IOP Conference Series: Materials Science and Engineering

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To cite this article: A Knoks *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **503** 012009

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# Electro-catalytic and photo-catalytic reformation of $CO_2$– reactions and efficiencies processes (Review)

**A Knoks, P Lesnicenoks, J Kleperis, L Grinberga, J Hodakovska, J Klavins, G Cikvaidze and I Lukosevics**

Institute of solid state physics, University of Latvia, Kengaraga street 8, Riga, LV – 1063, Latvia

E-mail: ainars.knoks@cfi.lu.lv

**Abstract**. Energy harvesting with lowest environmental impact is one of key elements for cleaner future. Photocatalytic as well as electrocatalytic $CO_2$ reformation processes are considered as prominent methods. Thus, extensive research of $CO_2$ reformation is being done to find the right materials that holds crucial qualities. For photocatalysis that includes pronounced separation of light-generated opposite sign charge carriers, sensitivity to visible light, high quantum yield. In electrocatalysis high $CO_2$ adsorption, chemical stability, multielectron reaction catalysts are necessary. Additionally, materials participating in the reaction process must be provided with charge carriers at proper reduction and oxidation potentials. To meet the set goal of lowering environmental impact and lower $CO_2$ amounts exhausted into the atmosphere by human activities, it is necessary to find right technology for capturing, storing, and reusing carbon dioxide. Various technologies and materials in different levels of readiness are available and under development, such as CuO loaded $TiO_2$ nanotubes for photocatalytic reformation or electrocatalytic reduction on copper. Not only the proof of concept is necessary but estimation and more importantly determination of the efficiency of both electro and photo catalytic reformation of $CO_2$. In this work review of reactions and efficiency of both processes based on existing established technological methods is done.

## 1. Introduction

It is well known that proactive steps towards pollution reduction and shift from oil based energy are being pursued not only generally by legislation and agreements [1] but also by long term development strategy and research, such as EU climate-neutral plan by 2050. Not only energy harvesting with lowest environmental impact is on of key elements for cleaner future, but also use of accessible resources more efficiently. Electrocatalytic and photocatalytic $CO_2$ reformation are considered as prominent methods for lowering atmospheric pollution and providing possible shift to more sustainable energy production. $CO_2$ can be reformed into various hydrocarbons that can be directly used as fuel or substitute conventional chemical production. Extensive research on $CO_2$ reformation is being done to find the right materials for successful catalytic $CO_2$ reduction. It is known that straightforward $CO_2$ reduction requires substantial amount of energy and special conditions such as high pressure and temperature [2,3]. It is possible to increase efficiency of the process using catalytic reformation under lower temperatures and increase production yields. Materials participating in the reaction must possess adequate $CO_2$ adsorption properties, provide with charge carriers with proper reduction and oxidation potentials for successful reformation of $CO_2$.

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Various technologies and catalysts in different technology readiness levels are available or are under development, such as CuO loaded $TiO_2$ nanotubes for photocatalytic reformation [4] or electrocatalytic reduction on various forms of copper [5,6]. Estimation and more importantly determination of the efficiency of both electrocatalytic and photocatalytic reformation of $CO_2$ is necessary.

In this work review of reactions and efficiency of both processes based on existing technological methods was done.

## 2. Electrocatalytic process

$CO_2$ electrocatalytic reduction has been under investigation for decades, but many uncertainties still remain, such as the reformation pathway from $CO_2$ to higher hydrocarbons, electrolyte influence, etc. The question has been tackled by deWulf and Bard looking into copper electrode using electrochemical methods [7], Firet et al. investigation of silver thin films through spectroscopic methods [8], Shen et al. investigating cobalt protoporphyrin immobilized on a pyrolytic graphite [9] or Kuhl et al. investigating various metal surfaces [10]. It has come to classifications of $CO_2$ reduction products into two categories: 1) gaseous; 2) liquid products, requiring different physical separation and characterization/identification methodologies. On the other hand, the reformation reactions also can be classified by the required number of electrons necessary for a product. Then the reactions can be written as

$$CO_2(g) + 2H^+ + 2e^- = HCOOH(l) \quad E = -250\ mV \quad (1)$$
$$CO_2(g) + H_2O(l) + 2e^- = CO(g) + H_2O(l) \quad E = -1078\ mV \quad (2)$$
$$CO_2(g) + 2H^+ + 2e^- = CO(g) + H_2O(l) \quad E = -110\ mV \quad (3)$$
$$CO_2(g) + 2H_2O(l) + 2e^- = CO(g) + H_2O(l) \quad E = -930\ mV \quad (4)$$
$$CO_2(g) + 4H^+ + 4e^- = CH_2O(l) + H_2O(l) \quad E = -70\ mV \quad (5)$$
$$CO_2(g) + 3H_2O(l) + 4e^- = CH_2O(l) + 4OH^- \quad E = -900\ mV \quad (6)$$
$$CO_2(g) + 6H^+ + 6e^- = CH_3OH(l) + H_2O(l) \quad E = +20\ mV \quad (7)$$
$$CO_2(g) + 5H_2O(l) + 6e^- = CH_3OH(l) + 6OH^- \quad E = -810\ mV \quad (8)$$
$$CO_2(g) + 8H^+ + 8e^- = CH_4(g) + 2H_2O(l) \quad E = +170\ mV \quad (9)$$
$$CO_2(g) + 6H_2O(l) + 8e^- = CH_4(g) + 8\,OH^- \quad E = -660\ mV \quad (10)$$
$$2CO_2(g) + 2H^+ + 2e^- = H_2C_2O_4(aq) \quad E = -500\ mV \quad (11)$$
$$2CO_2(g) + 2e^- = C_2O_4^{2-}(aq) \quad E = -590\ mV \quad (12)$$
$$2CO_2(g) + 12H^+ + 12e^- = CH_2CH_2(g) + 4H_2O(l) \quad E = +60\ mV \quad (13)$$
$$2CO_2(g) + 12H^+ + 12e^- = CH_3CH_2OH(l) + 3H_2O(l) \quad E = +80\ mV \quad (14)$$
$$2CO_2(g) + 12H^+ + 12e^- = C_2H_4(g) + 4H_2O(l) \quad E = +80\ mV \quad (15)$$

here electrode potential E vs standard hydrogen electrode (SHE) in normal conditions [11–14].

We clearly see that hydrocarbons such as ethanol and ethylene reactions require multi-electron transfer. In addition, overpotential plays an important role in the propagation of a reaction, especially involving higher number of electrons. Other parameters, such as electrolyte composition and concentration, pH, temperature, catalyst crystalline facets, dopants, must be considered. For example, majority products on Ag is CO, Cd produces $HCOO^-$, on the other hand, various forms of Cu can produce wide variety of products [11,12,15–17]. Let's assume interest in hydrocarbons, such as $C_2H_4$, then appropriate catalyst will be selected by majority product, faradaic efficiency (FE), overpotential and catalyst synthesis process.

In early work of Hori et al [18] the reformation of CO to $CH_2$ and $C_2H_4$ was discussed. Process was carried out at copper electrode in aqueous electrolyte. It was reported that CO electrocatalytic reduction didn't proceed as the cathodic currents were on scale of $10^{-5}$ $Acm^{-2}$ [18]. Nowadays the current densities reported are with magnitude of $10^{-2}$ [19] and up to $10^{1}$ [13].

In later work of Hori et al. it was pointed out that $CO_2$ must initially be reduced to CO, which is adsorbed on the catalyst. Only then further reformation to C2 and C3 products are possible. Investigation of pH showed that $CH_4$ production is promoted at low pH and $C_2H_4$ at high pH, due to increase in electrolyte concentration of $KHCO_3$. Dependency was explained as $^-OH$ neutralization by nearby $HCO_3^-$

. It is noteworthy that current densities for $C_2H_4$ and $C_2H_5OH$ were reported independent of pH level [20].

Electrolyte concentration influence on FE and production of hydrocarbons was investigated by Zhong et al. where they suggested that higher electrolyte concentrations provide with lower overpotentials at the same time increasing $H_2$ production FE [21]. At the same time it was reported that $C_2H_4$ production is more favourable under low overpotentials [5]. Thus, indicating that if we are interested in $C_2H_4$ production, a catalyst with low overpotential must be chosen and an electrolyte with high pH level can be used, due to reported current density independence of pH. But high concentration and pH promotes $H_2$ production, that sometimes is considered the rate determining step.

It was proposed as $H_2^+$ (ads) or $H_{ads} + H^+$ in comparison with previously assumed $H_2^+(ads) + e^- \rightarrow H_2$, where $H_2^+$ (ads) is transition state. If carbon adsorption on electrode followed by OH electronation and not $H_2^+$ (ads) or $H_{ads} + H^+$ is the rate determining step for ethylene, a formation diagram was proposed (See Figure 1) [20].

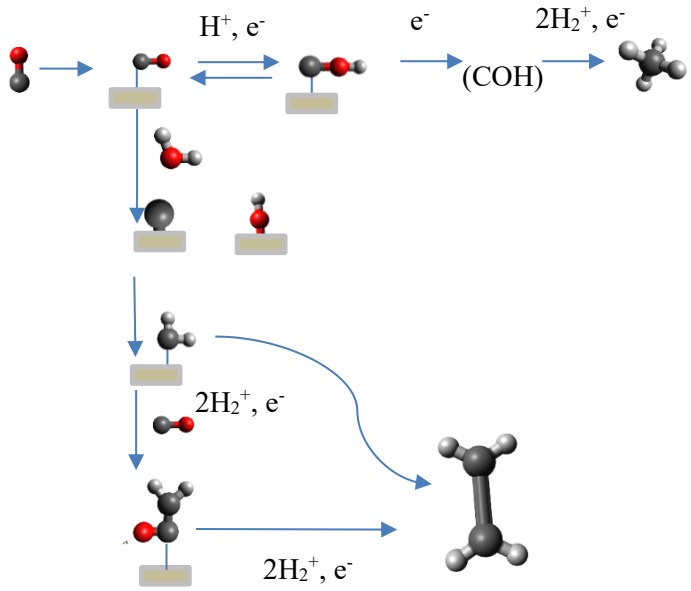



**Figure 1**. Reaction pathway of $CO_2$ reduction with intermediate adsorbed CO, COH, C and OH. Adopted from [20], molecules were drawn by using [24].

In case of pathway depicted in Figure 1, the rate determining step can be CO adsorption and following reformation into $CH_4$ in addition to various intermediates. It is noteworthy that other authors also came to similar conclusions and results for Cu nanoparticles [22,23].

Kortlever et al. suggested that $CO_2$ reduction can be viewed as multiple proton-electron reactions with products C1, C2+ and water, summarizing all probable product equations as equation (16)

$$kCO_2 + n(H^+ + e^-) \leftrightarrows P + mH_2O \quad (16)$$

where P is the C1 and C2+ products [12].

Reaction involving more than 2 electrons (and protons) will involve intermediate steps, thus it will cause catalytic irreversibility. The role of intermediates in the $CO_2$ reduction was discussed. For example, ethylene formation starts with *CO and *$CH_2$ intermediates, which follows abovementioned pathway [12]. But during investigation three unexplained observations were made. First, formation of methane from CO shows different pH dependency compared to ethylene. Second, often ethylene formation happened at more positive (less negative) potential without methane formation. Third, there is a structure sensitive and pH dependent pathways on Cu. Cu(111) reduction of CO to methane and ethylene is observed simultaneously, but on Cu(100) different pathway is observed, where only ethylene is formed, especially at high pH values [12]. On the electrode surface due to $CO_2$ reduction there is a

pH gradient that influences product selectivity. The pH value and ion presence can stabilize reaction intermediates, thus promoting formation of one or the other product [25]. Due to proton consumption during the reduction process and hydrogen evolution reaction (HER) the local pH at the electrode deviates from bulk, thus $CO_2$ can react with $OH^-$ and form bicarbonate or carbonate [12]. On the other hand, Resasco et al. did an extensive investigation on production of CO, $HCOO^-$, $C_2H_4$ and $CH_3CH_2OH$ on Cu electrode, and concluded that the concentration of electrolyte anions has very little influence on production. Attributing it to lack of involvement of hydrogen atoms. At the same time providing with evidence for hydrogen and $CH_4$ production high sensitivity to anion concentration [26].

Malik et al [27] described electrochemical reduction of $CO_2$ process on various Cu morphologies, with FE of 26% at -2.75V. It was reported that grown dendrites on the surface capture some of gaseous products lowering overall efficiency. In addition, the use of Cu nanoparticles increased CO production, with selectivity dependence on size [27,28] attributing it to low-coordination site activity. Similar results concerning increase in CO production was found by Reske et al. decrease in particle size promotes $H_2$ and CO production, at the same time providing with higher current density in comparison with bulk Cu [28].

Authors investigation $CO_2$ reformation on metals as Fe, Au, Zn, Ni, Pt and Ag propose similar reformation pathway [29,30] as seen in Figure 1. Leading to conclusion that first step in $CO_2$ reformation is adsorption of $CO_2$, then CO is formed and desorbed or transformed into *CHO or *CHO species, that later forms into hydrocarbons as methane and methanol. It is noteworthy that metals as Pt, Pd, and Ni were reported to bind CO too strongly, which leads to electrode poisoning by *CO [25,31]. As previously mentioned crystallographic facets show selectivity for production: Cu (111) for $CH_4$ and Cu (100) for $C_2H_4$, suggesting that CO adsorption and lower surface energy is the reason of selectivity [27,32,33]. An overview of FE of different materials in various formations is presented in Table 1.

**Table 1**. FE and major product summary NP – nanoparticle, NW – nanowire, D – dendrite, NR – nanorods, NC – nanocubes, NF – nanoflowers,

| Ref | Catalyst | electrolyte | pH | U, V vs RHE | FE | Product | Ref nr |
|---|---|---|---|---|---|---|---|
| Chen et al | Cu0 - $Cu_2O$ | 0.1M $KHCO_3$ | 6.8 | -1 | 32.1 | $C_2H_4$ | [34] |
| Chen et al | Cu0 - $Cu_2O$ | 0.1M $KHCO_3$ | 6.8 | -1 | 16.4 | $C_2H_5OH$ | [34] |
| Chen et al | $Cu_2O$-PdClx | 0.1M $KHCO_3$ | 6.8 | -1 | 30.1 | $C_2H_6$ | [34] |
| Chen et al | Graphite-$PdCl_2$ | 0.1M $KHCO_3$ | 6.8 | -1 | 4.7 | $HCOO^-$ | [34] |
| Chen et al | Graphite-$PdCl_2$ | 0.1M $KHCO_3$ | 6.8 | -1 | 8.1 | CO | [34] |
| Chen et al | Graphite-$PdCl_2$ | 0.1M $KHCO_3$ | 6.8 | -1 | 0.2 | $CH_4$ | [34] |
| Hori et al | Cu | KCl | 5.9 | -1.44 | 47.8 | $C_2H_4$ | [5] |
| Hori et al | Cu | $KHCO_3$ | 6.8 | -1.41 | 30.1 | C2H4 | [5] |
| Tang et al | Cu NP | | | | 30 | CO | [35] |
| Tang et al | Cu NP | | | | 35 | $C_2H_4$ | [35] |
| Reske et al | Cu NP | 0.1 M $KHCO_3$ | 6.8 | -1.1 V | 20/70 | $CO/H_2$ | [28] |
| Raciti et al | Cu NW | | | -0.6 V | 30.7 | HCOOH | [36] |
| Raciti et al | Cu NW | 0.1M $KHCO_3$ | | -0.4 V | 60 | CO | [36] |
| Chen et al | Cu mesocrystal | 0.1M $KHCO_3$ | | -0.99 V | 81 | $C_2H_4$ | [37] |
| Roberts et al | Cu NC | 0.1M $KHCO_3$ | | -0.6 V | | $C_2H_6$ | [38] |
| Sen et al | Cu foam | 0.5M $KHCO_3$ | | -0.5 V | 26 | HCOOH | [39] |
| Sen et al | Cu smooth | 0.5M $KHCO_3$ | | -0.5 V | 3 | HCOOH | [39] |
| Sen et al | Cu foam | 0.5M $KHCO_3$ | | -0.9 V | 37 | HCOOH | [39] |
| Kas et al | | 0.1 M $KHCO_3$ | 6.8 | -1.1 V | 40 | $C_2H_6$ | [40] |
| Malik et al | Cu NR | 0.5 M $KHCO_3$ | | -2.75 V | 24.5 | CO | [27] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Malik et al | Cu D | 0.5 M $KHCO_3$ | | -3 V | 7 | $C_2H_6$ | [27] |
| Malik et al | Cu D | 0.5 M $KHCO_3$ | | -2.75 V | 7 | $C_2H_4$ | [27] |
| Malik et al | Cu octahedral | 0.5 M $KHCO_3$ | | -3,0 V | 5 | CO | [27] |
| Malik et al | Cu D | 0.5 M $KHCO_3$ | | -2,5 V | 2,8 | $CH_4$ | [27] |
| Lui et al | $Sn/Sn_{O2}$ | 0.5 M $KHCO_3$ | 7.2 | -1.4 V | 70 | $HCOO^-$ | [41] |
| Mistry et al | Au/Cu NP | 0.1 M $KHCO_3$ | 6.8 | -1.2 V | 20 | $CO/CH_4$ | [42] |
| Wang et al | $Cu_2Cd/Cd/Cu$ | 0.1 M $KHCO_3$ | | -1.0 V | 84 | CO | [43] |
| Bernal et al | CuCo NP | 0.1 M $KHCO_3$ | | -1.1 V | 11 | HCOOH | [44] |
| Bernal et al | CuCo NP | 0.1 M $KHCO_3$ | | -1.1 V | 7.5 | CO | [44] |
| Yang et al | Co NF | 0.1 M $KHCO_3$ | | -0.456 V | 63.4 | Formate | [45] |
| Ge et al | $Sn_{O2}$ | | | -0.8 V | 80 | CO/Formate | [46] |
| Kaneco et al | Cu NP with Pb | NaOH in $CH_3OH$ | 14 | -2.3 V | 80 | HCOOH | [47] |
| Kaneco et al | Cu NP with Zn | NaOH in $CH_3OH$ | 14 | -2.1 V | 12 | $CH_4$ | [47] |
| Cook et al | Cu on GDE | 1 M KOH | 14 | - 2.8 V | 69 | $C_2H_4$ | [48] |

Particle size also influence not only selectivity but also FE. CuCo NP showed decrease in HER, with increase of Cu content NP. On the other hand increased Cu content lead to increase in production of CO and HCOOH [44]. Flower like structures were proven to improve production of formate up to 63% FE. From Table 1 we can see that Cu is promising material for $CO_2$ reformation. Similar results were presented by Zhang et al. not only for Cu, but also for Zn and Sn based catalysts [49].

## 3. Photocatalytic $CO_2$ reduction

One of the problems in photocatalytic $CO_2$ reduction is that hydrogen donors, such as $H_2O$, $CH_4$, and alcohols, act as hole scavengers, thus it is necessary to separate reduction products from bulk electrolyte. This correlates with hydrogen production problems. Assuming that the $CO_2$ reduction reaction can proceed without limits set by charge carrier potentials (valence band (VB) and conduction band (CB) band position) [50].

Electrons are excited into the CB, with that, a hole is created in VB, where these charge carriers could be trapped in shallow or deep sites. In $TiO_2$ it could be $Ti^{III}OH$ and $Ti^{IV}OH^{\bullet}$ shallow sites. $Ti^{III}$ also could trap electrons in bulk material. If no site is found, charge carriers recombine and create excess heat on the material surface. Hydrocarbons can be produced only if hydride reductants are oxidized simultaneously. Thus, there is a need of oxidizing agents and oxidizing mechanism [50,51].

Direct oxidizing species are holes, but there are additional molecules with similar oxidizing properties: hydroxyl radicals ($^{\bullet}OH_{free}$ and $^{\bullet}OH_{ads}$ [52]), superoxide ($^{\bullet}O_2^-$ [53]), singlet oxygen ($^{-}O_2$ [54]), also some authors report hydrogen peroxide and oxygen [55]. Karamian et al summarizes that $^{\bullet}OH$ radicals are mostly product of surface hydroxyl and adsorbed water oxidation process. In this process peroxide can be produced and oxidized as described by equations (17) to (21).

Superoxides are supposed to be a weak oxidizing species as a product of one CB electron reduction of molecular oxygen or oxidizing hydrogen peroxide by VB hole (equation 22 to 24), whereas single oxygen is a strong oxidant and can be a product of $\bullet O_2^-$ and a trapped hole, though it has a short lifetime 2 μs on the surface, especially compared with hydroxyl radical with lifetime 5 times longer [50,54,55].

$$H_2O_2 + h\nu \rightarrow \bullet OH_{free/ads} + \bullet OH_{free/ads} \quad (17)$$
$$H_2O_2 + e_{CB}^- \rightarrow \bullet OH_{ads} + OH^- \quad (18)$$
$$H_2O_2 + \bullet O_2^- \rightarrow \bullet OH_{free/ads} + OH^- + O_2 \quad (19)$$
$$H_2O_2 + h_{VB}^+ + 2OH^- \rightarrow \bullet O_2^- + 2H_2O \quad (20)$$
$$H_2O_2 + \bullet OH + OH^- \rightarrow \bullet O_2^- + 2H_2O \quad (21)$$

$$OH^- + h^+_{VB} \rightarrow {}^{\bullet}OH_{ads} \quad (22)$$
$$O_2 + e^-_{CB} \rightarrow {}^{\bullet}O_2^- \quad (23)$$
$$O_2 + 2e^-_{CB} + 2H^+ \rightarrow H_2O_2 \quad (24)$$

It must be remembered that $CO_2$ is very stable molecule, difference between lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital states is 13.7 eV. Adsorption of $CO_2$ onto catalyst is the best way to lower its energy due to the bend in LUMO level. One electron transfer initiates the adsorption and following chemical reactions. Electron or proton transfer provides with C-O bond breaking and C-H bond creation. It is believed that capturing electron from CB of photocatalyst is the first step in $\bullet CO_2^-$ anion radical as described in the following equation (25). Additional reductant is necessary, it is supposed that carbon-free reductants such as $H_2$ or water allow C1 products and carbon containing reductants such as $CH_4$ can promote C2, C3 products [50].

$$CO_2 + e^-_{CB} \rightarrow \cdot CO_2^- \quad (25)$$

P-type photocathodes and earth-abundant n-type anodes such as $WO_3$, $Fe_2O_3$, $TiO_2$ can be used for photocatalytic $CO_2$ reduction. By utilizing metallic and composite catalysts as cathodes one can gain high FE and products as $CH_4$ and $C_2H_4$. In a photocatalytic cell using $WO_3$ and Cu or $Sn/SnO_x$ electrodes $CO_2$ reduction potential of -3.0 V and +0.2V *vs* Reversible hydrogen electrode (RHE) has been reported. Thus the photocatalytic $CO_2$ reduction is described by equations (1)-(15) with lower bias potential due to photocatalytic charge carrier generation [56]. FE and necessary bias potentials for photocatalytic $CO_2$ reduction are provided in Table 2.

**Table 2** Summary of FE and bias potentials in photocatalytic $CO_2$ reduction.

| Ref | Catalyst | electrolyte | pH | Potential V vs RHE | FE | Product | Ref nr | λ, nm |
|---|---|---|---|---|---|---|---|---|
| Magesh et al | $WO_3$-Cu | $KHCO_3$ | 7.5 | +0.87 | 42.3 | $CH_4$ | [57] | >420 |
| ''-'' | $WO_3$-Cu | $KHCO_3$ | 7.5 | +0.65 | 64.6 | $CH_4$ | [57] | >420 |
| ''-'' | $WO_3$-Cu | $KHCO_3$ | 7.5 | +0.75 | 67 | $CH_4$ | [57] | >420 |
| ''-'' | $WO_3$-Cu | $KHCO_3$ | 7.5 | +0.87 | 4 | $C_2H_4$ | [57] | >420 |
| ''-'' | $WO_3$-Cu | $KHCO_3$ | 7.5 | +0.65 | 4.5 | $C_2H_4$ | [57] | >420 |
| ''-'' | $WO_3$-Cu | $KHCO_3$ | 7.5 | +0.75 | 2.7 | $C_2H_4$ | [57] | >420 |
| ''-'' | $WO_3$-Sn/$SnO_x$ | KCl | 7.5 | +0.6 | 27.5 | HCOOH | [57] | >420 |
| ''-'' | $WO_3$-Sn/$SnO_x$ | KCl | 7.5 | +0.7 | 27.5 | HCOOH | [57] | >420 |
| ''-'' | $WO_3$-Sn/$SnO_x$ | KCl | 7.5 | +0.8 | 26.8 | HCOOH | [57] | >420 |
| Hinogami et al | p-Si | 0.1 M $KHCO_3$ | 6.8 | -0.62 | 12 | CO | [58] | >420 |
| ''-'' | Cu/p-Si | 0.1 M $KHCO_3$ | 6.8 | -0.52 | 25 | $CH_4$ | [58] | >420 |
| ''-'' | p-Si | 0.1 M $KHCO_3$ | 6.8 | -1.026 | 73.5 | $H_2$ | [58] | >420 |
| ''-'' | Ag | 0.1 M $KHCO_3$ | 6.8 | -1.49 | 75.9 | CO | [58] | >420 |
| ''-'' | part-Ag/p-Si | 0.1 M $KHCO_3$ | 6.8 | -0.806 | 50.9 | CO | [58] | >420 |
| ''-'' | Au | 0.1 M $KHCO_3$ | 6.8 | -0.966 | 82.2 | CO | [58] | >420 |
| ''-'' | part Au/p-Si | 0.1 M $KHCO_3$ | 6.8 | -0.496 | 62.2 | CO | [58] | >420 |
| Yoneyama et al | p-CdTe | 0.1 M $Na_2CO_3$ | n.a. | -0.55 | 48.4 | HCOOH | [59] | >450 |
| ''-'' | p-CdTe | 0.1 M TEAP | n.a. | -0.55 | 65.6 | CO | [59] | >450 |
| ''-'' | p-InP | 0.1 M TEAP | n.a. | -0.55 | 17.5 | HCOOH | [59] | >450 |
| ''-'' | p-InP | 0.1 M $Na_2CO_3$ | n.a. | -0.55 | 36.2 | HCOOH | [59] | >450 |
| Tan et al | 5GO-O$TiO_2$ | Gaseous $CO_2$ with $H_2O$ | n.a. | 0 | 3.45 | $CH_4$ | [60] | >400 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| ''-'' | 5GO-OTiO$_2$ | Gaseous $CO_2$ with $H_2O$ | n.a. | 0 | 9.07 | CO | [60] | >400 |
| ''-'' | 5GO-OTiO$_2$ | Gaseous $CO_2$ with $H_2O$ | n.a. | 0 | 1.75 | $C_2H_4$ | [60] | >400 |

## 4. Conclusions

Catalytic $CO_2$ reformation is yet to be fully understood. The pathways of electrocatalytic and photocatalytic reduction are similar but requires different parameter control and thus have different production efficiency.

In electrocatalytic reduction higher hydrocarbons are produced under more negative overpotentials than -1.3 V vs NHE. Low carbonate and KCl concentrations provide higher FE for $C_2H_4$ formation. pH influence is not determined but results suggest that flow of electrolyte should be applied for higher FE.

Electrocatalytic $CO_2$ reduction in liquid electrolytes is characterized by higher production rates and photocatalytic reduction production volumes are substantially lower. Production of higher hydrocarbons is challenging in photocatalytic reduction, as the majority of products are C1 and C2. In addition, in many cases photocatalytic $CO_2$ reduction requires bias potential, which increases overall energy consumption. It is necessary to investigate materials that would allow $CO_2$ reduction without bias potential. Photocatalytic processes are not able to deliver high enough current densities for high volume production.

If the goal is $C_2H_4$ then nanostructured Cu should be chosen as catalyst material, higher concentration electrolyte should be used in electrocatalytic $CO_2$ reformation.

## 5. Acknowledgement

Funding from European Union`s Horizon 2020 Research and Innovation Program project under grant agreement No 768789 is greatly acknowledged.

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