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Progress in Plasma-Assisted Catalysis for Carbon Dioxide Reduction

Guoxing Chen, Ling Wang,
Thomas Godfroid and Rony Snyders

Abstract

Production of chemicals and fuels based on CO_2 conversion is attracting a special attention nowadays, especially regarding the fast depletion of fossil resources and increase of CO_2 emissions into the Earth's atmosphere. Recently, plasma technology has gained increasing interest as a non-equilibrium medium suitable for CO_2 conversion, which provides a promising alternative to the conventional pathway for greenhouse gas conversion. The combination of plasma and catalysis is of great interest for turning plasma chemistry in applications related to pollution and energy issues. In this chapter a short review of the current progress in plasma-assisted catalytic processes for CO_2 reduction is given. The most widely used discharges for CO_2 conversion are presented and briefly discussed, illustrating how to achieve a better energy and conversion efficiency. The chapter includes the recent status and advances of the most promising candidates (plasma catalysis) to obtain efficient CO_2 conversion, along with the future outlook of this plasma-assisted catalytic process for further improvement.

Keywords: green energy, plasma-based CO_2 conversion, plasma catalysis, oxygen vacancies, synergistic effect

1. Introduction

The utilization of CO_2 for production of fuels, energy storage media, chemicals or aggregates is attracting interest worldwide due to the essential contribution of the greenhouse gases to the global warming. CO_2 capture and utilization are considered as a promising option for the mitigation of CO_2 emissions, which provides a lower carbon footprint for the synthesis of value-added products than those produced by conventional processes using fossil fuels. In spite of the continuously increasing interest for CO_2 recycling, there are significant challenges to overcome due to its stable molecular structure and low chemical activity. There are several methods that can be used to convert CO_2, including traditional catalysis, photochemical, biochemical, solar thermochemical, electrochemical and plasma chemical. Snoeckx and Bogaerts recently made a detailed comparison of these technologies as shown in **Table 1** [1]. They concluded that the plasma technology fares very well in this comparison and is quite promising. Indeed, nonthermal plasma has attracted much attention of the scientific community as a non-equilibrium medium suitable for CO_2

	Use of rare earth metals	Renewable energy	Turnkey process	Conversion and yield	Separation step needed	Oxygenated products (e.g. alcohols, acids)	Investment cost	Operating cost	Overall flexibility
Traditional catalysis	Yes	-	No	High	Yes	Yes	Low	High	Low
Catalysis by MW-heating	Yes	Indirect	No	High	Yes	Yes	Low	Low	Low
Electro-chemical	Yes	Indirect	No[b]	High	Yes[c]	Yes	Low	Low	Medium
Solar thermo-chemical	Yes	Direct	NA	High	No	No	High	Low	Low
Photo-chemical	Yes	Direct[a]	Yes	Low	Yes	Yes	Low	Low	Low
Biochemical	No	Direct[a]	No	Medium	Yes[d]	Yes	High /low	High	Low
Plasma-chemical	No	Indirect	Yes	High	Yes[e]	Yes	Low	Low	High

[a]*Bio- and photochemical processes can also rely on indirect renewable energy when they are coupled with artificial lighting.*
[b]*Electrochemical cells are turnkey, but generally the cells need to operate at elevated temperatures and the cells are sensitive to on/off fluctuations.*
[c]*The need for post-reaction separation for the electrochemical conversion highly depends on the process and cell type used.*
[d]*Biochemical CO_2 conversion requires very energy-intensive post-reaction separation and processing steps.*
[e]*The need for post-reaction separation for plasma technology highly depends on the process.*

Table 1.
Comparing the advantages and disadvantages of the different technologies for CO_2 reduction (adapted from [1]).

conversion, which provides an attractive alternative to the conventional pathway for CO_2 recycling, such as traditional catalysis and solar thermochemical process.

Nonthermal plasmas have been successfully utilized in many applications for the environmental control (such as gaseous pollutant abatement), material science (such as surface treatment) and medical applications (such as wound and cancer treatment) [1–3]. Nowadays, an increasing interest has been focused on examining their use for CO_2 utilization [3–54]. In comparison to the other processes, plasma process is fast: plasma has the potential to enable thermodynamically unfavorable chemical reactions (e.g. CO_2 dissociation) to occur on the basis of its non-equilibrium properties, low-power requirement and its capacity to induce physical and chemical reactions at a relatively low temperature. In addition, plasma can be ignited and shut off quickly, which enables plasma technology powered by renewable energy to act as an efficient chemical switch for the conversion purposes. Although plasma technology shows great potential, there is always a trade-off between the energy efficiency and conversion efficiency in plasma-only process. Last but not least, the conversion efficiency can be significantly improved by combining plasma with catalyst while maintaining high-energy efficiency.

Plasma catalysis (also referred to as plasma-enhanced catalysis, plasma-driven catalysis or plasma-assisted catalysis) has gathered attention as a way of increasing energy efficiency and optimizing the byproduct distribution [55]. On one hand, the catalyst can increase reaction rates and overall process selectivity. The nonthermal plasma can provide energy to drive highly endothermic processes. Plasma-catalytic processes have great potential to reduce the activation barrier of different reactions and improve the conversion rates. In addition, the nonthermal plasma itself can influence the acid–base nature of the supports, enhance the dispersion of the
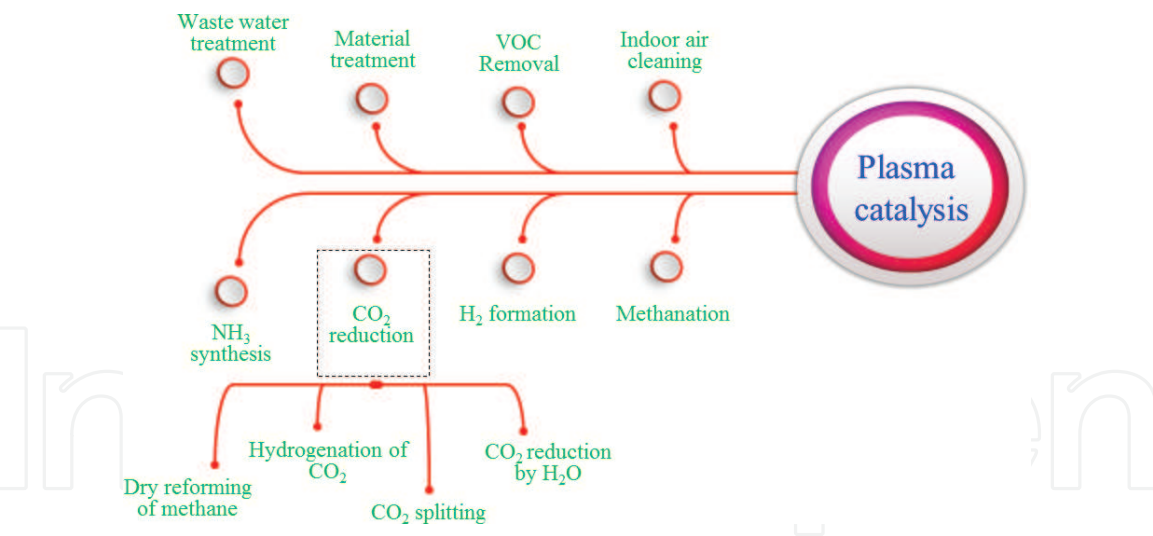
Figure 1.
Applications of plasma catalysis.

supported metals and even adjust the microstructure of the metal nanoparticles and metal-support interface [56, 57] and in this way change the catalyst properties. All these factors contribute in different ways to the enhancement of energy efficiency of the plasma process as well as the catalyst stability, due to a synergy that occurs between the catalyst and the plasma [58]. This novel technique combines the advantages of high product selectivity from thermal catalysis and the fast startup from plasma technique. Plasma catalysis has been widely investigated for many applications. **Figure 1** briefly summarizes the main application areas of plasma catalysis. In the domain of energy applications, the use of plasma catalysis for dry reforming, CO_2 reduction, hydrogen production, methanation and ammonia (NH_3) synthesis has been intensively studied. In this chapter, however, we focus only on their application for CO_2 conversion into value-added chemicals and fuels.

2. Brief theoretical background

2.1 CO_2 dissociation chemistry

As mentioned in Introduction, nonthermal plasma shows a great potential for an efficient CO_2 utilization. Different routes for CO_2 conversion have been investigated using plasma-catalytic process. **Table 2** summarizes some of the main reactions

Process	Reaction	Enthalpy (ΔH) kJ mol^{-1}	Enthalpy (ΔH) eV/molecule
CO_2 splitting	$CO_2 \rightarrow CO + \frac{1}{2}O_2$	279.8	2.9
Dry reforming of methane	$CO_2 + CH_4 \rightarrow 2CO + 2H_2$	247.4	2.6
Methanol synthesis	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	−128	−1.3
Methanation	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	−164.8	−1.7
Reverse water-gas shift reaction	$CO_2 + H_2 \rightarrow CO + H_2O$	41.2	0.4
Water-gas shift reaction	$CO + H_2O \rightarrow CO_2 + H_2$	−41.2	−0.4
Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	−205.8	−2.1
Water spitting	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	250.9	2.6

Table 2.
Chemical reactions related to CO_2 reduction and their enthalpies.

usually considered in plasma chemistry for CO_2 reduction using different pathways (such as dry reforming of methane, hydrogenation of CO_2). Significant attention has been given to plasma-catalytic dry reforming of methane (DRM) using supported Ni catalysts. However, most of these studies focused primarily on identifying plasma-catalytic chemical reactions to maximize process performance. Optical emission spectroscopy and plasma chemical kinetic modeling should be used to achieve a better understanding on the formation of a wide range of reactive species in this plasma-catalytic reforming process. Recently, Chung et al. had described the mechanisms of catalysis promotion, elucidated the synergistic effects between catalyst and plasma and proposed possible approaches to optimize DRM process performance [2]. As explained by Fridman [3], cumulative vibrational excitations of the CO_2 molecule can result in a highly energy-efficient stepwise dissociation. Thus, CO_2 splitting using nonthermal plasmas has been considered as another promising pathway to produce synthetic fuels via CO, as an intermediate product. As well-accepted in the literature, dissociation of a CO_2 molecule in plasma is represented by the following global reaction [3]:

$$CO_2 \rightarrow CO + \tfrac{1}{2}O_2, \Delta H = 2.9 \text{ eV/molecule} \tag{1}$$
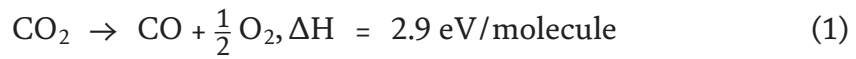
The main pathways for decomposition of CO_2 molecule include the electron impact dissociation:

$$CO_2 \rightarrow CO + O, \Delta H = 5.5 \text{ eV/molecule} \tag{2}$$

which is often accompanied by the further recombination of atomic O:

$$M + O + O \rightarrow O_2 + M \text{ (M is a particle)} \tag{3}$$

In addition to this, the vibrationally excited CO_2 molecules may also undergo decomposition via the collisions with atomic O:

$$O + CO_2{}^{vibr} \rightarrow CO + O_2, \Delta H = 0.3 \text{ eV/molecule} \tag{4}$$
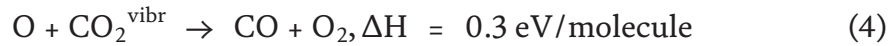
as well as with the plasma electrons:

$$e + CO_2{}^{vibr} \rightarrow CO + \tfrac{1}{2}O_2 \text{ (the energy required is } << 1 \text{ eV)} \tag{5}$$

Traditionally, to characterize the process efficiency, two main parameters reflecting the *conversion* efficiency and *energy* efficiency are used. The conversion efficiency (χ) and energy efficiency (η) of CO_2 are defined as follows:

$$\chi = \frac{\text{moles of } CO_2 \text{ input} - \text{moles of } CO_2 \text{ output}}{\text{moles of } CO_2 \text{ input}} \tag{6}$$

$$\eta = \frac{\chi * 2.9 \text{ eV}}{SEI} \tag{7}$$

Here the specific energy input (SEI) per molecule is given by the ratio of the discharge power (P) to the gas flow rate (F) through the discharge volume.

2.2 Plasma catalysis

When catalysts are combined with plasmas, they can be classified into three systems, i.e. single stage, two stage, and multistage, depending on the location of
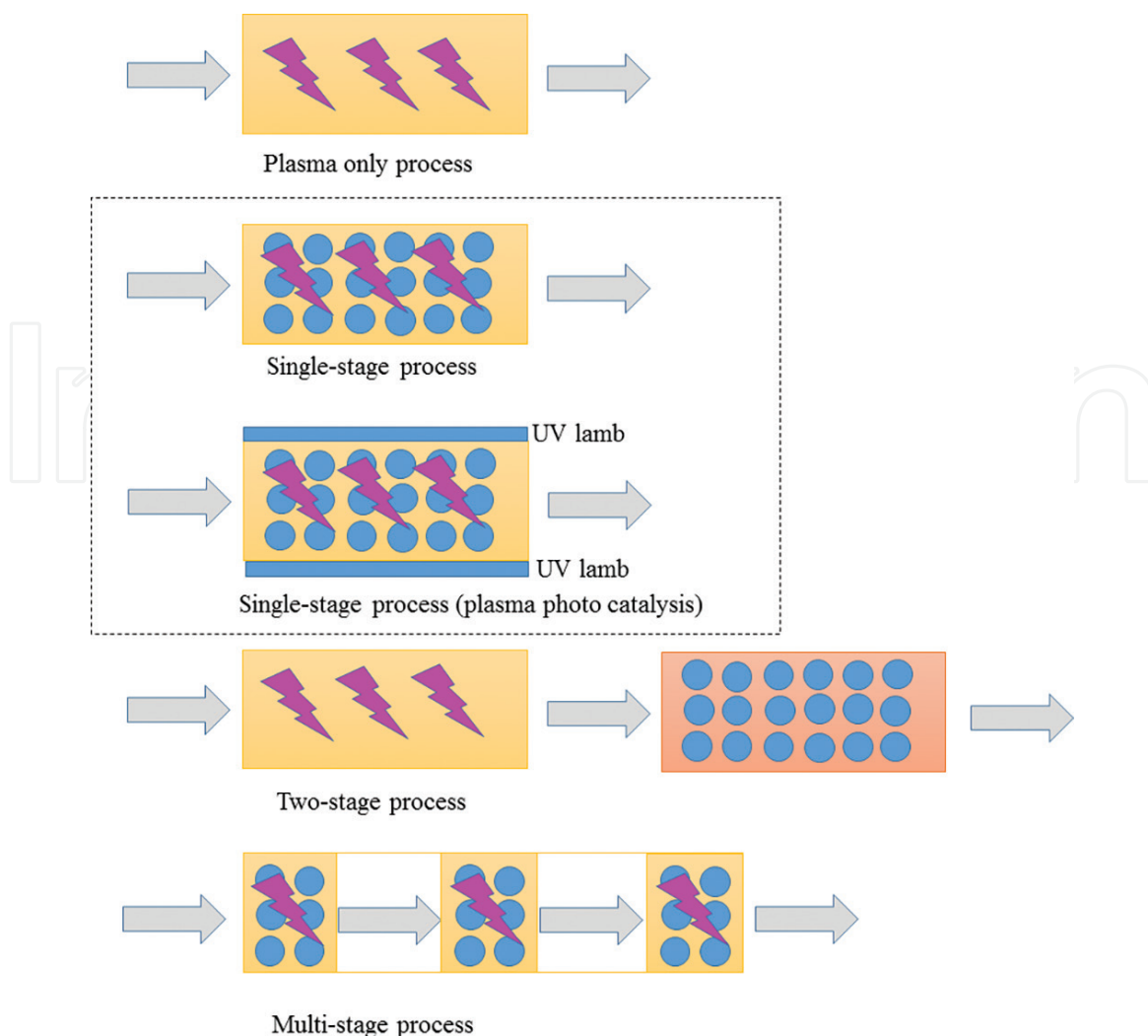
Figure 2.
Schematic diagram of different plasma-catalyst configurations according to the catalyst bed position and number.

the catalyst [59, 60]. These three configurations are illustrated in **Figure 2**. In all cases, the plasma can be used to supply energy for catalyst activation, and it can also provide the reactive gas species needed for reactions on the catalyst surface. The single-stage type is constructed by coating catalyst on the surface of electrode(s) or packing catalyst within the plasma zone, which is also called in-plasma catalysis (IPC). The catalysts could completely or just partially overlap with the plasma zone. In this manner, the plasma and catalysis could directly interact with each other. This single-stage system is also easy to combine with the UV irradiation, which is known as plasma photo catalysis, as shown in **Figure 2**. For the two-stage type, the catalyst is placed after the plasma discharge region; it is also called post-plasma catalysis (PPC). The plasma provides chemically reactive species for catalysis or pre-converts reactants into the easier-to-convert products to accelerate the catalysis. In the nonthermal plasma catalysis system, the long-lived reactive species produced by plasma, e.g. vibration-excited species, radicals, and ionized molecules, can react with the catalyst to induce catalytic reactions via either the Eley-Rideal mechanism or Langmuir-Hinshelwood mechanism [2, 59]. The multistage plasma catalysis system is a promising option for the industrial use in the future. Different functions of the catalysts can be combined to achieve certain expected reaction in the multi-stage system.

In the context of plasma catalysis, the synergy is referring to a surplus effect of combining the plasma with catalyst, namely, when the resulting effect has a higher
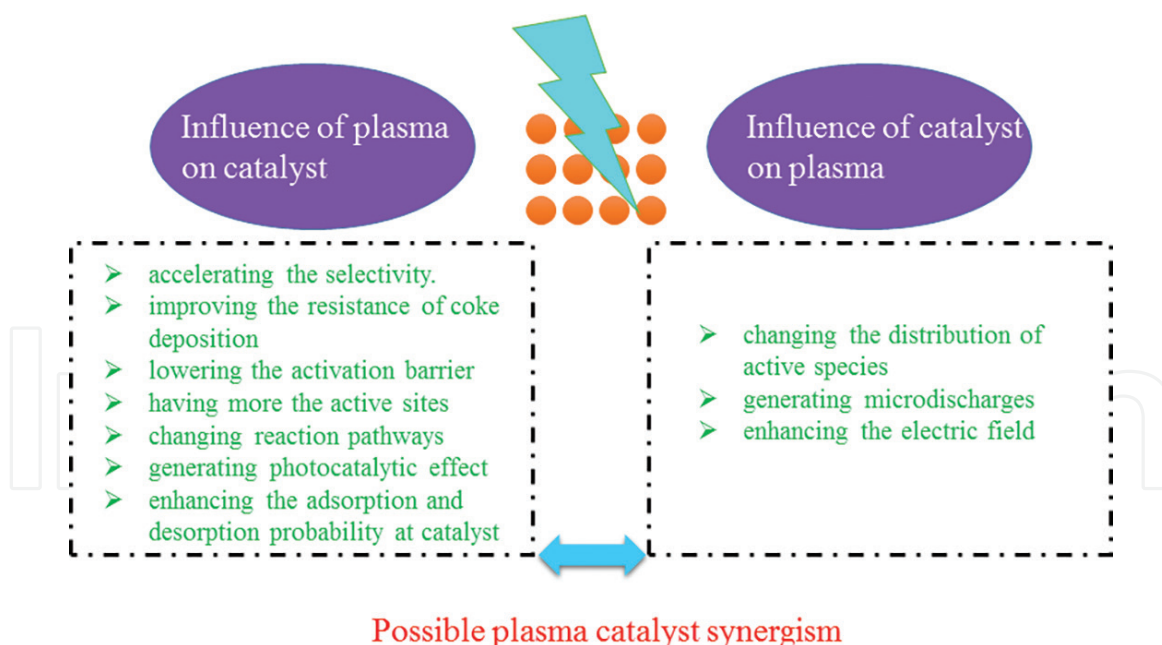
Figure 3.
Interaction between catalyst and plasma.

impact than the sum of their individual impacts. In several studies, the combination of plasma and catalysts has been found to have synergistic effects [34, 35, 61, 62]. A highly important synergistic effect of plasma catalysis is promotion of catalyst activity at reduced temperatures, and hence, a significant reduction in the energy cost for activating the catalyst [34]. For example, Wang et al. illustrated such synergy for plasma catalysis of dry reforming methane (DRM) in the single-stage system with Ni/Al_2O_3 catalyst but did not observe this synergy in the two-stage system or when the catalyst is only placed at the end of the plasma zone [62]. Typical synergistic effect factors of 1.25–1.5 were obtained. Zhang et al. presented the results on the plasma-catalyst synergy in the case of dry reforming methane using different $Cu-Ni/\gamma-Al_2O_3$ catalysts [63]. The effect was observed on the conversions of CH_4 and CO_2, where the result for the plasma-catalytic reaction was greater than the sum of the catalyst-only or plasma-only results. The selectivity towards H_2 and CO production was also enhanced by the use of plasma catalysis. In general, the enhanced performance of plasma catalysis can in part be attributed to vibrational excitation of CO_2 in the plasma, which enables easier dissociation at low temperature on the catalyst surface. The plasma electrons in turn affect the catalyst properties (chemical composition or catalytic structure). Synergistic effects in the plasma and catalyst are illustrated in **Figure 3**. Plasma can alter the physicochemical characteristics of catalyst via several routes, which are induced mainly by energetic electron generation. In the meantime, a catalyst can induce electric field concentration due to its pore structure and dielectric properties. Hence, both electric field distribution and catalyst characteristics are modified to have better DRM performance.

3. Plasma-assisted catalytic conversion of CO_2

Nonthermal plasma technology provides an attractive alternative to the other (classical) technologies for converting inert carbon emissions. Different types of plasmas have already been used for CO_2 reduction, including dielectric barrier discharges (DBDs), glow discharges, radio frequency (RF) discharges, microwave (MW) discharges and gliding arc plasma (GAP) and corona discharges [8–39]. In this section, the most widely used discharges for CO_2 conversion are presented.

DBDs have been known for more than a century. They were first reported in 1857 by Siemens for the use in ozone production and were originally called 'silent' discharges [64]. The DBD is the most widely used discharge type for CO_2 conversion among the variety of other plasma sources because it is easy to handle with relatively cheap equipment and it operates at atmospheric pressure [34]. Even though the conversion efficiencies obtained in DBDs are generally quite low [1, 4, 5, 8, 9, 12, 13], the possibility to work at atmospheric pressure under non-equilibrium conditions is still a very strong advantage of these discharges. Combined with plasma catalysis, these discharges should also improve the selective production of the targeted compounds.

An atmospheric pressure GAP discharge can be formed between two flat knife-shaped electrodes with a gas flowing between them. These discharges are suitable for applications that require relatively large gas flows (several l/min). The gliding arc plasma can be operated in the thermal and nonthermal regime depending on the applied power and flow rate. Furthermore, the arc can be operated in the transition regime, which is an evolving arc starting in the thermal regime going to the nonthermal regime. This transition regime makes the discharge energy efficient for gas treatment. An energy efficiency of 43% was reported by Nunnally et al. for the decomposition of CO_2 in a reverse vortex flow gliding arc discharge, which is quite high compared to the efficiency obtained with DBDs (about 10%) [31]. The high level of efficiency can be attributed to non-equilibrium vibrational excitation of CO_2 and a high-temperature gradient between the gliding arc and the surrounding gas that results in fast quenching.

Plasmas generated by the injection of microwave power, i.e. electromagnetic radiation in the frequency range of 100 MHz–10 GHz, are called MW plasmas [65]. MW discharges are commonly generated using frequencies of 2.45 and 0.915 GHz. They can be operated over a wide pressure range (from few mTorr to the atmospheric pressure). The properties of the MW discharges operating at atmospheric pressure are close to those of thermal plasma. However, the MW discharges are far from thermodynamic equilibrium at low pressure. The performance of a microwave discharge in terms of efficiency of CO_2 dissociation process depends heavily on the plasma parameters such as power and operating pressure. The highest energy efficiency (about 90%) for pure CO_2 conversion was reported in a MW plasma operating with supersonic gas flows [22]. The ability to create a strong non-equilibrium environment in microwave discharges possesses highly vibrational states of CO_2 molecules, which are energy-efficient for CO_2 decomposition [3]. In general, the high efficiency of microwave plasmas is attained due to the high absorption of the applied power by electrons as well as relatively high excitation of the CO_2 asymmetric mode [24], which plays a key role for CO_2 decomposition [22]. In the low-pressure case, the microwave plasmas are typically characterized by an electron temperature around 1–2 eV and a gas temperature below 1500 K. Under these conditions, it has been estimated that about 95% of all the discharge energy is transferred from the plasma electrons to the CO_2 molecules, mostly to their asymmetric vibrational mode [3, 24].

Bogaerts et al. has presented some insights into how the electron energy is transferred to different channels of excitation, ionization or dissociation of the CO_2 molecules [1, 66]. **Figure 4** illustrates the fractional energy transferred from electrons to different channels of excitation, ionization and dissociation of CO_2, as a function of the reduced electric field (E/n) in a discharge. This plot is calculated based on the cross sections of the corresponding electron impact reactions [1, 37, 66]. In microwave plasma, the reduced electric field is typically around 50 Td, which is most appropriate for the vibrational excitation of CO_2. Fridman has shown that up to 97% of the total nonthermal discharge energy can be transferred from the plasma electrons to vibrational excitation of CO_2 molecules at an electron temperature around 1–2 eV or a reduced electric field (E/n) of about 20–40 Td [3, 36]. This is indeed indicated by the calculated curve referred to as the 'sum of all vibrations'
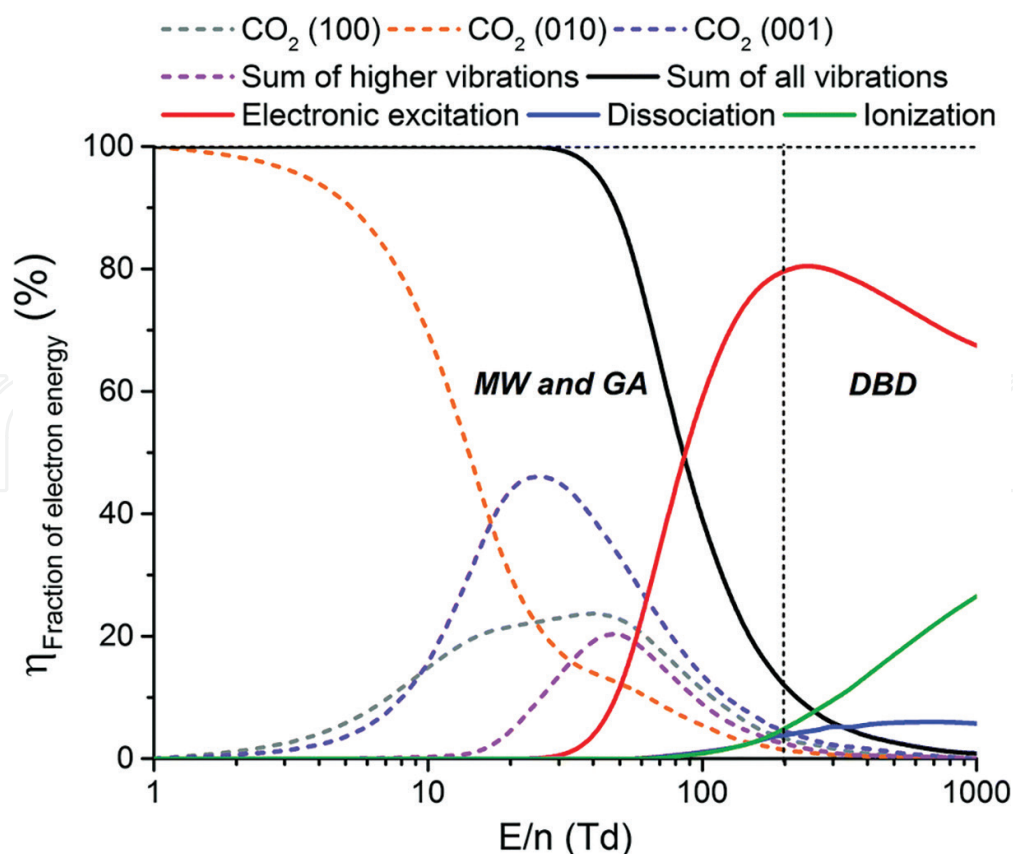
Figure 4.
The fraction of electron energy transferred to different channels of excitation as a function of the reduced electric field (E/n) (adapted from [1]).

shown in **Figure 4**. Moreover, the purple curve in **Figure 4** has its particular importance as it represents the first vibrational level of the asymmetric vibrational mode of CO_2, which represents the most important channel for the dissociation [66]. The energy efficiency for the dissociation of CO_2 is quite limited in a DBD plasma [3, 4, 11–13]. The electron temperature in a DBD is about 2–3 eV, which is somewhat high for efficient population of the CO_2 vibrational levels. The reduced electric field values are being typically about 200 Td or even higher, indicated as 'DBD region' in the figure. As a result of previous studies on CO_2 decomposition in plasma, it was concluded that higher pressures and lower values of reduced electric field make the vibrational excitation mechanism more favorable than the electronic excitation mechanism, explaining the higher energy efficiency of these types of discharges (e.g. MW, GAP) [1, 3, 22, 26, 28, 32, 33, 35, 37, 38].

3.1 MW region

In this chapter we have summarized the results from the recent publications on plasma set-ups with and without combining a catalyst for CO_2 conversion in **Table 2** and discussed the current research status on this topic. Porous Al_2O_3 (α-Al_2O_3 and γ-Al_2O_3) has been investigated in a pulsed corona discharge reactor for CO_2 conversion by Wen et al. [39]. γ-Al_2O_3 was found to enhance CO_2 conversion due to its high surface area and strong adsorption capability. Zhang et al. investigated CO_2 decomposition to CO and O_2 in a DBD reactor packed with a mixture of Ni/SiO_2 catalyst and $BaTiO_3$ spheres. In comparison to the reaction in the absence of a Ni/SiO_2 catalyst, introducing a Ni/SiO_2 catalyst to the plasma reactor packed with $BaTiO_3$ spheres slightly increase the CO_2 conversion from 19 to 23.5% at low temperatures [17]. Van Laer demonstrated a packing of ZrO_2 beads in a DBD reactor. The best combination of conversion (37.8%) and energy

(6.4%) efficiency was reached at a flow rate of 20 mL min^{-1} and an input power of 60 W [16]. Their simulation results suggest that the increased CO_2 conversion is caused by the presence of strong electric fields and thus high electron energies at the contact points, which thereby lowers the breakdown voltage. These findings suggest that the interactions between plasma and packing materials play an important role in the plasma conversion of CO_2. Brock et al. studied the catalytic effect of metallic coating on the decomposition of CO_2 in fan-type AC glow discharge plasma reactors, using a gas mixture of 2.5% CO_2 in He [19]. They showed that an Rh-coated reactor has the highest activity for the CO_2 decomposition compared to the reactors coated with Cu, Au, Pt and Pd and mixed rotor/stator systems (Rh/Au and Au/Rh).

In relation to microwave plasmas, Chen et al. reported that placing a NiO/TiO_2 catalyst in the downstream of a low-pressure microwave plasma significantly increased the CO_2 conversion efficiency and energy efficiency [25, 28]. They concluded that the oxygen vacancies provide the sites for adsorption of oxygen atoms from CO_2. The energetic electrons supplied by the plasma enhance the dissociative electron attachment of CO_2 at the surface. Recently, Ray et al. found that CO_2 conversion was enhanced upon packing CeO_2 into the discharge region of a DBD reactor. They also suggest this enhancement can be mainly attributed to the formation of oxygen vacancy defects on the surface of CeO_2, to stabilize the produced atomic oxygen, thereby preventing the revise reaction [18]. Spencer et al. experimentally investigated the conversion of CO_2 in an atmospheric pressure microwave plasma-catalytic system [21]. The results showed that Rh/TiO_2 coating on a monolithic cordierite structure used as a catalyst actually caused a drop in conversion efficiency due to reverse reactions occurring on the surface. Mei et al. demonstrated that the combination of plasma with $BaTiO_3$ and TiO_2 catalysts has a synergistic effect, which significantly enhances the conversion of CO_2 and the energy efficiency by a factor of 2.5 compared to the plasma reaction in the absence of a catalyst [7]. The overall synergistic effect resulting from the integration of DBD with catalysis for CO_2 conversion can be attributed to the dominant catalytic surface reaction driven by energetic electrons from the CO_2 discharge. Theoretical and experimental studies consistently showed that the CO_2 adsorption, activation and dissociation processes were significantly enhanced by the presence of oxygen vacancies [7, 23, 28, 67, 68]. The mechanism of plasma-catalytic CO_2 conversion can be described by **Figure 5**. The oxygen vacancies provide sites for the adsorption of
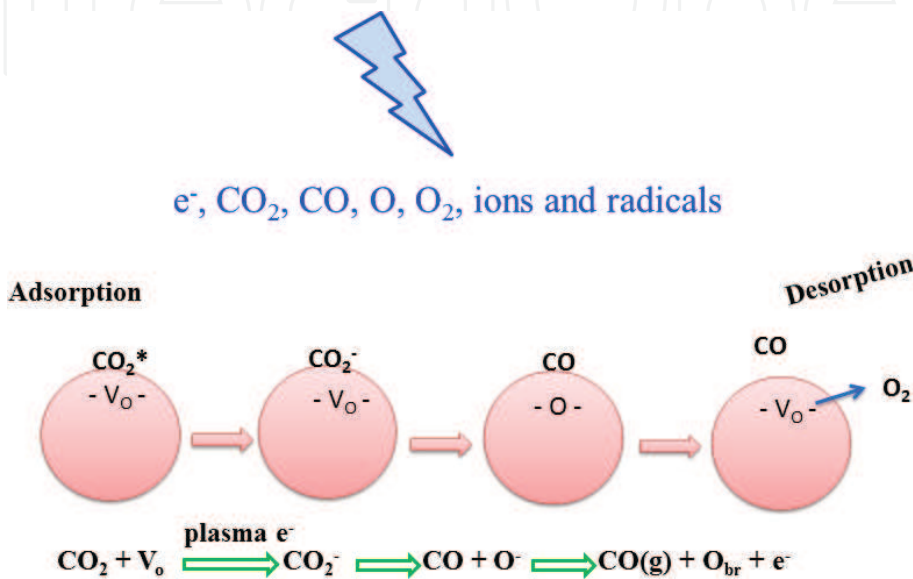

Figure 5.
Schematic mechanism of plasma-assisted catalytic process for CO_2 conversion.

Plasma type	Comments	Gas mixture	Catalyst	χ (%)	η (%)	SEI eV/ molecule	Ref.
DBD		CO_2	—	17	9	5.8	[4]
DBD		CO_2	—	30	1	87	[5]
DBD		CO_2	γ-Al_2O_3	20	4.9	12	[6]
DBD		CO_2	$BaTiO_3$	38	17	6.5	[7]
DBD		CO_2	—	18	4	13	[8]
DBD	Low flow rate	CO_2	—	14	8	5.2	[9]
DBD	10% CO_2 in the gas mixture	CO_2-H_2O-Ar	Ni/γ-Al_2O_3	36	23	4.5	[10]
DBD		CO2	—	35	2	50.8	[11]
DBD		CO_2	—	28.2	11.1	7.4	[12]
DBD		CO_2-N_2	—	4.5	4.5	2.9	[13]
DBD		CO_2	CaO	39.2	7.1	16	[14]
DBD		CO_2	—	20	10.4	5.6	[15]
DBD		CO_2	ZrO_2	2.9	9.6	9.6	[16]
DBD		CO_2	Ni/ SiO_2 + $BaTiO_3$	23.5	2.31	29.5	[17]
DBD		CO_2	CeO_2 (2 mm)	10.6	27.6	1.11	[18]
DBD		CO_2	TiO_2 (3–4 mm)	8.2	15.54	1.53	[18]
Glow		CO_2-Ar	Rh-coated	30	1.4	62	[19]
RF		CO_2	—	20	3	19	[20]
MW		CO_2-Ar	—	10	20	1.4	[21]
MW	Supersonic flow	CO_2	—	10	90	0.3	[22]
MW		CO_2	NiO/TiO_2	42	18	7.0	[23]
MW		CO_2-N_2	—	80	6	39	[24]
MW		CO_2	—	20	20	2.9	[25]
MW		CO_2	—	12	45	0.8	[26]
MW	CO_2:H_2O = 1:1	CO_2-H_2O	—	12	8.7	4	[27]
MW		CO_2	NiO/TiO_2	45	56	2.3	[28]
MW		CO_2	—				[29]
Corona		CO_2	—	11	2	16	[30]
Gliding arc		CO_2	—	4.6	43	0.3	[31]
Gliding arc		CO_2	—	15	19	2.3	[32]
Gliding arc		CO_2	—	10	34	0.85	[33]

Table 3.
Summary of the plasma-assisted catalytic CO_2 conversion for different discharge types.

oxygen atoms from CO_2. The energetic electrons supplied by the plasma enhance the dissociative electron attachment of CO_2 at the surface. Subsequently, CO desorbs or moves from the reactive site while the other O (bridging) atom 'heals' the oxygen vacancy. The oxygen vacancy can be regenerated via the recombination

on the surface of a bridging oxygen atom with a gaseous oxygen atom. Such regeneration maintains the equilibrium of the active sites in the catalyst and controls the CO_2 conversion [23]. If the catalyst is placed in the plasma zone (single stage), the electron–hole pairs can be created by highly energetic electrons from the discharge upon the surface of photocatalysts once plasma can generate electrons of very similar energy (3–4 eV) to the photons. In this case, oxygen vacancy can be regenerated by oxidizing the surface O_2^- anions using holes, followed by releasing O_2 [7]. Plasma-catalytic conversion of CO_2 is a complex and challenging process involving a large number of physical and chemical reactions. The performance of the process is controlled by means of plasma parameters and the properties of the catalysts as well. This suggests that more systematic studies on both the plasma effects and the chemical effects of the catalyst are highly needed (**Table 3**).

4. Conclusions and perspectives

Plasma-assisted catalytic processes used for CO_2 reduction are gaining increasing interest worldwide. There is still a room, however, for further improvement of the CO_2 conversion and energy efficiencies through the optimization of the plasma parameters (e.g. high pressure and high flow rate) as well as through modification of catalysts.

The plasma-catalytic activities can be controlled by numerous factors such as the nature of the catalyst support, active metal sites, surface area and the nanoparticle size. Let us note that the catalyst preparation (sometime called 'activation') plays a very important role in this regard. In addition to these factors and also due to their existence, the fine-tuning of a given catalyst is inevitable and crucial factor for enhancing plasma-catalytic process efficiency. Several methods, such as loading different metal nanoparticles, using different catalyst preparation schemes (sol gel, co-precipitation, deposition-precipitation or hydrothermal synthesis), using larger surface area of the support, etc., can be mentioned to realize the mentioned tuning.

An important factor which cannot be omitted here is that a chosen catalyst material should have rather low costs to be potentially commercialized and implemented in the industrial scale. Moreover, as a result of recent development of the microwave discharges, namely, a possibility to place catalyst packing directly in the discharge zone can be a powerful way to take advantage of the stepwise vibrational excitation on the catalyst surface. In addition, using plasma as a tool for the preparation (activation) of the catalyst surface may be another promising way. To improve its application, a better insight into the underlying mechanisms of the plasma catalysis is desirable. A greater understanding of the plasma chemistry, both by plasma modeling and by coupling with other techniques such as catalysis and membrane materials, will allow this field to expand. We expect that the results presented in this chapter will provide useful insights into the plasma-assisted CO_2 conversion in the presence or the absence of catalysts, which may be used for greenhouse gas conversion in the industry.

Acknowledgements

Author details

Guoxing Chen[1,2]*, Ling Wang[4], Thomas Godfroid[3] and Rony Snyders[1,3]

1 Chemistry of Plasma Surface Interactions, University of Mons, Belgium

2 4MAT, Universite Libre de Bruxelles, Belgium

3 "Materia Nova" Research Center, Belgium

4 Institute for Materials Science, University of Stuttgart, Stuttgart, Germany

*Address all correspondence to: guoxchen@ulb.ac.be

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