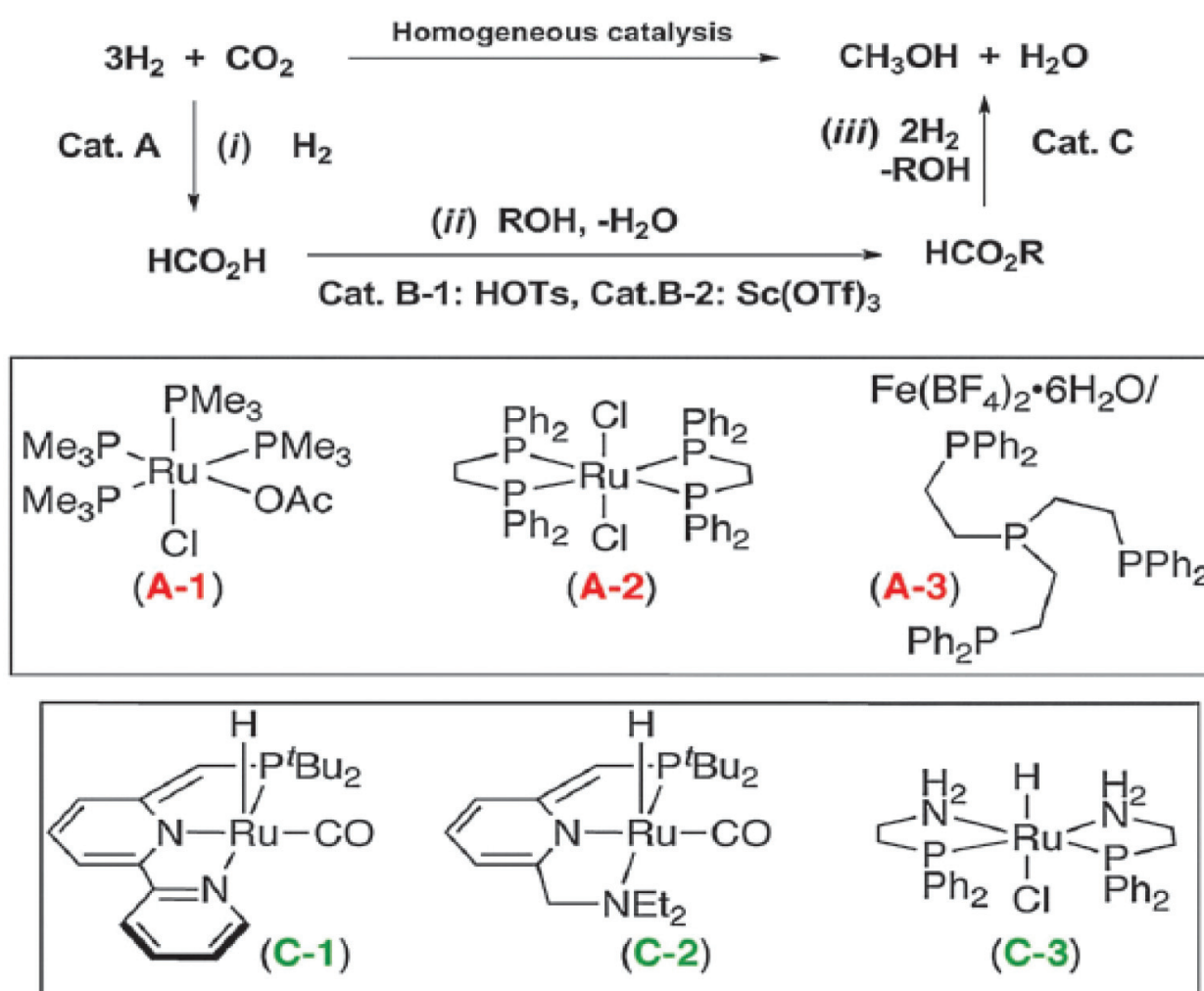
Although different heterogeneous catalysts were tested for the direct CO<sub>2</sub> conversion to methanol, yet very limited homogeneous catalysts have been mentioned in the literature. Tominaga et al. [34] reported an example of direct CO<sub>2</sub> conversion to methanol using homogeneous catalysts. They studied the ability of Ru<sub>3</sub>(CO)<sub>12</sub> catalyst precursor in the presence of KI additive for the CO<sub>2</sub> hydrogenation to form methane, methanol, and CO. Also, it was proved by the same authors that the performance of Ru<sub>3</sub>(CO)<sub>12</sub>–KI for CO<sub>2</sub> conversion is much better than the other transition metal carbonyl catalysts such as W(CO)<sub>6</sub>, Fe<sub>2</sub>(CO)<sub>9</sub>, Ir<sub>4</sub>(CO)<sub>12</sub>, Mo(CO)<sub>6</sub>, Co<sub>2</sub>(CO)<sub>8</sub>, and Rh<sub>4</sub>(CO)<sub>12</sub> [35]. Recently, cascade process has been used to reduce CO<sub>2</sub> to



**Figure 5.** Heterogeneous catalytic process for conversion of CO<sub>2</sub> to methanol using Cu/ZrO<sub>2</sub> and Cu-ZnO/ZrO<sub>2</sub> [33].

methanol instead of six electrons process [36]. Cascade process using homogeneous catalysts can be divided into three steps, which are hydrogenation of CO<sub>2</sub> to formic acid; then, the formic acid will be esterified to generate formate esters; and finally, the formate ester will be hydrogenated to produce methanol (**Figure 6**) as mentioned by Huff and Sanford [36].

Different catalysts will be used in each step of this approach under specific reaction conditions which are high temperature (135°C) and pressure (40 bars). Wesselbaum et al. [37] reported the hydrogenation of CO<sub>2</sub> with 60 bars of H<sub>2</sub> and 20 bars of CO<sub>2</sub> at 140°C in the presence of [(triphos)Ru-(TMM)] (TMM = trimethylenemethane, Triphos = 1,1,1-tris(diphenylphosphino)methyl) ethane) giving a maximum turnover number of 221. Therefore, it has been proved by the same authors that this catalyst can be used in the hydrogenation process to convert formate esters to methanol. In addition to the direct CO<sub>2</sub> conversion to methanol, the conversion of CO<sub>2</sub> derivatives by hydrogenation, such as polycarbonates, carbonates, formates, and carbamates, has gained a huge attention due to the small barriers of these reactions (**Figure 7**) [38, 39].



**Figure 6.** CO<sub>2</sub> hydrogenation to produce methanol via cascade system [36].



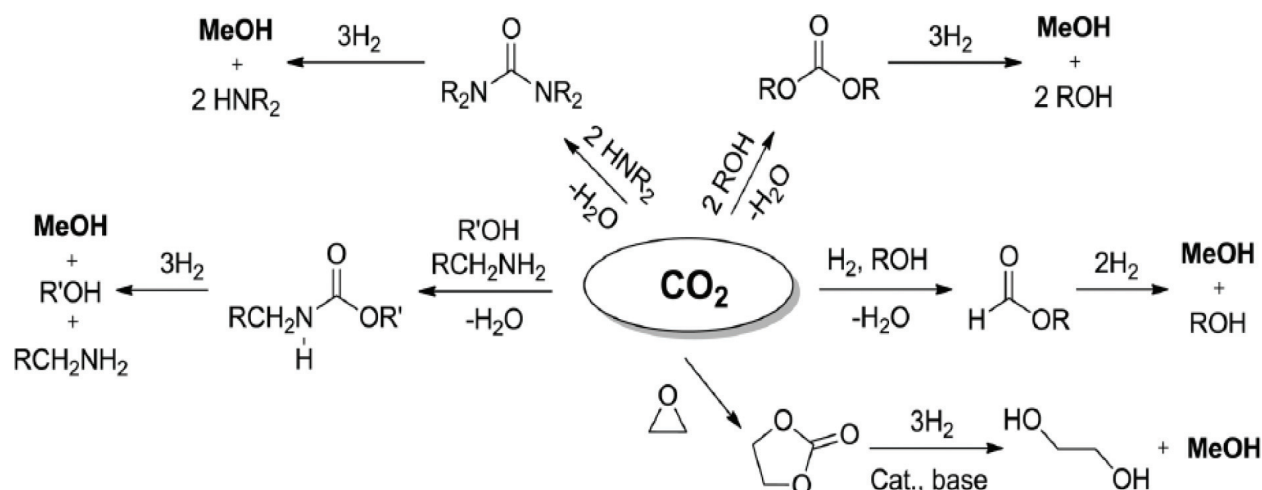


Figure 7. Indirect hydrogenation of  $\text{CO}_2$  for methanol production [39].

#### 2.1.2.2. Homogeneous chemical conversion of $\text{CO}_2$ to methanol

Silanes and hydrides are the main reducing agents to be used in the homogeneous chemical reduction of  $\text{CO}_2$  to methanol in the presence of organocatalysts such as N-heterocyclic carbenes (NHC). Although the cost of the silanes is high, it was proved that the NHC-catalyst has the ability to reduce  $\text{CO}_2$  to methoxides under ambient conditions as mentioned by Zhang et al. [40]. As shown in **Figure 8**, the derivatives of silanol and methanol will be produced by the hydrolysis of methoxysilanes.

The application of frustrated Lewis pairs to reduce  $\text{CO}_2$  to methanol is considered to be another example of the metal-free catalysis (**Figure 9**) [41]. In the first step, the formatoborate derivative is produced via the reaction between  $\text{CO}_2$  and  $[\text{TMPH}] + [\text{HB}(\text{C}_6\text{F}_5)_3]^-$ . The coordinatively unsaturated  $\text{B}(\text{C}_6\text{F}_5)_3$  attacks the nucleophile and formate-bridged intermediate forms.

After that, the latter will react with  $[\text{TMPH}] + [\text{HB}(\text{C}_6\text{F}_5)_3]^-$  to produce the formaldehyde acetal derivative. Schwartz's reagent ( $((\text{Cp})_2\text{Zr}(\text{H})(\text{Cl}))$ ) was used as a hydride source for the two-step

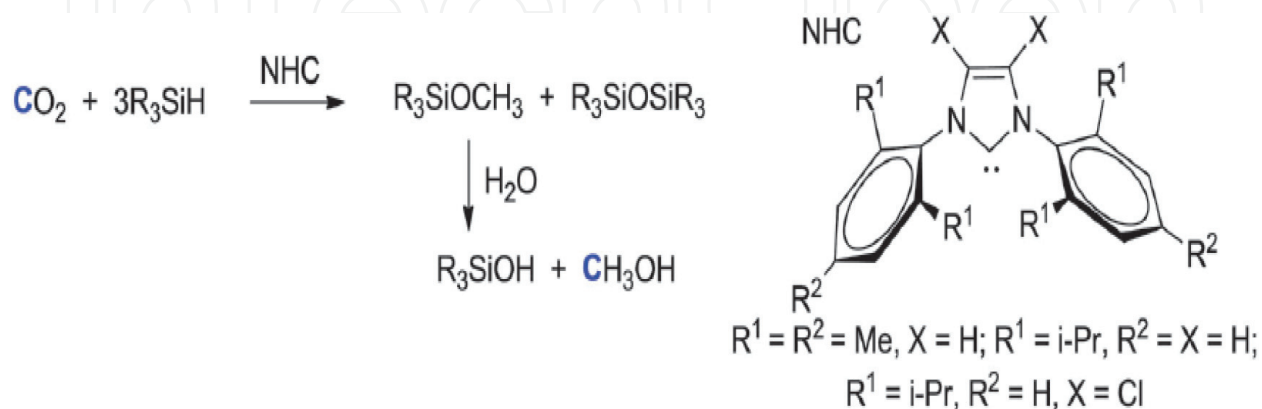


Figure 8. NHC-catalyzed  $\text{CO}_2$  conversion and the subsequent methanol hydrolytic [40].

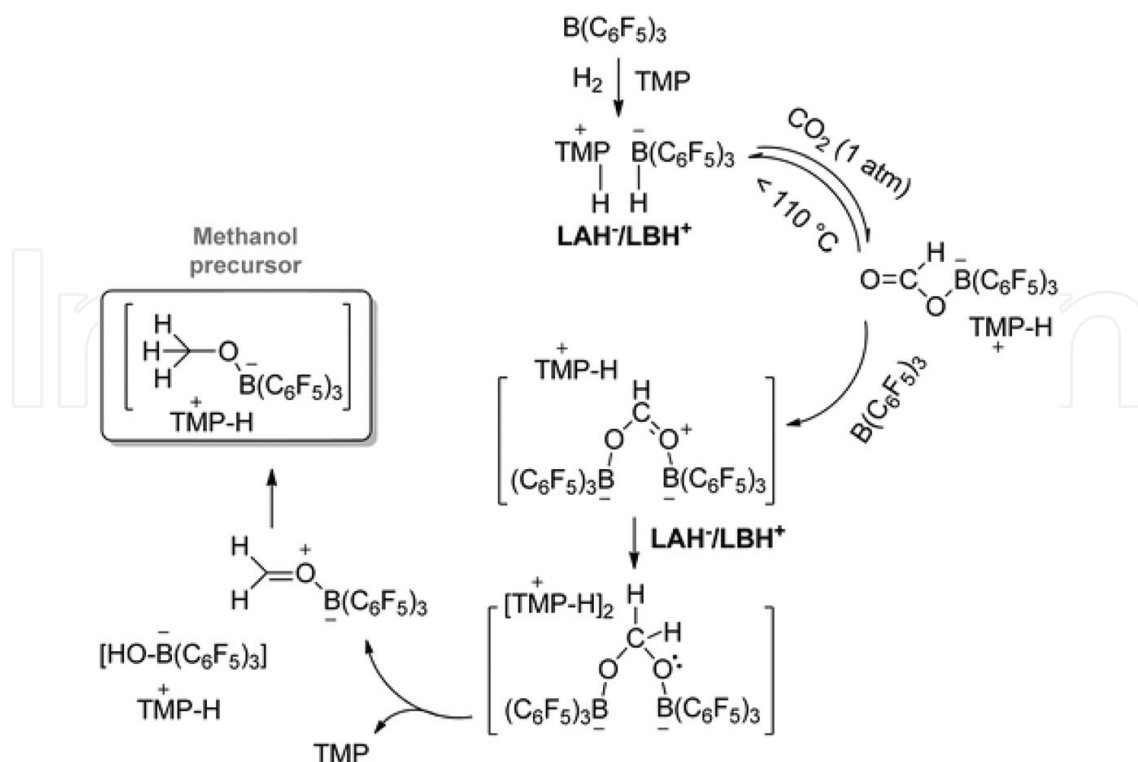


Figure 9. Lewis acid/Lewis base-catalyzed CO<sub>2</sub> hydrogenation [44].

reduction of CO<sub>2</sub> to formaldehyde and methanol, respectively as shown in (Figure 10) [42, 43]. In the first step, the conversion of CO<sub>2</sub> to formaldehyde produces some of the m-oxo complexes. Then, the deeper reduction of formaldehyde can be achieved by adding more Schwarz's reagent which leads to form zirconium methoxide in the second step.

## 2.2. Electrochemical reduction of CO<sub>2</sub> to methanol

During the last decades, electrochemical CO<sub>2</sub> conversion has been widely used on a laboratory scale, but it has not yet been successfully used in the industrial processes (large scale). The electrochemical reduction method is used for CO<sub>2</sub> conversion to valuable chemicals and fuels

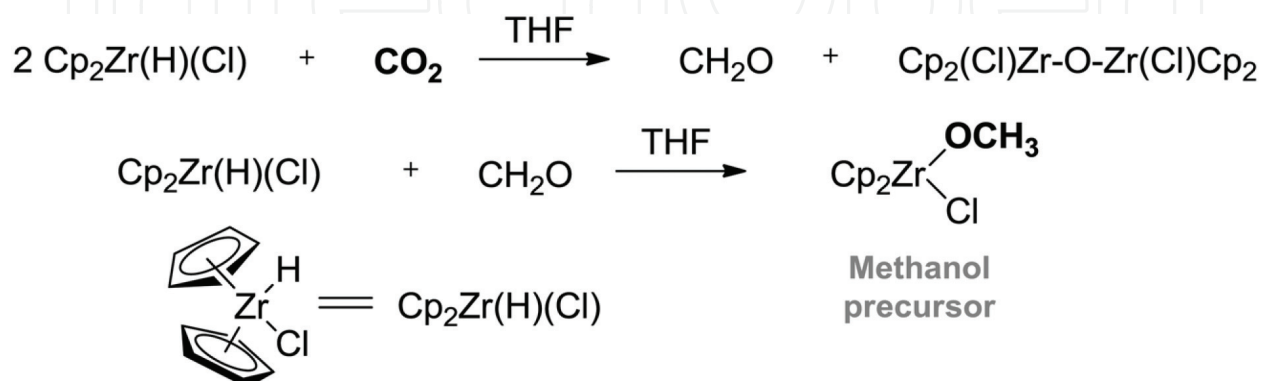


Figure 10. Two-step CO<sub>2</sub> reduction to methanol with Schwarz's reagent [44].

Half-cell reaction	E° vs. SHE
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	+0.17
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	+0.031
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$	−0.028
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	−0.10
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	−0.11

**Table 1.** Standard potentials for CO<sub>2</sub> reduction [49].

such as methanol using electricity as the main source of energy [45–47]. Many experiments with different conditions and electrocatalysts have been conducted for CO<sub>2</sub> reduction on metal electrodes [48]. Different reduced products can be formed electrochemically from CO<sub>2</sub>, and some of these products are presented in **Table 1**. The selection of catalyst and reaction conditions plays a significant role as compared to the potential in controlling between various reduced products. However, all the listed standard potentials in **Table 1** are relatively close to the hydrogen evolution standard potential [49]. The hydrogen evolution reaction (HER) is very important during CO<sub>2</sub> electrocatalyst reduction in which H<sub>2</sub>O is typically present as an electrolyte (and proton source). For this reason, the reported metals that can be used as an electrocatalyst for CO<sub>2</sub> reduction have relatively high HER overpotentials. A huge effort must be conducted in order to find the optimum electrode for CO<sub>2</sub> electrochemical reduction which will reduce the selectivity of CO<sub>2</sub> at low overpotentials and high rates without reducing water simultaneously [44].

There is a distinct advantage of directly converting the captured CO<sub>2</sub> into methanol of producing a useful product that can be used in many energy-consuming devices. This process allows for recycling captured CO<sub>2</sub> and produce methanol that could be used as a renewable energy instead of fossil fuel in energy-consuming devices. In other words, by electroreduction process, CO<sub>2</sub> could be reduced directly in the electrolysis cell back to methanol in one step. Different electrodes can be used to achieve methanol directly from CO<sub>2</sub> [44], as shown in **Table 2**. In 1983, Canfield and Frese [50] proved that some semiconductors such as *n*-GaAs, *p*-InP, and *p*-GaAs have the ability to produce methanol directly from CO<sub>2</sub> although at extremely low current densities and faradaic efficiencies (FEs). Many other researchers did some efforts to increase both the current density as well as faradaic efficiency of the process. Seshadri et al. [51] found that the pyridinium ion is a novel homogeneous electrocatalyst for CO<sub>2</sub> reduction to methanol at low overpotential. Recently, Pyridine has been widely explored in which it is used to act as co-catalyst to form the active pyridinium species in situ [52–56]. Generally, the one-electron reduction products of CO<sub>2</sub> show lower current density than the two-electron reduction products such as CO. The direct electrochemical reduction of CO<sub>2</sub> to methanol is a promising process to reduce the amount of captured CO<sub>2</sub>.

Popić et al. [57] proved that the Ru and Ru modified by Cd and Cu adatoms can be used as an electrode for CO<sub>2</sub> reduction at relatively small overpotentials. The obtained results showed that on the surface of pure Ru, Ru modified by Cu and Cd adatoms, and RuOx+IrOx modified

Electrode	Type of electrode	E vs. NHE (V)	Current density (mA cm <sup>-2</sup> )	Faradaic efficiency (%)	Electrolyte	Reference
<i>p</i> -InP	Semiconductor	-1.06	0.06	0.8	Sat. Na <sub>2</sub> SO <sub>4</sub>	[50]
<i>n</i> -GaAs			0.16	1.0		
<i>p</i> -GaAs			0.08	0.52		
CuO	Metal oxide	-1.3	6.9	28	0.5 M KHCO <sub>3</sub>	[59]
RuO <sub>2</sub> /TiO <sub>2</sub> Nanotubes		-0.6	1	60	0.5 M NaHCO <sub>3</sub>	[58]
Pt-Ru/C	Alloy	-0.06	0.4	7.5	Flow cell	[60]
<i>n</i> -GaP	Homogeneous catalyst	-0.06	0.27	90	10 mM pyridine at pH = 5.2	[61]
Pd		-0.51	0.04	30	0.5 M NaClO <sub>4</sub> with pyridine	[51]

**Table 2.** CO<sub>2</sub> electrochemical reduction to methanol.

by Cu and Cd adatoms, the reduction of CO<sub>2</sub> was achieved to produce methanol during 8 h of holding the potential at -0.8 V. Therefore, in case of CO<sub>2</sub> reduction on Ru modified by Cu and Cd adatoms, the production of methanol was depended on the presence of adatoms at the surface of ruthenium. RuO<sub>2</sub> is a promising material to be used as an electrode for CO<sub>2</sub> reduction to methanol due to its high electrochemical stability and electrical conductivity. For that reason, Qu et al. [58] prepared RuO<sub>2</sub>/TiO<sub>2</sub> nanoparticles (NPs) and nanotubes (NTs) composite electrodes by loading of RuO<sub>2</sub> on TiO<sub>2</sub> nanoparticles and nanotubes, respectively. The obtained results showed that the current efficiency of producing methanol from CO<sub>2</sub> was up to 60.5% on the RuO<sub>2</sub>/TiO<sub>2</sub> NTs modified Pt electrode. Therefore, RuO<sub>2</sub> and RuO<sub>2</sub>/TiO<sub>2</sub> NPs composite electrodes showed lower electrocatalytic activity than RuO<sub>2</sub>/TiO<sub>2</sub> NTs composite modified Pt electrode for the electrochemical reduction of CO<sub>2</sub> to methanol. In order to increase the selectivity and efficiency of CO<sub>2</sub> electrochemical reduction process, nanotubes structure is suggested to be used as an electrode as the studies proved.

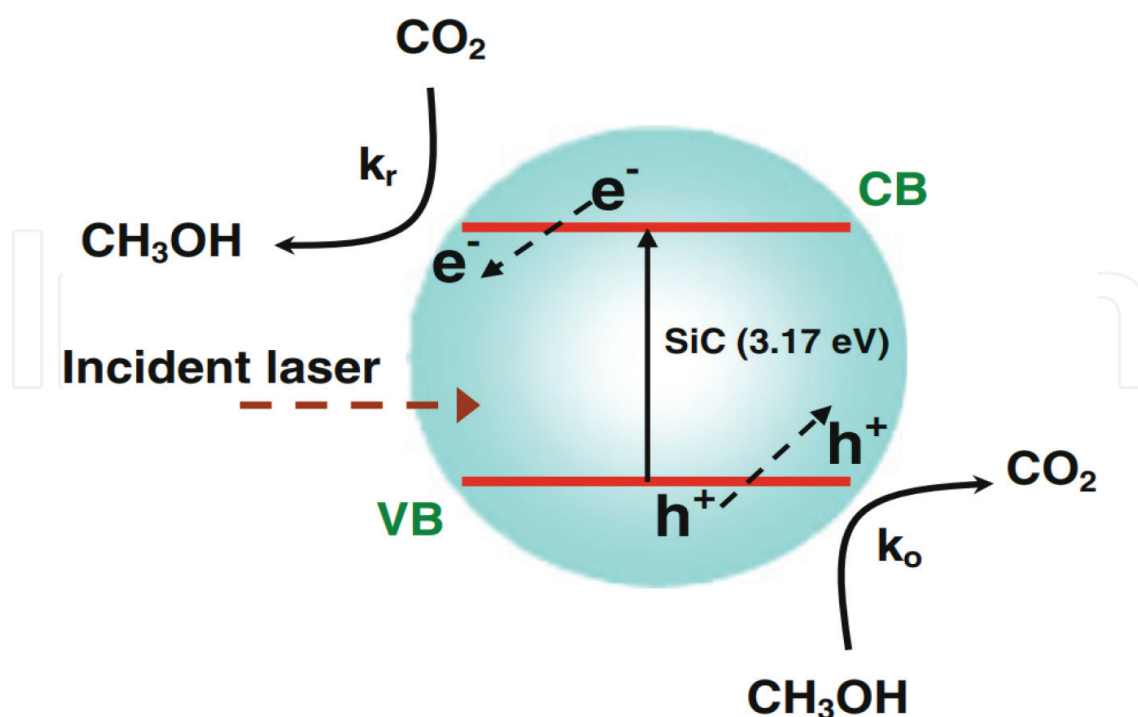
### 2.3. Photochemical reduction of CO<sub>2</sub> to methanol

Typically, the photochemical (or photocatalytic) CO<sub>2</sub> conversion method is used to convert captured CO<sub>2</sub> to methanol and other valuable products by using solar energy such as light or laser [62, 63]. Even if the selectivity for methanol is relatively low, the direct conversion of CO<sub>2</sub> to methanol using photocatalytic method has been studied [64]. However, recently, this method has received a great attention, and it is considered to be as the most attractive method for CO<sub>2</sub> utilization. The photocatalytic CO<sub>2</sub> conversion process is a complex combination of photophysical and photochemical processes together [62]. Therefore, this method has some similarities with electrocatalytic CO<sub>2</sub> reduction in which the molecular catalysts are used in both cases. Sacrificial hydride source is considered to be the major limitation to reduce CO<sub>2</sub> by photocatalytic method. Ascorbic acid, amine, and 1-benzyl-1,4-dihydronicotinamide are examples of sacrificial hydride source, which must be added to the solution to substitute for the

anode, that would be used in electrocatalytic  $\text{CO}_2$  reduction process [65]. Several experiments have been conducted to test the ability of some semiconductors and metal oxides for  $\text{CO}_2$  conversion to methanol. This include silicon carbide [66],  $\text{TiO}_2$  [67–70],  $\text{WO}_3$  [71],  $\text{NiO}$  [70],  $\text{ZnO}$  [70], and  $\text{InTaO}_4$  [72] either by themselves or they can be combined with different heterogeneous catalysts to achieve the same goal. The main challenge in methanol production on semiconductors by using solar energy is that the formation reaction is reversible. Thus, in order to mitigate the methanol oxidation, it is very essential to find new strategies to achieve a practical industrial process [66, 70].

Gondal et al. [66] proved that the granular silicon carbide is a promising photocatalyst for  $\text{CO}_2$  reduction to methanol. The granular silicon carbide ( $\alpha\text{-6H-SiC}$ ) has been tested as a photocatalyst to reduce  $\text{CO}_2$  and convert it into methanol using a 355-nm laser. The reaction cell was filled with  $\alpha\text{-6H-SiC}$  granules, pressurized with  $\text{CO}_2$  gas at 50 psi and distilled water. Therefore, they mentioned that a pair of competitive reactions which are photo-oxidation and photo-reduction are existed in the photochemical process, as shown in **Figure 11**. When the reaction starts, the photooxidation rates ( $k_o$ ) will be slower than the photoreduction rates ( $k_r$ ) because of the low concentration of produced methanol. The obtained results showed that the maximum molar concentration of methanol and photonic efficiencies of  $\text{CO}_2$  conversion into methanol achieved was around 1.25 mmol/l and 1.95%, respectively.

$\text{CdS/TiO}_2$  and  $\text{Bi}_2\text{S}_3/\text{TiO}_2$  nanotube photocatalysts were tested by Li et al. [67], and their photocatalytic activities that reduce  $\text{CO}_2$  to methanol under visible light irradiation have been studied. The obtained results proved that the synthetical TNTs are almost a good material to be act as photoreduction to convert  $\text{CO}_2$  into methanol. The largest methanol production on



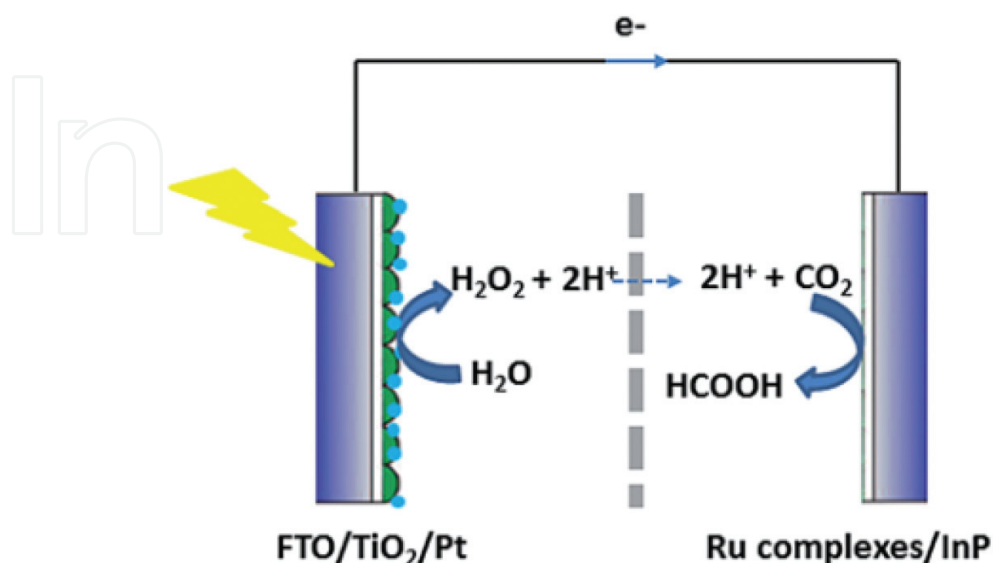
**Figure 11.** Schematic illustration of the photoreduction and photooxidation reactions in the photochemical process [67].



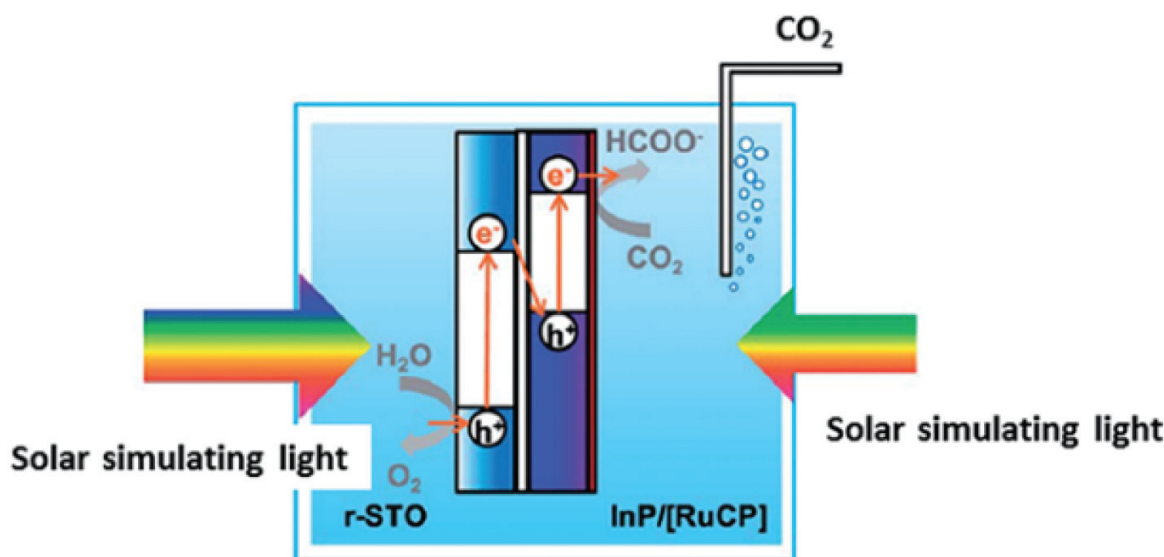
TNTs–CdS and TNTs–Bi<sub>2</sub>S<sub>3</sub> photocatalysts by using visible light irradiation for 5 h were 159.5 and 224.6  $\mu\text{mol/L}$ , respectively. Luo et al. [68] studied the ability of Nd/TiO<sub>2</sub>, which is synthesized via the sol-gel method, to reduce CO<sub>2</sub> into methanol in an aqueous solution under UV irradiation. The experiment showed that the maximum methanol yield under UV irradiation for 8 h was 184.8  $\mu\text{mol/g}$ , proving that the Nd/TiO<sub>2</sub> can increase the efficiency of CO<sub>2</sub> photocatalytic reduction compared to pure titanium oxide.

#### 2.4. Photoelectrochemical reduction of CO<sub>2</sub> to methanol

The photoelectrocatalytic CO<sub>2</sub> reduction process is a combination of the photocatalytic and electrocatalytic methods together. Many research works were focused to find the best semiconductor material that can be used as a photoelectrode to convert CO<sub>2</sub> into methanol using any solar energy in PEC cell; however, no tested semiconductor met the desired stability and efficiency [73]. In fact, the photoelectrochemically reduction of CO<sub>2</sub> need around 1.5 eV of thermodynamic energy input. Therefore, the PEC cell needs greater energy input to make up the losses that causes by band bending (which is needed for charge separation at the surface of semiconductor), overvoltage potentials, and resistance losses [61, 74–81]. The first important step for the reduction of CO<sub>2</sub> to methanol by the photoelectrochemical (PEC) method is the hydrogen ions and electrons generation by the solar irradiance of semiconductor which is used as photocathode. The semiconductor (e.g., GaP, SiC) is illuminated by light as the source of energy that is higher than the semiconductor's band gap. In that case, the electrons in semiconductor will be excited and transferred to conduction band from the valance band, and it will reach the cathode counter electrode through an external electrical wire. Furthermore, in order to produce the electrochemical reduction and oxidation reactions, the produced electron-hole pairs at or near the interface will be separated by the semiconductor and will be injected into the electrolyte [82–84]. A major problem in using the photoelectrochemical cells is the ability of n-type semiconductor materials to generate holes on the surface that can oxidize the



**Figure 12.** The two-compartment photoelectrochemical cell for CO<sub>2</sub> reduction [87].



**Figure 13.** The one-compartment photoelectrochemical cell for CO<sub>2</sub> reduction [87].

semiconductor itself [85]. Recently, the hybrid system which consists of a semiconductor light harvester and a complex of metal co-catalyst has received a huge attention. In this system, the water is considered the main source of electron donors and protons for the reduction of CO<sub>2</sub> at the surface of cathode. An example of hybrid system has been discussed by Zhao et al. [86]. They studied the full cell of photocathode with InP/Ru-complexes that was coupled with a TiO<sub>2</sub>/Pt based photoanode, as shown in **Figure 12**. In this full cell, in order to avoid the formate re-oxidation at the surface of photoanode, the proton exchange membrane was used as a separator. However, Arai et al. constructed a wireless full cell for photoelectrochemical CO<sub>2</sub> reduction in which the system consists of the InP/Ru-complex as a hybrid photocathode and a photoanode of SrTiO<sub>3</sub> (**Figure 13**). In this system, the redox reactions of CO<sub>2</sub> and H<sub>2</sub>O will occur via sunlight irradiation without applying any bias. The obtained results showed that the conversion efficiency from solar to chemical energy in these two full cells was 0.03% and 0.14% for TiO<sub>2</sub>-InP/[RuCP] and SrTiO<sub>3</sub>-InP/[RuCP], respectively. Barton et al. [61] successfully reduced CO<sub>2</sub> to methanol by using catalyzed p-GaP-based photoelectrochemical (PEC) cell in a process called chemical carbon mitigation. Chemical carbon mitigation term describes the photoinduced CO<sub>2</sub> conversion to methanol without the use of additional CO<sub>2</sub> generating power source. The obtained results showed that the methanol selectivity and CO<sub>2</sub> conversion were found to be 100 and 95%, respectively.

### 3. Future prospective and conclusions

Carbon dioxide conversion is presenting both an opportunity and a challenge worldwide for the sustainability of environment and energy. The main strategies of CO<sub>2</sub> reduction should focus on the utilization of CO<sub>2</sub>, the CO<sub>2</sub> recycling combined with the renewable energy to save carbon sources, and the useful chemicals production from CO<sub>2</sub>. Therefore, the conversion of CO<sub>2</sub> into energy product such as methanol will consume large amount of captured CO<sub>2</sub> in which the market scale of methanol is potentially extensive. Furthermore, the generated

methanol can be used instead of the fossil fuel, thus reducing the dependence on fossil fuel and contribute in the market growth of CO<sub>2</sub> utilization. Herein, a complete literature of different methods for CO<sub>2</sub> conversion into methanol is reported in this section. This include homogeneous/heterogeneous catalytic, electrochemical, photochemical, and photoelectrochemical reduction. However, the high performance in CO<sub>2</sub> conversion process can be achieved by using an effective catalyst. In general, the development of required catalyst can be used as a solution if the catalyst is already used, but it is required high cost to be scaled up or it does not exist and await discovery thus the challenges in catalytic processes are huge indeed. The poor product selectivity and the low/high reaction temperatures are considered to be the main barriers in the heterogeneous CO<sub>2</sub> reduction process. However, the above discussion shows that among various methods proposed for CO<sub>2</sub> conversion to methanol or to any valuable chemical, the electrochemical cells are the preferable over other methods. Nevertheless, many barriers still exist in the CO<sub>2</sub> electrochemical reduction in which the electrocatalyst is needed to be used at higher selectivity as well as lower over potentials. Various heterogeneous electrocatalysts are selective, fast and energy-efficient, but they are considered to be unstable catalysts. Therefore, in the future, the electricity needed for electrochemical CO<sub>2</sub> reduction process on a large scale can come from different renewable energy sources such as hydro, wind, wave, geothermal, tides, and so on. In this sense, many research works should be focused on new electrocatalytic materials that can be used to allow working at higher current densities without loss of Faradaic efficiency. On the other hand, photochemical processes offer an attractive approach to reduce CO<sub>2</sub> to methanol using solar energy. However, this method is not widely used due to its critical conditions to absorb the required amount of solar energy. Otherwise, the prospects to develop the successful technologies for the efficient CO<sub>2</sub> conversion using solar energy are certainly long term (>5 years out). Nonetheless, photoelectrochemical reduction processes are discovered to be attractive approaches for the reduction of CO<sub>2</sub> to methanol. At present, the applications of solar photoelectrochemical devices are very limited due to its high cost and several reasons, as discussed above. However, it is very important for research efforts to continue in these areas because this technology will be extremely needed for efficient reduction of CO<sub>2</sub> in the coming years.

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