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Chapter title: Plasma-based CO₂ conversion

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1. Introduction

Plasma technology is gaining increasing interest for CO₂ conversion. Plasma is an ionised gas, consisting of a variety of different species, including electrons, various types of radicals, ions, excited species, photons, besides neutral gas molecules. This reactive cocktail makes it useful for a myriad of applications ^[1]. Furthermore, as plasma is generated by electrical power, and can easily be switched on/off, this combination makes it suitable for using intermittent renewable electricity. Hence, it may provide a solution for the current challenges on efficient storage and transport of renewable electricity, i.e., peak shaving and grid stabilisation.

So let us consider in more detail what plasma is and which promises it carries for chemical transformations in general and of CO₂ in particular. In short, plasma is ionised gas and generally sustained by the application of electric fields, as depicted in the cartoon in Figure 1.

Fig. 1: Plasma is ionised gas and generally sustained by acceleration of the light electrons in an electric field (here indicated as microwaves). Ionisation is indicated by positively charged atoms/molecules (in red) and free electrons (in yellow) and is a small fraction compared to the neutral particle density.

Energy transfer from the external electric field starts with acceleration of the free electrons. Subsequent collisions with (blue) feedstock molecules passes their kinetic energy on. However, the large mass difference between electrons and molecules makes momentum transfer extremely inefficient. Instead, energy transfer occurs predominantly via excitation of internal degrees of freedom, such as molecular vibration. On the microscopic scale, it means that the free electron modifies the configuration of the bound electrons of the atom or molecule. Internal energy is subsequently transferred to translational and rotational degrees of freedom, of which the rates are highly dependent of molecular properties, cross sections, pressure and temperature. In effect, a hierarchy in excitation of the different degrees of freedom of the system is typically found. The free plasma electrons are hottest, typically 1-3 eV. Rotational and translational degrees are coldest whilst molecular vibration temperatures are necessarily intermediate. It goes without saying that at all time

energy might be consumed (or released) in chemical reactions, which is the overall purpose and hence to be optimised.

In the present context of plasma-based CO₂ transformations, especially those cases in which the strongest non-equilibrium between the different modes is found are highly interesting. These are generally referred to as Non-Thermal Plasma (NTP). It is under the far from thermodynamic equilibrium conditions that it is possible to intensify traditional chemical processes and to achieve the highest values of energy efficiency^[2]. In the most ideal situation, one would have room temperature rotation and translation, whilst high vibration temperature still drives strongly endothermic reactions. Simply spoken, this saves energy that is otherwise to be invested in these modes and likely to be lost as heat to the environment. It has the additional advantage of inherent quenching of the reaction products. Both aspects makes the approach particularly advantageous for thermodynamically unfavorable or energy-intensive chemical reactions, such as CO₂ splitting or dry reforming of methane (DRM), to proceed in an energy-efficient way. The strong non-equilibrium situation is opposed to Thermal Plasma (TP), in which all degrees of freedom are in thermal equilibrium.

The nature of the excitation process depends on the energy of the electrons. In the tail of the electron energy distribution function, the energy is high enough to excite the heavy gas particles into higher electronic states or even induce ionisation, as shown in Figure 2. Obviously, ionisation is required for sustaining the plasma discharge. For efficient CO₂ reforming it should not become a dominant pathway as it is an energetically inefficient way of initiating chemical reactions. After all, ionisation of CO₂ requires ~14 eV/molecule, whereas its “net” dissociation energy is ~3 eV (considering the “net” reaction $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2$). This simple consideration implies a maximum energy efficiency of at most 20% for each dissociation event via ionisation. In practice, due to the fact that only the high energy tail would drive dissociation and all other energy input would be “lost”, it would limit efficiencies to even lower values of ~5%.

Fig. 2: *Cross sections for electron collisions with CO₂ after^[3]. Average plasma electron energies are usually of few eV, exactly where the cross section of vibrational excitation peaks. This confirms the hand waving picture of preferential vibrational excitation in low temperature plasma. Ionisation to replenish plasma losses requires energies over 10 eV and is still possible by electrons in the high energy tail of the electron energy distribution function. The different approaches to plasma generation vary all in shape and mean of the distribution, which determines the balance between power deposited in vibration versus power consumed by ionisation and other high energy excitations.*

The majority of the electrons are however at lower energy, typically a few eV. These are responsible for collisions that predominantly excite vibrational modes in the molecule. The resulting vibrationally excited molecules will further interact with each other and exchange vibrational energy or convert vibrational energy into translational. Of special interest here is the asymmetric stretch vibration of CO₂, which carries two important properties. Firstly, the vibrational quanta are too large to be easily converted into translational energy in a low energy collision. Secondly, the vibration is anharmonic, which means that the vibrational level spacing of highly excited molecules is smaller than that of molecules at a lower level. This results in a slight preference of highly excited molecules gaining additional quanta compared to losing it to (the majority) molecules at the first levels.

In effect, it is the asymmetric stretch vibrational mode that can be brought to the highest degree of non-equilibrium and in which vibrational energy can be driven up along the energy scale to reach the dissociation limit. In this ladder climbing scheme, illustrated in Figure 3, the electrons, that were

energetically "expensive" to create, are used many times to deliver energy to overpopulate the lower asymmetric stretch levels and essentially to the bond that is to be broken up to the point where dissociation of the molecule is achieved. It is this qualitative mechanism that has been put forward to explain the ultimate energy efficiencies that have been demonstrated in the former Soviet Union in the 1970s^[4-9] for the net reaction $\text{CO}_2 \rightarrow \text{CO} + \text{O}_2$, i.e., with over 80% energy efficiency.

Fig. 3: Schematic illustration of some CO_2 electronic and vibrational levels. Illustrated is stepwise vibrational excitation, i.e., the so-called ladder-climbing process. It is initiated by plasma electron excitation and carried by vibrational exchange up to the point of dissociation. Opposed to energetically advantageous ladder climbing is dissociative excitation, which involves a large activation barrier. Reproduced from^[10] with permission.

The fraction of charge is usually small, often 10^{-5} or even less compared to the neutral species. Ionisation is therefore not significant in the power balance and the plasma acts as a *power transfer medium*, converting electric energy into internal energy of molecules.

Having explained why plasma is promising for CO_2 conversion, we will briefly present the most common types of plasma reactors with their characteristic features in the next section. Referred will be to the non-equilibrium nature of the discharges to illustrate why some plasma types exhibit better energy efficiency than others. Subsequently, we will discuss the state-of-the-art on plasma-based CO_2 conversion, including the combined conversion of CO_2 with CH_4 , H_2O or H_2 . Finally, we will discuss the major limitations and steps to be taken for further improvement.

2. Plasma reactor types for CO_2 conversion

Plasma is created, in its simplest form, by applying an electric potential difference between two electrodes, positioned in a gas. The gas pressure can range from a few Torr up to (above) 1 atm. The potential difference can be direct current (DC), alternating current (AC), ranging from 50 Hz over kHz to MHz (radio-frequency; RF), or pulsed. Furthermore, the electrical energy can also be supplied in other ways, e.g., by a coil (inductively coupled plasma; ICP) or as microwaves (MW).

Three types of plasma reactors are most often studied for CO_2 conversion, i.e., dielectric barrier discharges (DBDs), microwave plasmas and gliding arc (GA) discharges. Below, we will briefly present their working principles and typical operating conditions, to explain why they are particularly interesting and what their current limitations are. Furthermore, besides these three major types of plasma reactors, other plasma types are being explored as well for CO_2 conversion, and they will also be very briefly discussed. Finally, we will introduce the concept of plasma catalysis, for the selective production of value-added chemicals.

2.1. Dielectric barrier discharge (DBD)

A dielectric barrier discharge is created by applying an AC potential difference between two electrodes, of which at least one is covered by a dielectric barrier. The latter limits the amount of charge transported between both electrodes, and thus it prevents that the discharge would undergo a transition into a thermal plasma, which is a less efficient regime for CO_2 conversion. The electrodes can be two parallel plates, but a more common design for CO_2 conversion is based on two concentric cylindrical electrodes (cf. Figure 4(a)), in which the inner electrode is surrounded by a dielectric tube with a mesh or foil electrode wrapped around it. The gap between inner electrode and dielectric tube is in the order of a few millimeter. One of the electrodes is connected to a power supply, while the

other electrode is grounded. The gas flows in from one side, and is gradually converted along its way through the gap between inner electrode and dielectric tube, and flows out from the other side.

A DBD typically operates at atmospheric pressure, which is beneficial for industrial applications. Furthermore, it has a very simple design, making it suitable for upscaling, and thus industrial implementation, as demonstrated already for ozone synthesis, by placing a large number of DBD reactors in parallel ^[11].

On the other hand, a DBD has only a limited energy efficiency for CO₂ conversion, typically around 10 %, with some exceptions up to 20 % ^[12]; see also next section. The reason is that the reduced electric field (i.e., ratio of electric field over gas number density) is typically above 100-200 Td (1 Td = 10⁻²¹ V m²), creating high-energy electrons, which mainly give rise to electronic excitation, ionisation and dissociation of CO₂ molecules in the ground state, and this is not the most energy-efficient CO₂ dissociation pathway (see below).

By introducing a packing of dielectric material in the discharge gap, the energy efficiency can in principle be improved, due to polarisation of the dielectric packing beads resulting from the applied potential difference. Indeed, this will enhance the electric field near the contact points of the packing beads, and thus the electron energy ^[13], causing more electron impact excitation, ionisation and dissociation, and thus more CO₂ conversion for the same applied power. In addition, such a packed bed DBD is very suitable for plasma catalysis, as will be discussed in section 2.5. However, it should be noted that the CO₂ conversion efficiency is not always enhanced in a packed-bed DBD ^[14, 15], due to the competing effect of reduced residence time in the smaller discharge volume, when comparing at the same gas flow rate, as well as the loss of electrons and reactive plasma species at the surface of the packing material.

Fig. 4: Schematic illustration of the three plasma reactors most often used for CO₂ conversion, i.e., dielectric barrier discharge (a), microwave plasma (b), and gliding arc discharge, in classical configuration (c) and cylindrical geometry, called gliding arc plasmatron (GAP) (d). Reproduced from ^[16] with permission.

2.2. Microwave plasma

In a microwave plasma, electromagnetic radiation with frequency between 300 MHz and 10 GHz is applied to a gas, without using electrodes. Depending on the configuration, there exist different types of MW plasmas, i.e., cavity induced plasmas, free expanding atmospheric plasma torches, electron cyclotron resonance plasmas and surface wave discharges. The latter are most frequently used for CO₂ conversion. In this configuration, the gas flows through a quartz tube, which is transparent to MW radiation, intersecting with a rectangular waveguide, to initiate the discharge (see Figure 4(b)). The microwaves propagate along the interface between the quartz tube and the plasma column, and the wave energy is absorbed by the plasma.

MW plasmas can operate in a wide pressure regime, ranging from very low pressure (e.g., 10 mTorr) up to atmospheric pressure. The low pressure regime yields very efficient CO₂ conversion. Energy efficiencies up to 90 % were reported for very specific conditions, i.e., supersonic gas flow and pressures around 100-200 Torr ^[17]. This is attributed to the role of the vibrational kinetics (discussed in above in section 2) ^[2, 10, 12, 18]. Indeed, a MW plasma is characterised by typical reduced electric fields below 100 Td. This yields electron energies around 1 eV, which are most beneficial for vibrational excitation of CO₂ ^[2, 10, 12]. Hence, the electrons populate the lower vibrational levels of CO₂, which collide with each other in so-called vibrational-vibrational (VV) relaxation, gradually populating the higher levels. This so-called ladder climbing process requires 5.5 eV for CO₂ dissociation, which is exactly the C=O bond dissociation energy, while electronic excitation to a dissociative level, which is

the main process in a DBD (see above), would require 7-10 eV. As the latter is much more than the C=O bond dissociation energy, this extra energy is just waste of energy. This explains why the energy efficiency in a DBD is much more limited (see above).

Note, however, that the vibrational levels can also get lost by vibrational-translational (VT) relaxation. This becomes especially important at high gas temperature, as revealed by computer simulations^[19], and it results in a vibrational distribution function (VDF) in (near) thermal equilibrium with the gas temperature. When the MW plasma operates at atmospheric pressure, it exhibits a quite high gas temperature (in the order of several 1000 K), resulting in a VDF that is indeed close to thermal^[19, 20]. Deviation from a thermal distribution can be realised by increasing the power density, reducing the pressure and the gas temperature^[19]. At atmospheric pressure, it is not straightforward to realise a low gas temperature. A solution could be to apply a pulsed power, so that the gas can cool down in between the applied pulses, or to apply a supersonic gas flow, as demonstrated by Azivov et al.^[17], so that the gas has not enough time to be heated. On the other hand, the gas must have a sufficiently long residence time for the conversion to take place as well.

2.3. Gliding arc discharge

A gliding arc discharge is a transient type of arc discharge. A classical (two-dimensional) GA discharge is created between two flat diverging electrodes (see Figure 4(c)). The arc is initiated at the shortest interelectrode distance, and it “glides” towards larger interelectrode distance under influence of the gas, which flows along the electrodes, until it extinguishes and a new arc is created at the shortest interelectrode distance.

The classical GA discharge yields only limited CO₂ conversion, because only a limited fraction of the gas passes through the arc. Therefore, other types of (three-dimensional) GA discharges have been designed, such as a gliding arc plasmatron and a rotating GA, operating between cylindrical electrodes. Figure 4(d) schematically illustrates the operating principle of a GAP. The cylindrical reactor body acts as cathode (powered electrode), while the reactor outlet is the anode (grounded). The gas enters tangentially between both cylindrical electrodes. When the outlet diameter is (significantly) smaller than the diameter of the reactor body, the gas flows in an outer vortex towards the upper part of the reactor body, followed by a reverse inner vortex towards the outlet, with a smaller diameter because it has lost some speed, and therefore it can leave the reactor through the outlet. The arc is again initiated at the shortest interelectrode distance, and expands till the upper part of the reactor, rotating around the axis of the reactor until it stabilises in the center after about 1 ms, due to the vortex gas flow. Ideally, the inner gas vortex passes completely through this stabilised arc, allowing most of the gas to be converted. However, the fraction of gas passing through the arc is still too limited, thereby limiting the CO₂ conversion^[21, 22].

The GA discharge operates at atmospheric pressure, which makes it suitable for industrial implementation. Moreover, it shows a good energy efficiency, i.e., around 30 % for CO₂ splitting^[21] and 60 % for DRM^[22]. The reason is the same as in the MW plasma, i.e., due to the favorable reduced electric field, creating electrons of about 1 eV, which mainly give rise to vibrational excitation of CO₂, and thus, the vibrational pathway of CO₂ dissociation is again promoted. Nevertheless, the gas temperature is also fairly high (typically a few 1000 K), which limits the energy efficiency, due to VT relaxation, yielding a VDF too close to a thermal distribution, just like in a MW plasma (see above). More efforts are thus needed to better exploit the non-equilibrium behavior of a GA plasma, by reducing the gas temperature.

2.4. Other plasma types used for CO₂ conversion

Besides these three types of plasma reactors explained above, other plasma types are also increasingly being used for CO₂ conversion, such as nanosecond (ns)-pulsed discharges^[23], spark discharges^[24], corona discharges^[25] and atmospheric pressure glow discharges (APGDs)^[26].

Ns-pulsed discharges are basically generated by repetitive ns-pulsed excitation, leading to a high non-equilibrium with very high plasma densities for a relatively low power consumption due to the short pulse duration. The short pulses offer good control of the electron energy, depending on the pulse length, so that more energy can be directed towards the desired dissociation channels.

Spark discharges consist of an initiation of streamers between two electrodes, developing into highly energetic spark channels, which extinguish and reignite periodically, just as lightning, even without pulsed power supply.

Corona discharges are created near sharp edges or thin wires used as electrode. Either a negative or a positive voltage can be applied to the electrode, yielding a negative or positive corona discharge. Corona discharges are non-uniform discharges, with a strong electric field, ionisation and luminosity close to the sharp electrode, while the charged particles are dragged to the other electrode by a weak electric field. Their performance towards CO₂ conversion is similar as for DBDs.

The name "APGD" stands for a collection of several types of plasmas, including miniaturised DC glow discharges, microhollow cathode DC discharges, RF discharges, as well as DBDs. They typically operate at not too elevated temperature, and can exist either in stable homogeneous glow or filamentary glow mode. They can exhibit a typical electron temperature around 2 eV, thus still suitable for vibrational excitation of CO₂, while the gas temperature is limited to about 900-1000 K, hence lower than for GA and MW plasmas. This guarantees more pronounced thermal non-equilibrium, and makes them promising for CO₂ conversion.

2.5. Principle of plasma catalysis

As explained above, plasma on its own is very reactive, due to the cocktail of chemical species (electrons, various types of molecules, atoms, radicals, ions and excited species), but for the same reason, it is not selective in the production of targeted compounds. This problem can be solved by so-called plasma catalysis, which combines the high reactivity of a plasma with the selectivity of a catalyst^[27-29]. Plasma catalysis is most straightforward in a DBD plasma, more specifically in a packed bed DBD, because the packing beads can be covered by a catalytic material or they can have catalytic properties from their own. This is called one-stage plasma catalysis, but the catalyst can also be placed after the plasma reactor, in so-called two-stage plasma catalysis. In the first case, short-lived plasma species, such as excited species, radicals, photons, and electrons, can interact with the catalyst, providing more possibilities for synergy than in the latter case, where only long-lived species can interact with the catalyst. On the other hand, the two-stage configuration can also be applied to other plasma types, such as MW and GA discharge, where one-stage plasma catalysis is not so straightforward, among others due to the high gas temperature in the plasma (cf. above). Nevertheless, the latter may also provide other opportunities; it can open the way for thermal activation of catalysts, either inside the discharge zone (if the temperature could be somewhat reduced, and when using thermally stable catalysts) but also downstream, when the gas leaving the MW or GA reactor is still hot, in two-stage plasma catalysis.

Although plasma catalysis is a quite promising combination, not only to improve the selectivity of product formation, but also to enhance the overall plasma performance in terms of conversion and energy efficiency, the underlying mechanisms, especially in one-stage plasma catalysis, are very complicated and far from understood.

On the one hand, the plasma can affect the catalyst performance in several ways:

a) changes in the physicochemical properties of the catalyst, i.e., a higher adsorption probability^[30],

- a) a higher surface area ^[31], due to reduced metal particle size and enhanced dispersion of metal particles at the catalyst surface ^[32], a change in the oxidation state ^[33], reduced coke formation ^[34], and a change in the work function due to the presence of a voltage and current (or charge accumulation) at the catalyst surface ^[35];
- b) the formation of hot spots, modifying the local plasma chemistry ^[36];
- c) lower activation barriers, due to the existence of short-lived active species, such as radicals and vibrationally excited species ^[33].

On the other hand, the catalyst will also affect the plasma performance, by:

- a) enhancement of the local electric field in the plasma, because the catalyst is mostly present in a structured packing (e.g., pellets, beads, honeycomb,...; so-called packed-bed reactor), or simply due to the porosity of the catalyst surface ^[36-38];
- b) change of the discharge type from streamers inside the plasma to streamers along the catalyst surface, resulting in more intense plasma around the contact points ^[39-42];
- c) formation of microdischarges in the catalyst pores, resulting in more discharge per volume, increasing the mean energy density of the plasma ^[36, 43];
- d) adsorption of plasma species on the catalyst surface, affecting the residence time and hence the concentration of species in the plasma ^[44], while new reactive species might be formed at the catalyst surface.

Figure 5 presents a schematic overview of some of these plasma-catalyst interaction processes, in one-stage plasma catalysis ^[45]. Roughly speaking, we can distinguish two types of effects, i.e., physical and chemical effects. While the physical effects, such as enhanced electric field, are mainly responsible for gaining a better energy efficiency, the chemical effects can lead to improved selectivity towards value-added products. In case of CO₂ splitting, mainly CO and O₂ are formed, so the primary added value of the catalyst is to increase the energy efficiency, although the conversion can also be improved by chemical effects, such as enhanced dissociative chemisorption due to catalyst acid/basic sites. When adding a co-reactant (e.g., CH₄, H₂O, H₂), the catalyst allows to modify the selectivity towards value-added products.

Fig. 5: Schematic illustration of some plasma-catalyst interaction mechanisms. Adopted from ^[45] with permission.

The plasma-catalyst interactions can lead to synergy in plasma catalysis, when the combined effect is larger than the sum of the two separate under the same operating conditions, but this is not always realised up to now. Indeed, a lot of research, by combined experiments and computer modeling, will be needed to understand all these mechanisms and to fully exploit the possible synergy. Furthermore, more dedicated research is needed to effectively design catalysts tailored for the plasma environment, which make profit of the typical plasma conditions, instead of using commercial catalysts typically used in thermal catalysis. Indeed, nowadays this is still too often the case, limiting the real potential of plasma catalysis in selectively producing the desired products. Examples of successful plasma catalytic CO₂ conversion will be given later in this Chapter.

3. CO₂ conversion processes: reactions, reactors and performance

3.1. CO₂ splitting

CO₂ splitting in the plasma phase was pioneered around the 70s for a two-step hydrogen production process in the former Soviet Union. It remained largely unknown to the rest of the world until it was summarised in the book by A. Fridman in 2008 ^[2]. The potential of vibrational excitation to intensify

chemical reactions is a recurring theme in this work and CO₂ reduction forms its showcase. Since that moment, the promise to address the current global challenges regarding CO₂ emissions has been well recognised by the international plasma chemistry community and a number of groups started investigating the maximally achievable energy efficiency for the reduction of CO₂ in plasma.

A graph summarising the great promise of plasma chemistry on the basis of work from the 80s^[2] and some first results since the revival of the field^[18, 46] is shown in Figure 6. It is clear that the unprecedented high energy efficiency of ~85% has been the food for inspiration and is extremely promising for opening pathways to CO₂ reuse. The explanation of the ultimate energy efficiencies has been the preferential excitation of vibrational modes that drives ladder climbing of vibrational quanta all the way to dissociation, as explained in section 2.

Other remarkable features of the early data are the superior performance of microwave discharges compared to other approaches (here only RF shown) and an apparent trade-off between energy efficiency and conversion. Both observations align with the mechanism of vibrational ladder climbing. Microwave discharges are recognised to have an average electron energy that is optimal for preferential vibrational excitation, although it requires sub-atmospheric pressures. Degrading efficiency at higher input power levels can be expected due to gas heating that quenches the vibrational non-equilibrium and reduces performance to thermal values^[2].

Fig. 6: Energy efficiency of plasma assisted CO₂ reduction as a function of the specific energy input. The black and white markers are from the summary by Fridman^[2]. The red markers show initial modelling results of vibrational ladder climbing by Kozak^[18] and the orange markers first experimental microwave results by Bongers^[46]. Dashed lines indicate contours of conversion degree.

Some first results since the revival have also been included in the figure and are topical for many more findings since. Firstly, zero-dimensional modelling of vibrational kinetics in microwave plasma that included 25 vibrational levels (of the asymmetric stretch mode) up to the dissociation limit could not reproduce the record efficiencies but predicted a maximum efficiency of ~25%^[18]. Secondly, experimental characterisation of microwave plasma achieved higher efficiencies of ~50%^[46], however, temperature measurements in similar configurations revealed gas temperatures of typically 3500 K^[47]. The latter means that thermal decomposition must have been of importance too whilst vibrational ladder climbing cannot be expected to dominate at such high temperatures^[19]. Noteworthy is that also for the early experiments that yielded 85% efficiency a high temperature core was observed and that vibrational dynamics were assumed to be important in the colder surroundings^[2]. In other words, ultimate thermal conversion performance of 50% energy efficiency has been achieved in recent experiments. However, the older record of 85% has not been reproduced yet and it seems that schemes in which vibrational excitation are dominant are probably non-uniform and involve transport of power and species.

Mechanisms of CO₂ dissociation

Let us summarise the main pathways that lead to dissociation in a plasma. Here, we start with the electron driven processes. Important for the present is that these differentiate largely from each other in their threshold energy E_{th} :

- i. Electron impact ionisation followed by dissociative recombination,

$$e + \text{CO}_2 \rightarrow \text{CO}_2^+ + 2e \rightarrow \text{CO} + \text{O} + e \quad E_{th} = E_{ion} = 13.8 \text{ eV} \quad (1)$$
- ii. Electron impact dissociative excitation,



iii. Vibrationally enhanced electron impact dissociative excitation, including vibrational ladder climbing,



It is clear that the first two of these are *a priori* not beneficial for achieving high energy efficiency. The high threshold energies have to be compared with the reaction enthalpy of the net elemental dissociation reaction,



Thus, (i.) dissociative recombination of ions as well as (ii.) dissociative excitation are highly inefficient dissociation mechanisms and convert 6-8.3 eV into heat and/or internal energy per event. In fact, more than one excited state will probably contribute to dissociative excitation, with (slightly) lower threshold energy, and ${}^1\text{D}$ or ${}^3\text{P}$ oxygen atoms being created. These excited states have bent structures of which still little is known, which means that their Franck-Condon overlap with the electronic ground state is unknown and their electron impact energy threshold cannot be predicted.

The third mechanism is evidently favourable, providing potentially the smallest threshold energy. Here, we include within (iii.) vibrationally enhanced electron impact dissociative excitation also the aforementioned vibrational ladder climbing mechanism. The latter was explained in detail in Figure 3, invoking the potential energy diagram of CO_2 along one O-CO coordinate. A subtle addition here is the decrease of the activation barrier of dissociative excitation by more favourable Franck Condon overlap of a vibrationally excited level. Dissociative excitation from the ground state produced in this example roughly 2.5 eV of kinetic energy in the fragments and an ${}^1\text{S}$ oxygen radical. A molecule excited in the first vibrational level benefits not only from a lower threshold energy due to its initial vibrational energy (0.3 eV for the asymmetric stretch vibration), but also from Franck Condon overlap with reduced energy of the upper state. In the schematic representation of Figure 3, it means a reduction in threshold energy of ~ 1 eV and in released kinetic energy of ~ 0.7 eV.

The energy threshold vanishes as molecules get into the highest vibrational (asymmetric stretch) levels, close to the dissociation limit. The non-adiabatic transition ${}^1\Sigma^+ \rightarrow {}^3\text{B}_2$ in the point of crossing of the ${}^1\text{B}_2$ and ${}^3\text{B}_2$ terms opens the most effective dissociation pathway $\text{CO}_2({}^1\Sigma^+) \rightarrow \text{CO}({}^1\Sigma^+) + \text{O}({}^3\text{P})$. As was briefly touched upon before, this can become a significant channel by virtue of the vibrational ladder anharmonicity under strongly non-equilibrium conditions in which the kinetic energy of the molecules remains low. Due to the anharmonicity, vibration-vibration (VV)-exchange is no longer resonant and Treanor has shown (although neglecting effects of dissociation and VT relaxation^[19], a boundary condition that determines the exact shape of the vibrational distribution [Diomedea2017]) that this results into strong deviation from a Boltzmann distribution, of overpopulation of high vibrational levels. Such strong overpopulation is indeed observed in the aforementioned state-to-state modelling of the asymmetric stretch manifold, which is shown in Figure 7. The depopulation of the highest levels is due to dissociative excitation.

Fig. 7: Vibrational distribution functions of the asymmetric mode vibrational levels of CO_2 in a microwave discharge after 8.0ms of power input at a rate of 20, 25 and 30 W/cm³, reproduced from^[18] with permission. The plateau behaviour around $10 < v < 17$ reflects the Treanor-like overpopulation. Dissociative excitation of the levels $v > 19$ causes strong depopulation of these highest levels and produces CO most efficiently.

Finally, atomic oxygen created in the plasma should be able to create a second CO molecule and molecular oxygen in order to optimise the overall efficiency and to explain the observed ultimate energy efficiencies close to 90% [2]. Again, this requires a vibrationally excited CO₂* molecule as the reaction is endothermic:



One should notice the large range that is given for the activation energy of the reaction. Its consequence is that it may well be limiting the overall efficiency, as has been discussed in [48, 49]. At sufficiently high power density, the neutral gas temperature in the plasma reactor can become high enough for thermal decomposition of CO₂ to set in. This requires temperatures exceeding ~1700 K, as is seen from the calculated equilibrium composition of a carbon dioxide mixture at 100 mbar in Figure 8. The thermal conversion optimum shown in the same graph is just over 50% at 3200 K, which requires ideal quenching of the reaction products. In fact, also here the plasma phase can help by providing a vibrational non-equilibrium and thus quenching atomic oxygen by producing additional CO in reaction (5). This is referred to as super-ideal quenching and would bring the efficiency limit of thermal conversion in plasma up to at least 60% [2].

Fig. 8: The equilibrium composition of CO₂ and its dissociation products as a function of temperature at a pressure of 100 mbar. Instantaneous quenching preserving all CO formed is assumed to calculate the efficiency. Reproduced from [47] with permission.

Dissociation performance in different plasma approaches

Recently, Snoeckx and Bogaerts reviewed the state of the art of plasma chemistry concerning CO₂ conversion [50]. Fig. 9 summarises the performance of the different plasma approaches in terms of combinations of efficiency and conversion.

Fig 9: Comparison of all the data collected from the literature for CO₂ splitting in the different plasma types as collected by Snoeckx and Bogaerts [50]. It shows combinations of energy efficiency and conversion grouping the data per discharge type.

Although DBDs have been widely researched in view of their strong non-equilibrium character, their successful commercial application for O₃ production and relatively ease of operation at atmospheric pressure, their performance stays significantly behind that of the other types. Although conversion can reach up to 40%, efficiency appears to be limited to ~18% (except for the DBD record of 23% by [51]). The effect of changing the applied frequency, power, gas flow rate, discharge length, discharge gap, reactor temperature, dielectric material, electrode material, mixing with gases, i.e. Ar, He, N₂, and by introducing (catalytic) packing materials has been studied extensively, as well as numerically modelling has been applied to gain understanding in the underlying reaction pathways. In general, it appears that conversion can well be controlled via specific energy input (or, equivalently, the residence time of the gas in the reactor), however, this goes on the expense of energy efficiency. The limited efficiency seems to be due to unfavourable plasma electron energy distribution (or E/n), which

causes *vibrational* non-equilibrium effects to be insignificant and reactions (1) and (2) the main dissociation pathways. This is despite the fact that gas temperatures remain low and in this respect the DBD discharge being non-equilibrium par excellence. The low gas temperatures, however, also cause thermal conversion insignificant.

Microwave discharges clearly span the largest parameter range and reach the highest energy efficiencies. This discharge type is known to be best suitable to channel most of the discharge power to vibrational modes and is thus best equipped to benefit from vibrational excitation. However, the best results (efficiency >60%) date from the early work ^[4-9] and have not been reproduced in recent years. All recent work is within the range of thermal equilibrium conversion and gas temperature measurements have indeed shown that 50% efficiency is well achievable up to high conversion values ^[47, 52-57]. As thermal regions have also been observed in the early work, it seems that a combination of thermal conversion with non-equilibrium chemistry in the periphery is an interesting route to further optimisation. It means that transport of power and particles in a complex 3D geometry is to be optimised.

A drawback that is often put forward to MW discharges is their preference to operate at reduced pressure. On the one hand, the lower operational pressure is compensated by high flow rates so that in effect the reactor power density is of the highest possible. On the other hand, also atmospheric pressure operation is well possible, but likely limits performance to thermal operational space.

GA discharges seem to succeed in exploiting vibrational excitation enhanced dissociation channels while operating at atmospheric pressure. Energy efficiencies up to 50% are common^[58] and also record values of 65% have been reported^[59]. Model calculations (e.g. ^[20, 60-63]) revealed that also GA discharges induce elevated temperatures. Just like for MW discharges, preventing gas heating to operate at lower gas temperatures might be the key for benefitting fully from the potential of the vibrational excitation pathways to dissociation. At the same time, it is very much likely that also in GA thermal conversion plays a significant role ^[20, 60-63].

3.2 Plasma conversion of CO₂ with CH₄

3.2.1 Plasma conversion



The conversion of CO₂ with CH₄, known as dry reforming of methane (DRM) has received significant interest as this reaction uses two abundant greenhouse gases CO₂ and CH₄ in the form of different sources (e.g., landfill gas, biogas and shale gas) to produce value-added fuels and chemicals, with syngas (H₂+CO) being the most common target product (6). Syngas is a vital chemical feedstock that can be used to produce a variety of platform chemicals and synthetic fuels, including via the Fischer-Tropsch process. However, both CO₂ and CH₄ are highly stable, therefore high temperature (>700 °C) is always required for thermal catalytic activation of CO₂ and CH₄ with reasonable conversions and syngas production due to the thermodynamic barrier of this process, resulting in high energy consumption. In addition, the rapid deactivation of reforming catalysts at high temperatures due to sintering and coke deposition remains a major challenge for the use of this process at a commercial scale. Non-thermal plasmas provide a promising alternative to the thermal catalytic process for the conversion of CO₂ with CH₄ into higher value chemicals and fuels at low temperatures and ambient pressure. Significant efforts have been devoted to the synthesis of syngas using different plasma

systems with or without catalyst^[64-68]. In addition to syngas production, noticeable amounts of higher hydrocarbons are often produced in the plasma DRM process, especially in the presence of a catalyst (e.g. zeolite)^[69]. CH_x radicals initially formed in the dissociation of CH₄ play a key role in the production of higher hydrocarbons^[10, 19, 70]. Thus, the content of CH₄ in the CO₂/CH₄ mixture is of primary importance for the synthesis of higher hydrocarbons in the plasma DRM reaction. Eliasson et al. investigated the synthesis of higher hydrocarbons from CO₂ and CH₄ using a DBD plasma. The selectivity of C₅₊ and oxygenates was up to 41.2% at a discharge power of 500 W and a CO₂/CH₄ molar ratio of 1:2^[69]. A mixture containing mainly C₂H₂ and synthesis gas with a H₂/CO ratio of 2:1 was produced in the plasma reaction using a point-to-point pulsed discharge at a CO₂/CH₄ ratio of 1:2^[71].

In addition, a few groups have reported the formation of trace oxygenates (e.g. alcohols and acids) along with the production of syngas and hydrocarbons in plasma-based DRM^[72, 73]. Zhang et al.^[72] reported the production of acetic acid, propanoic acid, ethanol and methanol in the plasma DRM using a DBD reactor. Acetic acid was the major liquid product with the highest selectivity of 5.2% achieved at CH₄ and CO₂ conversion of 64.3% and 43.1%, respectively^[72]. Acetic, formic, butanoic and propanoic acids were also formed, along with methanol and ethanol, in the plasma oxidation of CH₄ with CO₂ using a DBD^[74]. Zhou et al.^[75] developed a starch-enhanced plasma process for the conversion of CO₂ and CH₄ into a range of oxygenates, including primarily formaldehyde, methanol, ethanol, formic acid, and acetic acid. The total selectivity of the oxygenates was about 10-40% with the conversion of CH₄ and CO₂ of about 20%. They found that a lower methane concentration was favourable for the production of oxygenates, and a higher feed flow rate led to higher selectivity of oxygenates in the presence of starch^[75]. The direct conversion of CH₄ with CO₂ using a DBD plasmas was carried out by Li et al. The product includes syngas, gaseous hydrocarbons (C₂ to C₄), liquid hydrocarbons (C₅ to C₁₁₊), and oxygenates^[76]. Bogaerts et al. developed a 1D fluid model to understand the plasma chemistry of the DRM process in a DBD reactor. Their modeling results showed that oxygenates, including methanol, ethanol, acetaldehyde and ketene, can be formed in the plasma DRM reaction^{[10], [77]}. Very recently, Wang et al. have developed a water-electrode DBD plasma reactor for the direct, one-step reforming of CO₂ with CH₄ into oxygenates (e.g. acetic acid, methanol, ethanol and acetone) at atmospheric pressure (1 bar) and room temperature (30 °C). The total selectivity to oxygenates was approximately 50-60% without a catalyst, with acetic acid being the major liquid product at 40.2% selectivity^[78]. Two possible reaction pathways could contribute to the formation of acetic acid in this process (Figure 10). CO can react with a CH₃ radical to form an acetyl radical (CH₃CO) with a low energy barrier of 28.77 kJ mol⁻¹, followed by recombination with OH to produce acetic acid with no energy barrier. Direct coupling of CH₃ and carboxyl radicals (COOH) could also form acetic acid based on density functional theory (DFT) modelling^[74].

Fig. 10: Possible reaction pathways for the formation of oxygenates in plasma DRM using a DBD. Reproduced from^[78] with permission.

Carbon nanomaterials are often produced as a by-product in the plasma dry reforming reaction. Tu and Whitehead reported the production of multi-wall carbon nanotubes (MWCNTs) and spherical carbon nanoparticles with a diameter of 40-50 nm in the DRM reaction using an AC gliding arc discharge with knife-shaped Al electrodes (Figure 11(a))^[66]. Chung and Chang reported the synthesis of MWCNTs via plasma DRM using a spark discharge. They found that the stainless-steel electrodes of the spark discharge acted as a substrate for the deposition of MWCNTs (Figure 11(b))^[79]. Carbon

nanomaterials have a variety of applications and are higher value products in the plasma DRM process, which can further reduce the energy cost of the overall plasma DRM process and make this process more attractive.

Fig. 11: (a) The formation of carbon nanotubes using a gliding arc plasma; (b) The formation of MWCNTs using a spark discharge. Reproduced from ^{[66],[79]} with permission.

The conversion of CO₂ with CH₄ has been explored using different plasma systems. Most of previous works have mainly focused on the production of syngas via plasma DRM ^[80-85]. The reaction performance of the plasma dry reforming process has been affected by a range of operating parameters, such as plasma input power, total gas flow rate, SEI, CH₄/CO₂ molar ratio, and dielectric material. The plasma power is one of the most important parameters determining the effectiveness of the plasma DRM process. Increasing discharge power enhances the conversion of CO₂ and CH₄ regardless of the type of plasma system used ^[65-67, 86, 87]. A higher discharge power generates more energetic electrons and reactive species (e.g. O and OH radicals), which can activate the reactants and promote the conversion ^[69]. In addition, increasing discharge power would increase the temperature of the plasma reaction, which also contributes to the enhanced conversion of CO₂ and CH₄. In a DBD plasma reactor, increasing discharge power by changing the applied voltage at a fixed frequency increases the number of microdischarge and creates more reaction channels for chemical reactions, resulting in higher conversion of CO₂ and CH₄. This effect can be demonstrated by the increased magnitude and number of current pulses of the DBD plasma at a higher plasma power ^[88]. However, the discharge power can also affect the distribution of gas products produced in the plasma DRM process. Previous results showed that increasing discharge power decreases the selectivity of lower hydrocarbons (e.g., C₂) but increases the selectivity of higher hydrocarbons (e.g., C₄ and C₅) ^[89]. By contrast, the change of discharge power has a limited effect on the selectivity of syngas and the H₂/CO molar ratio, although the yield of syngas is enhanced at a higher discharge power ^[90].

Increasing the total feed flow rate decreases the conversion of CO₂ and CH₄ due to the decrease of the residence time of the reactants in the discharge region, which reduces the possibility of the reactant molecules colliding with energetic electrons and reactive species ^[66]. A lower gas flow rate is beneficial for producing more syngas and reducing the selectivity of higher hydrocarbons ^[89]. The increase of the residence time resulting at a lower feed gas flow rate increases the chance for C₂-C₄ hydrocarbons to be further dissociated via electron impact reactions and converted to produce more CO and H₂ ^[91]. By contrast, a high total feed flow rate is preferred for the production of C₂-C₄ hydrocarbons. In addition, the change of the feed flow rate does not significantly change the H₂/CO molar ratio ^[64, 82]. Although the conversion of the reactants decreases when increasing the feed flow rate, the energy efficiency of the plasma process increases as the total amount of reactants converted increases and more electric energy could be converted to chemical energy stored in the products ^[66].

Specific energy input (SEI) is a major determining factor for the conversion and energy efficiency in plasma chemical processes, as it combines the effect of power and gas flow rate. The variation of the SEI can be achieved by changing the discharge power and/or gas flow rate. However, previous findings showed that manipulating the SEI by changing the gas flow rate has a more pronounced effect on the conversion of the reactants compared to the change of discharge power ^[88]. Increasing the SEI at a constant gas ratio and frequency results in a higher conversion of CO₂ and CH₄ but with a decreased energy efficiency of the plasma process. The trade-off between the conversion and energy efficiency

was often reported in previous studies^[67, 87]. Therefore, both discharge power and gas flow rate should be considered when pursuing a suitable SEI to achieve higher conversion and energy efficiency simultaneously.

The reactant conversion and the H₂/CO molar ratio, along with the product yields and selectivities, are significantly affected by the molar ratio of CO₂/CH₄ in the feed^[81, 92]. Increasing the CO₂/CH₄ molar ratio significantly enhances the conversion of CH₄ but only weakly decreases the conversion of CO₂. At a higher CO₂ content in the feed, oxygen atoms generated from the dissociation of CO₂ can also react with CH₄, enhancing the CH₄ conversion. The CO₂/CH₄ molar ratio also significantly affects the yield of CO and H₂. Mei reported that the yield of H₂ and CO was more than doubled when increasing the CO₂/CH₄ molar ratio from 1:4 to 4:1 in the plasma DRM using a DBD (Figure 12)^[93]. Zhang et al. found that increasing the CO₂/CH₄ molar ratio from 2:3 to 3:1 significantly increased the H₂ yield from 11.4% to 20.4% and the CO yield from 7.3% to 31.3% in a DBD reactor^[64]. The CO₂/CH₄ molar ratio plays a key role in determining the H₂/CO molar ratio in the produced syngas. Thus, syngas with a desired H₂/CO molar ratio for the further synthesis of chemicals or fuels can be controlled by tuning the CO₂/CH₄ molar ratio in the feed.

Fig. 12: Effect of CO₂/CH₄ molar ratio on the yield of syngas and H₂/CO ratio in the plasma DRM using a DBD reactor (discharge power 50 W, total flow rate 50 ml/min). Reproduced from^[93] with permission.

Higher CO₂ content in the CO₂/CH₄ mixture leads to higher CO selectivity. In addition to direct CO₂ dissociation to CO, more C₂-C₄ hydrocarbons generated by CH₄ dissociation could be oxidised by O atoms from CO₂ dissociation, resulting in the enhanced CO selectivity and decreased selectivity to C₂-C₄. For instance, the CO selectivity was increased from ~20% to over 80% when changing the CO₂/CH₄ molar ratio from 1:4 to 4:1^[93]. On the other hand, the lower content of CO₂ in the feed gas leads to a higher selectivity of C₂-C₄ hydrocarbons. Zhang et al. suggested that lower CO₂/CH₄ ratio decreased the availability of O radicals in the reaction, which enhanced the possibility of recombination of CH_x (x=1-3) species to form C₂-C₄ hydrocarbons compared with that of direct CH₄ oxidation to form CO^[64]. This explanation is consistent with the decreasing trend in CO selectivity as a result of decreasing the CO₂ content in the feed gas. Wang et al. investigated the effect of CO₂/CH₄ molar ratio on the synthesis of oxygenates via DRM using a water-cooled DBD system. The selectivity of acetic acid and methanol increased initially and then decreased when changing the CO₂/CH₄ molar ratio from 3:1 to 1:2, with the highest selectivity achieved at a CO₂/CH₄ molar ratio of 1:1. By contrast, the selectivity of ethanol decreased continuously when decreasing the CO₂/CH₄ molar ratio^[78]. Zhang et al. also reported that there exists an optimum CH₄/CO₂ molar ratio for the maximum selectivity of target oxygenates^[72].

Other process parameters also affect the performance of the plasma DRM process. Khoja et al. evaluated the effect of discharge gap (1-4 mm) on the plasma DRM at a constant SIE in a DBD reactor. The highest conversion of CH₄ and CO₂ and H₂ selectivity was achieved at a discharge gap of 3 mm using quartz as a dielectric material^[94]. In most of the previous works, a discharge gap between 1 and 5 mm was used. The most appropriate discharge gap may be 2-3 mm for adequate residence time and effective collision between electron-molecules, as studied in many cases. Enlarging the discharge gap can increase the residence time of the reactants in the discharge zone, which can have a positive effect on the conversion. However, increasing the gap distance at a constant input power decreases the power density due to the increased discharge volume, which in turn negatively affects the conversion. The balance between these opposite effects determines whether the change of the gap distance has

a positive or negative effect on the conversion^[88]. A partial discharge is more likely to form at a larger discharge gap, resulting in reduced conversion of the reactants. Li et al. found that a wider discharge gap (1.8 mm) is more favourable for the formation of methanol and ethanol in the plasma reforming of CO₂ with CH₄ at a lower CO₂/CH₄ feed ratio, while a smaller discharge gap (1.1 mm) produced more acetic acid^[76]. In the first reactor, the roughness of the inner electrodes was demonstrated to play an important role on the conversion and efficiency levels of methane^[95]. Zhu et al. investigated the effect of pressure on plasma-based DRM using a kHz spark discharge plasma. Their results showed that increasing the pressure from 1 to 2 bars enhanced the conversion of CO₂ and CH₄ by 7-14.8% and reduced the energy costs by 7.7-15.2% for the conversion of the reactants^[80].

Considerable effort has been devoted to further improving the performance of the dry reforming process to maximise the conversion of CO₂ and CH₄ while reducing the energy consumption of the plasma process through the development of new plasma reactor designs. Wu et al. designed a novel rotating gliding arc co-driven by a magnetic field and tangential flow for the conversion of CO₂ with CH₄. A total conversion of 39% with an energy cost of 1 eV per molecule was achieved in this process^[96]. Very recently, Cleiren et al. applied a novel gliding arc plasmatron for the reforming of CH₄ with CO₂ with syngas being the major product. The CO₂ and CH₄ conversions reached their highest values of approximately 18 and 10 %, respectively, at 25 % CH₄ in the gas mixture, which corresponded to an energy efficiency of 66%. This value was above the required energy efficiency target (i.e. 60%) reported in literature to be competitive with thermal catalytic DRM processes^[22]. Modification of a plasma reactor design has been carried out to manipulate the product distribution with enhanced selectivity of target products. Wang et al. proposed a multi-stage ionisation design to enhance the conversion of reactants and syngas production. It was found that the multi-stage ionisation process favoured a higher conversion of CO₂, but lowered the conversion of CH₄. Meanwhile, the selectivity to CO and H₂ was increased, while the selectivity to the by-products (C₂-C₆) was decreased^[92]. Ozkan et al. developed a new geometry of a DBD reactor with multiple electrodes for the processing of high gas flow rates in DRM. In their work, the main products were syngas, C₂H₄ and C₂H₆ when Ar or He was used as the carrier gas^[97]. Wang et al. developed a specially designed coaxial DBD reactor using water as both the ground electrode and cooling for the direct synthesis of a range of oxygenates, with acetic acid being the dominant liquid chemical via plasma DRM reaction^[78].

3.2.2 Plasma-catalysis

The combination of non-thermal plasma with heterogeneous catalysis has been demonstrated as a promising solution to further enhance the conversion and energy efficiency of the plasma process, as well as the selectivity towards target products (*e.g.* syngas). Plasma-catalytic DRM has been carried out using different plasma systems, including DBD, corona discharge, glow discharge and gliding arc plasma. Those catalysts that have successfully demonstrated their activities in thermal catalytic dry reforming are generally used as a starting point in the plasma-catalytic DRM reaction.

Catalysts can be coupled with non-thermal plasma in different ways, which in turn affects the interaction between the plasma and catalyst and the formation of a plasma-catalytic synergy. Tu et al. found that a fully packed Ni/Al₂O₃ catalyst into the entire discharge region of a DBD reactor decreased the conversion of CH₄ and CO₂ in comparison to the plasma reaction without a catalyst^[86]. Packing catalyst pellets into the discharge area was found to shift the discharge mode from typical microdischarges in the gas to a combination of surface discharge and weak microdischarges, which could partly contribute to the negative effect of the plasma-catalyst coupling. A similar negative effect from the integration of plasma and catalyst was also reported in previous studies^[90, 98, 99]. These results

suggest that the generation of plasma-catalytic synergy at low temperatures (without extra heating) in the DRM reaction is conditional and depends on the balance between the change in discharge properties induced by the catalyst and the catalyst activity generated by the plasma^[86]. The former strongly depends on how the catalysts are packed into the discharge volume and the packing geometry significantly affects the interactions between the plasma and the catalyst. Tu and Whitehead compared the influence of three different catalyst packing methods on the plasma-catalyst interactions and the resulting plasma-catalytic synergy in the DRM reaction (Figure 13)^[65]. They found that partially packing a Ni/ γ -Al₂O₃ catalyst in flake form into the bottom of the discharge gap significantly enhanced the reaction performance with a doubled CH₄ conversion and hydrogen yield in comparison to a fully packed reactor. This is because the discharge in the partially packed-bed reactor retains the strong filamentary discharge, whereas the reduction in discharge volume in the fully packed bed DBD reactor strongly suppresses the formation of microdischarges and changes the discharge mode to surface discharge and spatially limited microdischarges^[65].

Fig. 13: Different catalyst packing methods in a DBD plasma reactor. Reproduced from ^[65] with permission.

Ray et al. also investigated the effect of catalyst packing volume (0%, 25%, 50% and 100%) on the plasma dry reforming reaction in a DBD reactor^[100]. They found that 25% catalyst packing showed the highest conversion of CH₄ and CO₂, while fully (100%) packing the catalyst into the discharge zone decreased the conversion of CH₄ and CO₂ compared to the plasma DRM reaction without packing. Wang et al. studied the synergistic effect of catalyst and non-thermal plasma on DRM in fluidised bed and packed-bed DBD reactors with a Ni/ γ -Al₂O₃ catalyst. They concluded that both interaction modes between the plasma and catalytic particles could promote the reaction at relatively low temperatures (e.g. 673 K)^[101].

The use of zeolites has been shown to be effective for enhancing selectivities towards higher hydrocarbons, particularly C₂-C₄ species. Zeolites are known for their adsorbent properties, which are beneficial to plasma reactions, because they allow species to be adsorbed onto the zeolite surface or inside the pore structure, which can increase the residence time of the reactant species in the plasma discharge. This can lead to an increased probability of successful collisions with active plasma species. Eliasson et al. reported the direct formation of higher hydrocarbons with reduced carbon formation in the plasma dry reforming of CH₄ when zeolite NaX was used. They found that the presence of zeolite NaX in the discharge zone reduced the overall conversion but increased the concentration of C₂ to C₄ hydrocarbons in the products^[69]. Zhang et al. compared the effects of zeolite X, zeolite HY, and zeolite NaY on the plasma DRM reaction at ambient conditions. Zeolite NaY was found to be the most promising catalyst for the production of syngas and liquid hydrocarbons (C₅₊)^[89], while Zeolite HY showed the best performance in the generation of syngas and C₄ hydrocarbons (C₄H₈, n-C₄H₁₀ and i-C₄H₁₀) with high selectivity^[102]. Jiang et al. reported that the coupling of a DBD with zeolite A inhibited the formation of carbon black and polymers and resulted in a higher selectivity towards valuable hydrocarbons (C₂-C₄) compared to the use of zeolite X in the DBD^[103]. Li et al. reported the formation of phenol in the plasma DRM combined with a HZSM-5 catalyst using a corona discharge^[98].

Supported metal catalysts have been extensively used in thermal catalytic dry reforming, with transition metals being prevalent due to their low cost and wide availability. Catalysts with high activity in the thermal catalytic process have been used as the starting point for the plasma-catalytic

DRM process. Ni/ γ -Al₂O₃ [64, 65, 68, 81, 86, 101, 104], Ag/Al₂O₃[99], Pd/Al₂O₃[99], Cu-Ni/Al₂O₃[102], Cu/Al₂O₃[82, 105], Co/ γ -Al₂O₃[82], Mn/ γ -Al₂O₃[82], Fe/Al₂O₃[106], La₂O₃/ γ -Al₂O₃[107] have been tested in the plasma DRM, with Ni/Al₂O₃ catalysts being the most commonly used. Song et al. reported that the presence of Ni/ γ -Al₂O₃ in a DBD reactor enhanced the CO selectivity by 22% but had a weak effect on the CO₂ conversion. In addition, they found that Ni loading (2-10 wt. %) had no effect on the conversion of CO₂ and CH₄, the selectivity of gas products and H₂/CO molar ratio^[90]. Mahammadunnisa et al. also investigated the effect of Ni loading (10, 20 and 30 wt. %) on the plasma DRM over partially packed Ni/Al₂O₃ catalysts in a DBD reactor. The coupling of the DBD with 20 wt.% Ni/Al₂O₃ showed the highest reactant conversion and syngas selectivity with doubled hydrogen yield and H₂/CO molar ratio^[108]. Zhu et al. reported that increasing the Ni loading of Ni/Al₂O₃ from 6 wt. % to 10 wt. % enhanced the conversion of CH₄ with maximum CH₄ conversion of 58.5% in the plasma DRM using a rotating gliding arc plasma, which could be attributed to the increased catalytic effect due to the decreased Ni particle size and enhanced Ni dispersion on the catalyst surface at a higher Ni loading (10 wt.%)^[84]. Tu and Whitehead evaluated the influence of calcination temperature (300-800 °C) of Ni/Al₂O₃ on the plasma-catalytic DRM at low temperatures (~250 °C) in a DBD reactor. The results showed a synergistic effect from the combination of the DBD with partially packed Ni/Al₂O₃ catalyst calcined at 300 °C, which almost doubled the conversion of CH₄ (56%) and hydrogen yield (17.5%) compared to the plasma reaction without a catalyst^[65]. Long et al. carried out the plasma DRM reaction using a cold plasma jet coupled with a 12 wt.%Ni/Al₂O₃ catalyst placed in the downstream of the plasma jet. Compared to the reaction using plasma only, the combination of the plasma jet and Ni/Al₂O₃ enhanced the conversion of CO₂ and CH₄ by 6-14% and the yield of hydrogen and CO by 11-18% at a discharge power of 700 W^[109]. Zeng et al. carried out the plasma DRM reaction over different supported metal catalysts, i.e., M/ γ -Al₂O₃ (M = Ni, Co, Cu and Mn), in a DBD reactor. They found that the combination of the plasma with Ni/ γ -Al₂O₃ or Mn/ γ -Al₂O₃ significantly enhanced the conversion of CH₄ in comparison to the reaction without catalyst. The presence of Ni/ γ -Al₂O₃ in the plasma showed the highest activity for syngas production^[81]. However, the use of these catalysts did not improve the CO₂ conversion^[81]. Sentek et al found that the presence of a Pd/Al₂O₃ catalyst in a DBD reactor slightly decreased the conversion of CO₂ and CH₄ compared to the reaction without packing, but significantly changed the distribution of C₂-C₄ hydrocarbons with the formation of more C₂ and less C₃-C₄^[99].

The catalyst support is of primary importance, as the support, along with its interactions with the active metal, can affect the reaction performance. Mei et al. investigated the use of a Ni catalyst supported on γ -Al₂O₃, TiO₂, MgO and SiO₂ in plasma-catalytic DRM^[110]. The results of this experiment concluded that the γ -Al₂O₃ support was most beneficial on the reaction performance, giving the highest CO₂ (26.2 %) and CH₄ (44.1 %) conversions, as well as the maximum energy efficiency and highest yields of CO and H₂ (Figure 14). This was attributed to the increased reducibility of the Ni/ γ -Al₂O₃ catalyst and the number of stronger basic sites present on its surface (which facilitate CO₂ chemisorption and activation), along with its higher specific surface area and greater dispersion of smaller NiO particles^[110]. Carbon deposition also occurred to a lower extent on this catalyst, as the increase in CO₂ chemisorption and activation may have resulted in adsorbed CO₂ undergoing gasification by surface adsorbed oxygen^[110]. Weaker interactions between the catalyst and support are favourable as this increases the reducibility of the catalyst, increasing its activity^[65].

Fig. 14: Effect of catalyst support on the yield of H₂ (a) and CO (b) as a function of discharge power in the plasma-catalytic DRM reaction (total flow rate 50 ml/min, CO₂/CH₄ molar ratio 1:1). Reproduced from ^[110] with permission.

The addition of dopants and use of bimetallic catalysts has also been studied in the plasma DRM reaction. Zhang et al. investigated the effect of Cu/Ni ratio in Cu-Ni/ γ - Al_2O_3 catalysts and found that the 12 wt. % Cu-12 wt. % Ni/ γ - Al_2O_3 catalyst gave the optimum results for both CH_4 and CO_2 conversion and showed a synergistic effect of plasma-catalysis at 450 °C (Figure 15)^[111]. This catalyst also achieved the maximum CO selectivity of 75 %. However, this selectivity was also achieved when using the 5 wt. % Ni-12 wt. % Cu/ γ - Al_2O_3 catalyst, whereas the maximum selectivity to H_2 was achieved with 16 wt. % Ni-12 wt. % Cu/ γ - Al_2O_3 and 20 wt. % Ni-12 wt. % Cu/ γ - Al_2O_3 catalysts^[111]. Ray et al. found that the addition of Mn to a Ni/ Al_2O_3 catalyst enhanced the conversion of CO_2 and CH_4 , and the yield of H_2 and CO in the plasma DRM^[100]. In addition, the coupling of the DBD with the Ni-Mn/ Al_2O_3 bimetallic catalyst reduced the carbon formation on the catalyst surface compared to Ni/ Al_2O_3 ^[100]. Zhang et al. investigated the effect of La_2O_3 / Al_2O_3 catalysts on the production of C_2 hydrocarbons in the plasma DRM using a pulsed corona discharge. They found that the La_2O_3 / Al_2O_3 catalysts with different La loadings (5-12 wt. %) gave a C_2 hydrocarbon selectivity of more than 60% with C_2H_2 being the major C_2 product, and maintained the methane conversion of ~24%. Note the La_2O_3 / Al_2O_3 catalysts with different La loadings showed no change in the distribution of C_2 products. Adding 0.01 wt. % Pd to 5 wt. % La_2O_3 / Al_2O_3 still gave a high C_2 selectivity of 70% but significantly changed the distribution of C_2 hydrocarbons with C_2H_4 being the major C_2 product (65 vol. %)^[112]. Kado et al. reported that packing a $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ catalyst into a flow-type tubular pulsed discharge reactor significantly changed the selectivity of gas products compared to the plasma reaction without a catalyst: the selectivity of C_2 drastically decreased from 33.6% to 1%, and the CO selectivity increased from 65.4% to 99%, at a CO_2/CH_4 molar ratio of 1:1^[113]. More recently, K-, Mg- and Ce-promoted Ni/ Al_2O_3 catalysts have also been evaluated in plasma-catalytic DRM at 160 °C^[85]. The addition of promoters (K, Mg and Ce) into the Ni/ Al_2O_3 catalyst enhanced the conversion of CH_4 , the yield of H_2 and the energy efficiency of the plasma process. The highest conversion of CO_2 (22.8%) and CH_4 (31.6%) was achieved by placing the K-promoted Ni/ Al_2O_3 catalyst in the plasma reforming process. In addition, compared to the un-promoted Ni/ Al_2O_3 catalyst, although the use of the promoted catalysts increased the carbon deposition on the surface of the spent catalysts by 22%-26%, the total amount of deposited carbon was still less than that reported in high temperature catalytic dry reforming processes. More than 80% of the increased carbonaceous species was in the form of reactive carbon species, which can be easily oxidised by CO_2 and O atoms and maintain the stability of the catalysts during the reforming reaction^[85]. In this study, the behaviour of K, Mg and Ce promoters in the low temperature plasma-catalytic DRM reforming was opposite to that in high temperature thermal catalytic DRM process in terms of the conversion of CH_4 and carbon deposition, which could be ascribed to the temperature-dependent character of the promoters^[85]. These results also suggest that those catalysts that have shown poor catalytic activity (e.g. conversion) in thermal catalytic reactions might work well in low temperature plasma-catalytic processes, and vice versa.

Fig. 15: DRM using plasma only, Cu-Ni/ Al_2O_3 catalyst only and plasma-catalysis at 450 °C (total flow rate 60 ml/min, argon flow rate 30 ml/min, CO_2/CH_4 molar ratio 1:1, discharge power 60 W, GHSV 1800 h^{-1} , CO_2 flow rate 60 ml/min, 50%Ar in the feed, CO_2/CH_4 molar ratio 1:1, GHSV 1800 h^{-1} , 0.1 g catalyst). Reproduced from ^[111] with permission.

Core-shell structured catalysts have attracted significant interest in DRM as the metallic active sites could be uniformly distributed within the shells. The strong interaction between the cores and shells is ascertained to be highly capable of preventing metallic nanoparticles (NPs) from carbon deposition and sintering even at high temperatures. Zheng et al. reported that the combination of a DBD plasma

with $\text{LaNiO}_3@\text{SiO}_2$ core-shell nanoparticle catalysts showed a better catalytic performance in plasma-based DRM with higher reactant conversion, product selectivity and catalytic stability, compared to the traditional Ni-based catalysts (Ni/SiO_2 , $\text{LaNiO}_3/\text{SiO}_2$ and LaNiO_3)^[114, 115]. The conversion of CH_4 and CO_2 reached 88.3% and 77.8%, and the selectivity of CO and H_2 was 92.4% and 83.7%, respectively. Their results suggest that the SiO_2 shell is capable of preventing Ni from sintering and mitigating carbon deposition in the plasma-catalytic reaction (Figure 16)^[114]. Compared to the supported Ni-based catalysts ($\text{Ni}/\gamma\text{-Al}_2\text{O}_3$, $\text{NiFe}/\gamma\text{-Al}_2\text{O}_3$, NiFe/SiO_2 , and NiFe_2O_4), the use of spinel nickel ferrite nanoparticles (NiFe_2O_4 NPs) embedded in silica ($\text{NiFe}_2\text{O}_4\#\text{SiO}_2$) also showed excellent catalytic performance and high resistance to carbon formation in the plasma dry reforming under ambient conditions without the involvement of extra heat. The results indicated that the special structure of the as-synthesised $\text{NiFe}_2\text{O}_4\#\text{SiO}_2$ catalyst was capable of restraining the aggregation of NiFe alloy and suppressing the carbon formation in the plasma reforming process^[83].

Fig. 16: *The conversion of CH_4 and CO_2 with time on stream over different Ni catalysts. Adopted from ^[114] with permission.*

In addition, the catalytic effect of electrode materials on the plasma DRM reaction has also been investigated. Li et al. evaluated the influence of different electrode materials (Ti, Al, Fe and Cu) on the production of syngas and higher hydrocarbons in the plasma DRM using a DBD reactor. They found that the Ti electrode showed the highest conversion of CH_4 and CO_2 , while the other electrode materials showed a similar performance^[116]. Scapinello et al. reported that nickel and copper electrodes are more efficient than stainless steel in producing carboxylic acids, in particular formic acid in the plasma DRM using a DBD reactor^[117]. However, no major catalytic effects of the metal surface on the conversion of reactants (CO_2 and CH_4) and the production of H_2 and CO were observed^[117].

The energy efficiency is higher in gliding arc discharges in comparison to other types of discharges, and catalysts can increase this even more^[81]. Placing a $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst in the afterglow of the gliding arc reactor was found to increase the energy efficiency by over 20 % in comparison to that achieved using plasma only^[81]. The H_2 yield, along with the CO_2 and CH_4 conversions, was also increased. The concentration of active metal was found to influence the reaction performance, as a 33 wt.% $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst resulted in a decrease in reaction performance in comparison to an 18 wt. % $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst; whilst a smaller catalyst diameter was found to be beneficial^[81]. Goujard et al. investigated the influence of the type of plasma power supply on the plasma-catalytic synergy for DRM. Their experiments were performed in a DBD reactor packed with a cordierite honeycomb monolith and excited by two different power supplies: a pulsed excitation and a sinusoidal excitation. In the absence of a Ni catalyst, higher CO_2 and CH_4 conversion was achieved using the pulsed power supply. However, when using a 2 wt.% Ni catalyst in the plasma, the reactive species generated by the AC power supply promoted the activation of CO_2 and CH_4 on the Ni catalyst surface, leading to a significant increase of CH_4 and CO_2 conversion^[118].

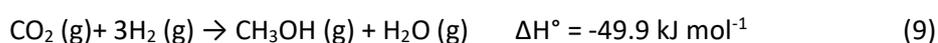
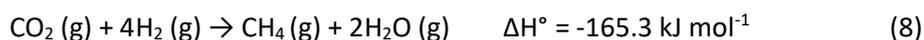
3.3 Plasma CO_2 Hydrogenation

CO_2 hydrogenation for the synthesis of higher value fuels and chemicals has provided an attractive

route for CO₂ conversion and utilisation, as this process has a lower thermodynamic limitation compared to direct CO₂ decomposition and dry reforming of methane. One of the key challenges facing this process is the cost and source of hydrogen. In order for this process to be both economically viable and sustainable, hydrogen must be generated using a low cost, environmentally friendly and sustainable process, such as from water electrolysis using wind or solar power or from bioenergy. The overall process should be CO₂ neutral, which means that CO₂ hydrogenation must convert a greater amount of CO₂ than renewable hydrogen production pathways generate. Although CO₂ reduction with H₂ using heterogeneous catalysis has been extensively investigated in the past few years, there are still significant challenges in developing active, selective and stable catalysts suitable for large-scale commercialisation. In addition, it is key to lower the operating temperature of the CO₂ hydrogenation to minimise the energy consumption of the process.

3.3.1 Plasma conversion

The direct hydrogenation of CO₂ mainly produces three types of C1 chemicals: CO via reverse water gas shift reaction (RWGS, (7)), CH₄ via CO₂ methanation (8), and CH₃OH via CO₂ hydrogenation (9). Up until now, very limited research has been concentrated on CO₂ hydrogenation using non-thermal plasmas^[119-123]. The majority of this research reports CO as the dominant chemical, with CH₄ formed as a minor product and no or trace CH₃OH detected^[124-126].



The reverse water-gas shift reaction converts CO₂ and H₂ to produce CO and H₂O. CO is an important chemical feedstock for Fischer-Tropsch synthesis (FTS) to produce higher hydrocarbons such as liquefied petroleum gas (LPG), naphtha, gasoline and diesel; or for the synthesis of valorised chemicals such as acetic acid, phosgene and formic acid. Recently, Porosoff et al. has proposed the combination of the RWGS reaction with FTS for the synthesis of hydrocarbons^[127].

Zeng and Tu investigated the influence of H₂/CO₂ ratio on the RWGS reaction using a DBD reactor^[128]. They found that the conversion of CO₂ increased almost linearly with the increase of the H₂/CO₂ ratio from 1:1 to 4:1. Increasing the H₂/CO₂ ratio significantly enhanced the yield of CO, while the CO selectivity was only slightly increased^[128]. The dependence of CO selectivity on the gas flow rate at a fixed H₂/CO₂ ratio of 4:1 was investigated using a low-pressure radio-frequency discharge^[129]. The selectivity of CO increased gradually when increasing the total flow rate. This phenomenon is most likely due to the decreased residence time associated with the increase of the flow rate, resulting in suppression of the recombination of CO and O. The effect of argon on the plasma RWGS was evaluated in a DBD plasma reactor at 150 °C. In the absence of a catalyst, the CO₂ conversion increased from 18.3% to 38% at a discharge power of 30 W and a fixed H₂/CO₂ ratio of 4:1 when increasing the Ar content from 0 to 60% in the gas mixture^[121]. The presence of metastable argon species in the DBD

creates new reaction pathways for the dissociation of CO₂, resulting in enhanced CO₂ conversion.

In the CO₂ methanation reaction, CO₂ reacts with hydrogen to produce methane and water. This reaction was first discovered by Sabatier and Senderens in 1902. The CO produced during methanation has been recognised as an important intermediate in the CO₂ methanation pathways (10).



However, limited efforts have been devoted to the use of non-thermal plasmas for CO₂ methanation, especially in the plasma reaction without catalyst. CO is the major product with CH₄ being the minor one in CO₂ methanation. Zeng and Tu showed that the selectivity of CH₄ (2-5%) was significantly lower than that of CO (>90%) in the plasma processing of CO₂ with H₂ at low temperature (150 °C)^[121]. In the plasma CO₂ methanation process, a higher H₂/CO₂ ratio is desirable as this increases the conversion of CO₂ and the selectivity of CH₄, which has been demonstrated both experimentally^[128, 130] and through the use of a 1D fluid model^[131]. Optimizing the total flow rate can also maximize the CH₄ selectivity and CO₂ conversion. A very low total flow rate can lead to reverse reactions occurring, reforming CO from CH₄ according to (11), due to the longer residence time, increasing the interactions between the CO₂ hydrogenation products and the reactive species in the plasma^[129].



Zeng and Tu reported that adding argon up to 60% in the CO₂/H₂ mixture significantly enhanced the CH₄ selectivity by 85%, which suggests that the presence of metastable argon species in the discharge creates new reaction routes for the production of methane. For DBD plasmas, the use of alumina as a dielectric material instead of quartz is beneficial on CO₂ methanation, which might be attributed to the relatively higher dielectric constant of alumina^[130]. Addition of a magnetic field to a plasma system enhanced the CO₂ conversion and CH₄ selectivity by over 10 % at a discharge power of 30 W, whilst the energy efficiency of the process was tripled^[124]. This process however employed low pressure (200 Pa), reducing simplicity of design and requiring extra energy input. Increasing input power generally results in a higher selectivity to CH₄ due to the increased power density^[124, 130]. However, it has been found that at high power input (>160 W), energy is transferred to the electrodes through heating rather than being used for plasma chemical reactions, resulting in the saturation of CH₄ selectivity^[124]. A smaller discharge gap is beneficial on the CO₂ conversion and CH₄ selectivity due to the rise in input power density and enhanced electric field^[124]. In fact, a smaller discharge gap can achieve the same CH₄ selectivity at a lower input power than when using a larger discharge gap^[124]. A reduction in discharge gap can also increase the production efficiency of the plasma process.

CO₂ hydrogenation to liquid fuels (e.g. methanol and ethanol) is one of the most attractive routes for CO₂ conversion and utilisation. CH₃OH is a valuable fuel substitute and additive, and is also a key feedstock for the synthesis of other higher value chemicals. In addition, methanol is considered a promising hydrogen carrier, suitable for storage and transportation^[132]. In the late 1990s, Eliasson and co-workers investigated CO₂ hydrogenation to CH₃OH using a DBD plasma reactor at pressures up to 10 bar^[133]. However, the major products were CO and H₂O with a CO selectivity of over 90%. Only trace amounts of CH₃OH were produced in the plasma CO₂ hydrogenation without a catalyst, with a maximum CH₃OH yield of 0.06% (selectivity 0.4-0.5%) obtained at 8 bars, a relatively high plasma power of 400 W, a total flow rate of 250 mL/min, and a H₂/CO₂ ratio of 3:1^[133]. Increasing the wall temperature from 100 to 220 °C had a limited effect on the selectivity and yield of methanol^[133]. The formation of trace amounts of CH₃OH in the plasma CO₂ hydrogenation was also reported using a radio frequency (RF) impulse discharge at low pressures (1-10 Torr)^[129]. Very recently, Wang et al. reported that the methanol production via plasma-assisted CO₂ hydrogenation was strongly dependent on the

structure of the DBD plasma reactor (Figure 17). The proposed single dielectric DBD reactor with a special design using water as a ground electrode and cooling significantly enhanced the production of methanol with the highest methanol selectivity of 54% achieved in the plasma hydrogenation of CO₂ without a catalyst at atmospheric pressure (1 bar) and room temperature (30 °C). The concentration and yield of CH₃OH, as well as the conversion of CO₂ were affected by the H₂/CO₂ molar ratio. Increasing the H₂/CO₂ molar ratio from 1:1 to 3:1 increased the yield of CH₃OH from 6.0% to 7.2%, while the selectivity of CO decreased from 40.0% to 30.0%^[123].

Fig. 17: Effect of DBD reactor structure (Reactor I, II and III) on plasma CO₂ hydrogenation to oxygenates without a catalyst at a fixed discharge power of 10 W and a H₂/CO₂ molar ratio 3:1 (a) concentration of oxygenates; (b) selectivity of gas products and oxygenates. Reproduced from ^[123] with permission.

3.3.2 Plasma-catalysis

Catalysts are the key to manipulate the selectivity of target products in the plasma hydrogenation of CO₂. Zeng and Tu investigated the influence of Al₂O₃ supported metal catalysts (Mn, Cu and Cu-Mn) on the plasma RWGS reaction in a DBD reactor at atmospheric pressure (1 bar). Compared to the reaction using plasma alone, the presence of these catalysts in the DBD enhanced the conversion of CO₂ by up to 36%, with the Mn/ γ -Al₂O₃ catalyst showing the best activity for CO₂ conversion at a H₂/CO₂ molar ratio of 1:1. The coupling of the DBD with Mn/ γ -Al₂O₃ also significantly enhanced the yield of CO by 114%, followed by Cu-Mn/ γ -Al₂O₃ (91%) and Cu/ γ -Al₂O₃ (71%). As a result, the energy efficiency for CO production was significantly enhanced by up to 116%^[128]. However, only the Cu/ γ -Al₂O₃ catalyst was found to enhance the selectivity of CH₄ compared to the reaction using plasma alone ^[128]. The weaker activity of Cu/ γ -Al₂O₃ in CO₂ conversion in comparison to the Mn/ γ -Al₂O₃ catalyst might be attributed to the increased prevalence of the water gas shift (WGS) reaction in the presence of Cu/ γ -Al₂O₃ as Cu catalysts are often used for catalysing the WGS reaction ^[128]. It is therefore important to select a catalyst that will suppress the WGS reaction and simultaneously increase the CO₂ conversion and the selectivity to CH₄.

The combination of plasma and suitable catalysts enables the CO₂ methanation reaction to occur at much lower temperatures than those required in the thermal catalytic process^[125]. Nizio et al. evaluated the activity of ceria and zirconia-promoted Ni-containing hydrotalcite-derived catalysts in the plasma-catalytic hydrogenation of CO₂ to methane using a low temperature DBD reactor. Below 250 °C, negligible CO₂ conversion occurs for the catalytic process using a Ce-Zr supported Ni catalyst. However, when combined with a DBD plasma the CO₂ conversion reached 80 %, with 90 % selectivity to CH₄ even at 110 °C^[125]. This is due to the creation of excited species in the plasma, which generate new pathways for CO₂ dissociation; hence the reaction is not limited by the rate of CO₂ dissociation at the catalyst surface as it is in the thermal catalytic process^[126]. The use of nickel containing hydrotalcite catalysts also showed promising results in the plasma-catalytic CO₂ methanation reaction, with a CO₂ conversion of 80 % and a CH₄ selectivity of nearly 100 % achieved^[134].

Eliasson et al. investigated the plasma-catalytic hydrogenation of CO₂ to methanol over a Cu/ZnO/Al₂O₃ catalyst in a DBD reactor at a relatively high pressure (up to 10 bar). Compared to the plasma reaction without catalyst (see previous section), the presence of the Cu/ZnO/Al₂O₃ catalyst in the DBD increased the methanol yield (from 0.1 to 1.0%), methanol selectivity (from 0.4 to 10.0%), and CO₂ conversion (from 12.4% to 14.0%) at 8 bars, 100 °C and a H₂/CO ratio of 3:1. However, the

methanol yield and selectivity were still significantly lower than those reported in thermal catalytic CO₂ hydrogenation processes [133]. Wang et al. has successfully demonstrated the synthesis of methanol with a high selectivity via plasma-catalytic CO₂ hydrogenation using a water-cooled DBD reactor at room temperature and atmospheric pressure (Figure 18). Packing Cu/γ-Al₂O₃ or Pt/γ-Al₂O₃ into the DBD significantly enhanced the CO₂ conversion and methanol yield compared to the plasma hydrogenation of CO₂ without a catalyst (Figure 19). The maximum methanol yield of 11.3% and methanol selectivity of 53.7% were achieved using the Cu/γ-Al₂O₃ catalyst with a CO₂ conversion of 21.2% in the plasma-catalytic process, while no reaction occurred at ambient conditions without using plasma^[123].

Fig. 18: Scheme of CO₂ hydrogenation to methanol. Reproduced from ^[123] with permission.

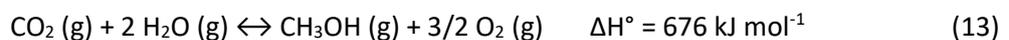
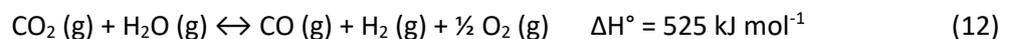
Fig. 19: Effect of H₂/CO₂ ratio and catalysts on the plasma-catalytic CO₂ hydrogenation to oxygenates at a discharge power of 10 W. (a) methanol yield and CO₂ conversion; (b) selectivity of gas products and oxygenates. Reproduced from ^[123] with permission.

In addition, the production of dimethyl ether (DME) from plasma CO₂ hydrogenation was reported using an atmospheric pressure surface discharge, with a CO₂ conversion of 15% and a H₂/CO₂ molar ratio of 1:1^[122]. Compared to thermal catalytic CO₂ hydrogenation to value-added fuels and chemicals, which has been carried out using a wide range of catalysts for a range of target products, very limited catalysts that are active for the thermal catalytic process have been examined in plasma hydrogenation of CO₂ at low temperatures.

3.4. CO₂ with water

3.4.1 Plasma conversion

Compared to the large amount of work performed for plasma-based DRM, only limited research has been performed for the simultaneous conversion of CO₂ and H₂O, i.e., so-called artificial photosynthesis.



Futamura et al. ^[135] investigated a CO₂/H₂O mixture diluted to 0.5–2.5 % in N₂ in a DBD reactor, and reported a CO₂ conversion of only 0.5 %, with product yields of 0.7 % for H₂, 0.5 % for CO and no O₂, and also no mention on oxygenated products. Mahammadunnisa et al. ^[136] obtained a CO₂ conversion of 12–25 % in a DBD reactor, depending on the SEI, with a selectivity of 18–14 % for H₂ and 97–99 % for CO, yield a syngas ratio of 0.55–0.18.

Snoeckx et al. ^[137] performed a combined experimental and computational study for CO₂/H₂O conversion in a DBD. Adding a few % of H₂O to the CO₂ plasma was found to cause a steep drop in the CO₂ conversion, and both the CO₂ and H₂O conversion were quite low. CO, H₂, O₂ and H₂O₂ (up to 2 %) were the major products and no oxygenates were detected. The experimental data could be explained by a chemical kinetics model (see Figure 20). The main reactive species created were OH, CO, O and H, and the model reveals that the OH radicals quickly recombine with CO into CO₂, which explains the limited CO₂ conversion upon H₂O addition. In addition, the O and H atoms recombine in a few

subsequent reactions to form H₂O again, explaining why also the H₂O conversion was limited. Finally, the fast reaction between O/OH and H atoms explains why no oxygenated products were formed.

Fig. 20: Reaction scheme to illustrate the main pathways for CO₂ and H₂O conversion and their interactions. The arrow lines represent the formation rates of the species, with full green lines being formation rates over $10^{17} \text{ cm}^{-3}\cdot\text{s}^{-1}$, orange dashed lines between 10^{17} and $10^{16} \text{ cm}^{-3}\cdot\text{s}^{-1}$ and red dotted lines between 10^{16} and $10^{15} \text{ cm}^{-3}\cdot\text{s}^{-1}$. Adopted from [137] with permission.

Ihara et al. [138] investigated a 1:1 CO₂/H₂O mixture in a MW plasma, and detected low yields of oxalic acid and H₂O₂. They also assumed that H₂ and O₂ are generated, but these products were not measured. In their follow-up study [139] they varied the CO₂/H₂O gas mixing ratio from 1:4 to 1:1, and detected methanol instead of H₂O₂ and oxalic acid, albeit again in very low concentrations < 0.01 %. However, a rise in the methanol yield by a factor 3.5 was observed upon increasing the pressure from 240 to 400 Pa. They suggested two pathways for methanol formation, i.e., (i) direct formation from CO₂ and H₂O in the plasma, and (ii) the reformation of deposited polymeric material on the walls during the plasma reaction with H₂O. Chen et al. [140] detected syngas (in a ratio close to 1, for a 1:1 CO₂/H₂O ratio) and O₂ in a surface-wave MW plasma, but no hydrocarbons or oxygenates. In a follow-up study [141], they reported that adding 10 % H₂O to a CO₂ MW plasma yielded a higher CO₂ conversion (i.e., 31 % vs. 23 %) and a lower energy cost (i.e., 22.4 eV/molec vs. 30.2 eV/molec), along with a lower gas temperature, which was attributed to the higher heat capacity of water and the induced endothermic reactions. This lower gas temperature can explain the higher conversion and lower energy cost, due to less VT relaxation (causing vibrational depopulation; see section 2.2 above) and a lower reaction rate of the recombination of CO back into CO₂.

Indarto et al. [142] reported that H₂O addition (in the range of 5 to 31 %) to a CO₂ plasma in a classical GA yielded a drop in CO₂ conversion (around 7.1 – 3.0 %, compared to 13.4 % in pure CO₂) and a higher energy cost (around 89 – 189 eV/molec, compared to 53 eV/molec in pure CO₂), which they attributed to instabilities in the plasma upon adding H₂O. Nunnally et al. [58] also found a higher energy cost when adding 1 % H₂O to a GAP, i.e., 14.8 eV/molec vs. 9.5 eV/molec in pure CO₂, but they did not observe arc instabilities. Instead, they attributed the higher energy cost to VT relaxation, causing depopulation of the CO₂ vibrational levels, which is much faster for collisions with H₂O than with CO₂ [2, 58].

Hayashi et al. [122] compared the conversion and product formation for a 1:1 mixture of CO₂/H₂O and CO₂/H₂ in a surface discharge, and reported much lower values in the CO₂/H₂O mixture than in the CO₂/H₂ mixture (i.e., 5 % vs. 15 %), but the same products were detected, i.e., CO, CH₄, dimethyl ether (DME) and formic acid. Finally, Guo et al. [143] studied the combined CO₂/H₂O conversion in a negative DC corona discharge, for H₂O contents between 10 and 43 % and pressures between 1 and 4 bar. Again, a drop in CO₂ conversion upon increasing H₂O content was observed. The main products formed were H₂ and CO, as well as ethanol and methanol, in roughly a 3:1 ratio, with a total molar yield up to 4.7 %, increasing with pressure.

In general, it is clear from the above literature overview that adding even small amounts of H₂O (1 – 2 %) yields a significant drop in CO₂ conversion, followed by a further drop upon addition of even more H₂O. For a DBD, this can be explained by the chemical pathways presented in [137] (see Figure 20 above). For a GA, the fast quenching of the CO₂ vibrational levels by VT relaxation with H₂O molecules is the most probable explanation [2, 58]. This would be expected in a MW plasma as well, but Chen et al. [141] reported a higher CO₂ conversion upon H₂O addition. However, this MW setup operates at low pressures (30-60 Torr), where VT relaxation and thus quenching is less important, and cooling upon H₂O addition might be the dominant effect, which reduces VT relaxation, and thus enhances the CO₂ conversion and corresponding energy efficiency.

The main products formed by the combined CO₂/H₂O conversion are H₂ and CO, like for DRM (see Section 3.2), as well as O₂, but some papers also report the production of hydrogen peroxide (H₂O₂)^[137, 138], oxalic acid (C₂H₂O₄)^[138], formic acid (CH₂O₂)^[122], methane (CH₄)^[122, 136], dimethyl ether (C₂H₆O, DME)^[122], methanol (CH₃OH)^[136, 139, 143], ethanol (C₂H₅OH) al.^[143], acetylene (C₂H₂)^[136], propadiene (C₃H₄)^[136] and even carbon nanofibres (CNFs)^[136]. However, most of these data are only qualitative and mainly incomplete, so we cannot deduce a general trend on product yields or selectivities. Nevertheless, the formation of oxygenates, and other value-added compounds, in a one-step process seems limited, in the absence of a catalyst. The reason is that too many steps are involved in creating these oxygenates, and all of them involve H atoms, which will rather recombine quickly with OH into H₂O or with O₂ into HO₂, which also reacts further with O into OH—and hence H₂O. In other words, the interactions of H atoms with oxygen species (i.e., OH, O₃, O₂ or O atoms) are too fast and their tendency to form H₂O is too strong.

On the other hand, the H₂/CO ratio produced in CO₂/H₂O plasmas can be very high (even up to 8.5, for sufficient amounts of H₂O addition), and they can be easily controlled, as revealed by computer modelling^[137], which might be useful for the production of value-added chemicals in a two-step process.

3.4.1. Plasma catalysis

It is clear from above that the direct production of value-added compounds in CO₂/H₂O plasmas requires suitable catalysts. Futamura et al.^[135] investigated the potential of a ferroelectric packed bed reactor with BaTiO₃ pellets for the diluted CO₂/H₂O mixture mentioned above. They obtained a CO₂ conversion of 12.3 %, with product yields of 12.4 % for H₂, 11.8 % for CO and 2.8 % for O₂, hence much higher than in the non-packed DBD reactor (cf. above), but nothing was mentioned on the formation of oxygenates. Likewise, adding a Ni/γ-Al₂O₃ catalyst, in both unreduced and partially reduced form, Mohammadunnisa et al.^[136] obtained a higher conversion and syngas ratio than without catalyst (see above), i.e., 18–28 % and 0.95–0.45 for the unreduced catalyst (NiO/γ-Al₂O₃), and 24–36 % and 0.66–0.35 for the partially reduced catalyst (Ni/γ-Al₂O₃). The NiO catalyst was found to yield a reduction of the produced CO to CH₄, CH₃OH, C₂H₂, propadiene, while the Ni catalyst also gave rise to carbon nanofibers.

Chen et al.^[141] studied the effect of NiO/TiO₂ catalysts (treated with an Ar plasma) in a MW plasma. Compared to their results without catalyst (see above), the CO₂ conversion was further enhanced to 48 %, with an energy cost of 14.5 eV/molec, but no oxygenated products were detected. The authors suggested that CO₂ is adsorbed at oxygen vacancies on the catalyst surface, reducing the threshold for dissociative electron attachment into CO, adsorbed O atoms at the vacancies and electrons. The adsorbed O atoms may subsequently recombine with gas phase O atoms or OH radicals into O₂ (and H atoms). Hence, the catalyst seems to have a beneficial effect in tuning O/OH from the plasma into O₂, by means of adsorbed O atoms at the vacancies, before they recombine again into CO₂ and H₂O, which seems the limiting step in CO₂/H₂O conversion, at least in a DBD, as revealed by computer modelling^[137] (see above).

Although the above papers use catalysts, and report beneficial effects, the production of oxygenates or other value-added compounds is very limited, if reported at all. Hence, clearly more research is needed for tailored catalyst design. These catalysts should allow the plasma-generated CO and H₂ to selectively react into oxygenates, such as methanol, and subsequently they should separate the methanol from the mixture. As mentioned in previous section, Eliasson et al.^[133] applied a CuO/ZnO/Al₂O₃ catalyst in a CO₂/H₂ DBD, which gave a 10 times higher methanol yield and selectivity. Other possible candidates could be Ni-zeolite catalysts, for which methanation is reported^[126], a Rh₁₀/Se catalyst, yielding an ethanol selectivity up to 83 %^[144], and a Ni-Ga catalyst for the conversion into methanol^[145].

4. Summary and steps to be taken for further improvement

It is clear from the above sections that plasma-based CO₂ conversion is promising, but more research is needed before it can be implemented in industry. Although plasma creates a very reactive environment, and is thus chemically not selective in producing value-added compounds, plasma is selective in another way, in the sense that it can selectively populate the vibrational levels of CO₂, without activating the other degrees of freedom, i.e., without the need to heat the gas. This selectivity induces thermal non-equilibrium, and explains the good energy efficiency compared to thermal conversion, at least for some plasma types, like MW and GA plasmas (and maybe APGDs).

To compete with classical and other emerging technologies, Snoeckx and Bogaerts ^[12] stated that an energy efficiency of 60 % (or an energy cost below 4.27 eV/molec for DRM) would be required (see also Figures 6 and 9 in sections 3.1). MW and GA plasmas already reach energy efficiencies close to, or above, this defined efficiency target. This shows their great potential, attributed indeed to the important role of vibrational excitation for energy-efficient CO₂ dissociation. This is especially true for MW plasmas at reduced pressure for CO₂ conversion, which clearly exhibit a thermal non-equilibrium between the vibrational and gas temperature. However, for DRM, very limited results have been reported in MW plasmas, while many promising results are published for GA discharges, and also ns-pulsed discharges, spark discharges and APGDs show potential.

DBDs are most frequently studied, both for CO₂ conversion and DRM, but we believe that even with further improvements the energy efficiency will remain too low for industrial implementation. Indeed, they have typical energy efficiencies of 5-10 %, with some exceptions up to 20 %, so significant improvements, by a factor 3-5, would still be needed to reach the defined efficiency target of 60 %, in order to make them competitive with other emerging technologies.

It should be realized, however, that the efficiency target of 60 % was defined for the production of syngas by DRM, which is indeed the major product in plasma-based DRM. Nevertheless, also other higher value products are formed in the plasma, although not selectively, but when suitable catalysts can be found, plasma catalysis can produce these value-added compounds, such as higher hydrocarbons or oxygenates, in a one-step process at low temperatures and ambient pressure. This would significantly reduce the energy efficiency target to be competitive with other technologies, if the latter would need a two-step process, because indeed, the subsequent Fischer-Tropsch or methanol synthesis from syngas is quite energy intensive.

In this sense, even DBD could become suitable, especially because of their simple design, allowing easy upscaling and straightforward implementation of catalysts. However, much more research is needed to design catalysts, tailored to the plasma environment, to directly produce such value-added chemicals with high selectivity. The latter does not only apply to DRM, but certainly also to CO₂ hydrogenation (CO₂/H₂) and artificial photosynthesis (CO₂/H₂O mixtures), where the formation of value-added compounds without catalyst seems even less straightforward.

To improve the capabilities of plasma-based CO₂ conversion, first of all the energy efficiency should be further improved. We believe this should be realized by a low enough reduced electric field (order of 5-100 Td), in combination with high enough plasma power for sufficient vibrational excitation, which is the most energy-efficient CO₂ dissociation pathway, and with a low gas temperature, to minimise vibrational losses upon collision with other gas molecules (so-called VT relaxation), i.e., strong thermal non-equilibrium. MW and GA plasmas already make use of this most energy-efficient dissociation pathway, but at atmospheric pressure, the VT relaxation is quite significant, and hence, the vibrational distribution function is too close to thermal, so for further improvement, the non-equilibrium should be further exploited.

In addition, the conversion should be further improved, along with the product yield/selectivity. Indeed, the major disadvantage of plasma-based CO₂ conversion is in our opinion the need for a post-

reaction separation step, as the gas conversion is typically (far) below 100 %, and many different reaction products can be formed. In case of CO₂ splitting, the separation of CO and O₂ was calculated to yield the largest energy cost^[146]. When a H-source is added (either CH₄, H₂ or H₂O), mainly syngas is formed, but some minor side-products are observed as well. The syngas mixture does not really pose a problem, when it is subsequently used for Fischer-Tropsch or methanol synthesis. Moreover, plasma technology can deliver a wide variety of syngas ratios, depending on the initial feed gas mixing ratio. However, when higher hydrocarbons or oxygenates could be directly produced with sufficient selectivity and yields, the post-reaction separation step would not be so critical, as these (liquid) compounds can more easily be separated. This brings us back, however, to the crucial need for tailored catalysts, specifically designed to the plasma environment.

In spite of the further improvement of energy efficiency or selectivity being required, we believe that plasma-based CO₂ conversion is very promising, especially because of its overall flexibility, in terms of (i) feed gas (i.e., pure CO₂ splitting, but also mixtures with any H-source are possible), (ii) energy source (solar, wind, hydro, wave and tidal power, as well as nuclear power), and (iii) fast on/off switching and modular upscaling capabilities. This flexibility makes plasma very useful as a so-called “turnkey” process, which might be able to use renewable electricity in a flexible way, following its intermittency, and convert it into fuels or chemicals. An example of how a (microwave) plasma based process for pure CO production could be implemented at industrial scale has been evaluated in terms of its economics^[146]. It indicates that CO production cost price translates into 0.22 \$/kWhr stored in CO at an electricity price of 0.05 \$/kWhr based on present day technology and performance.

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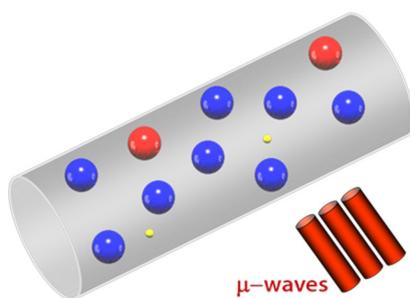


Fig. 1

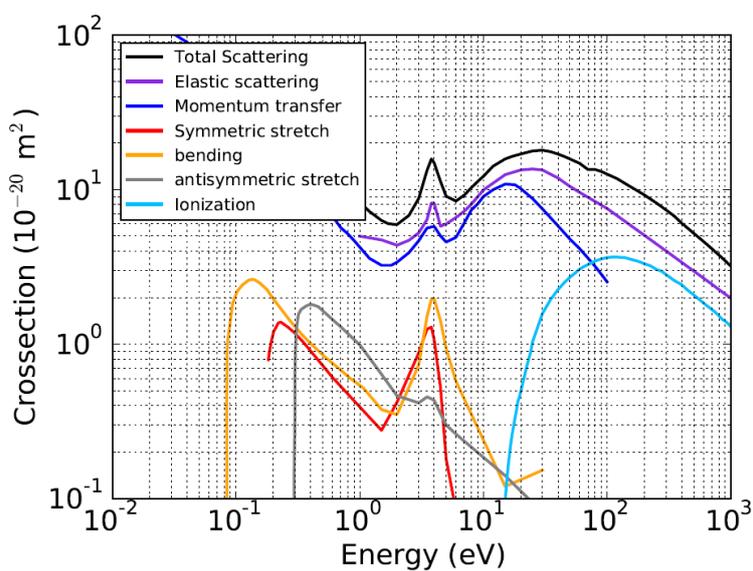


Fig. 2

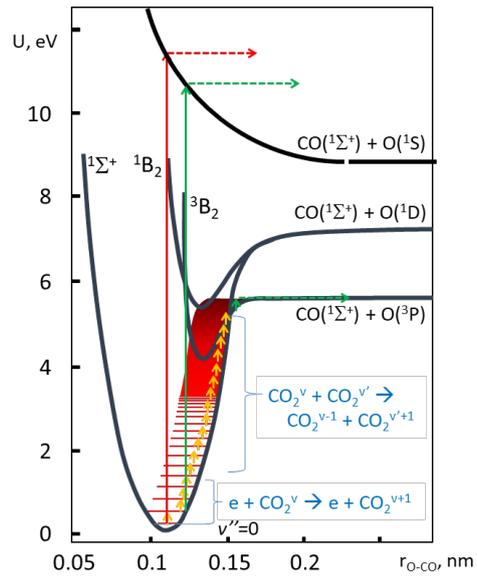


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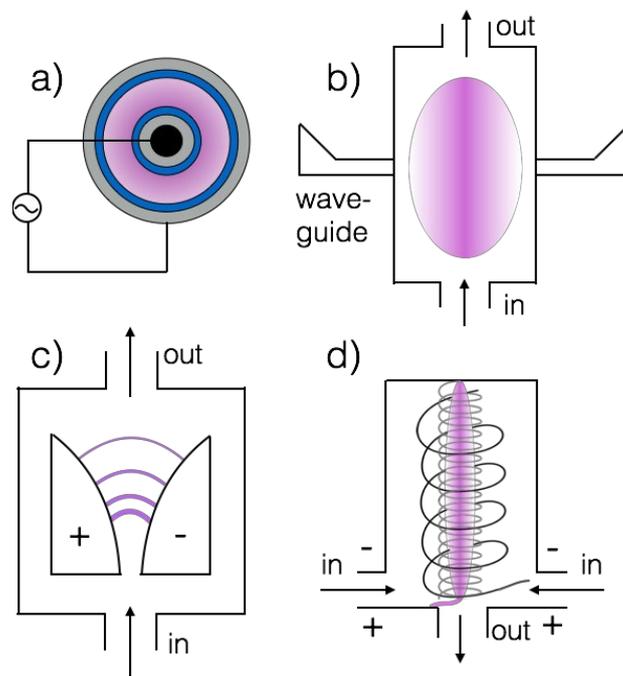


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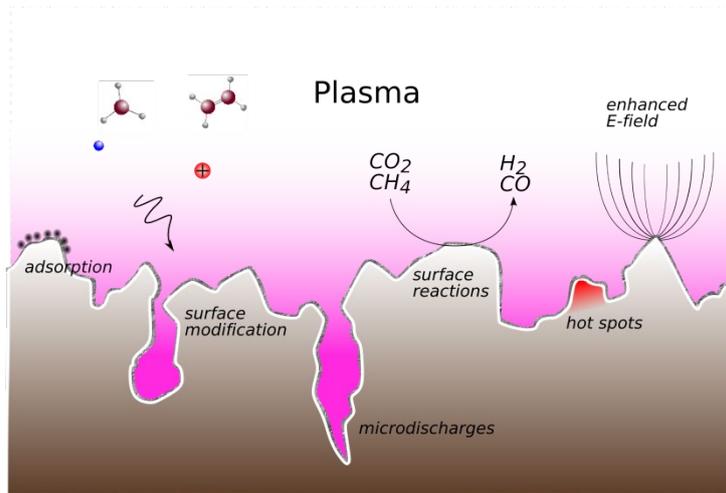


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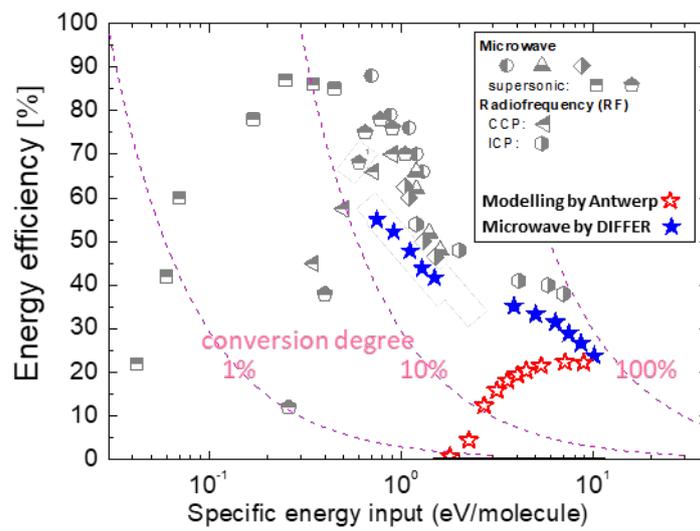


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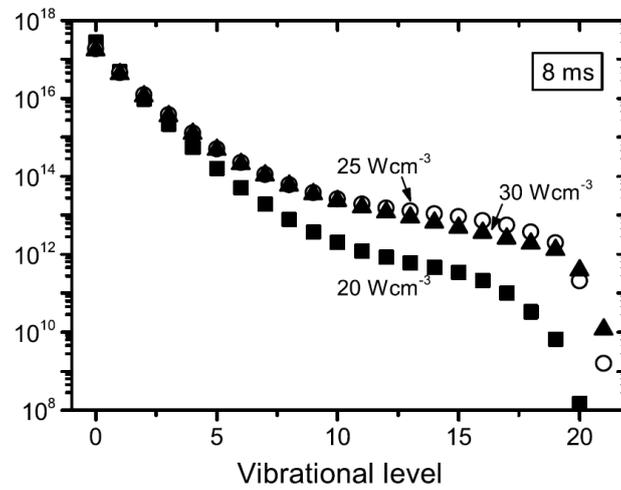


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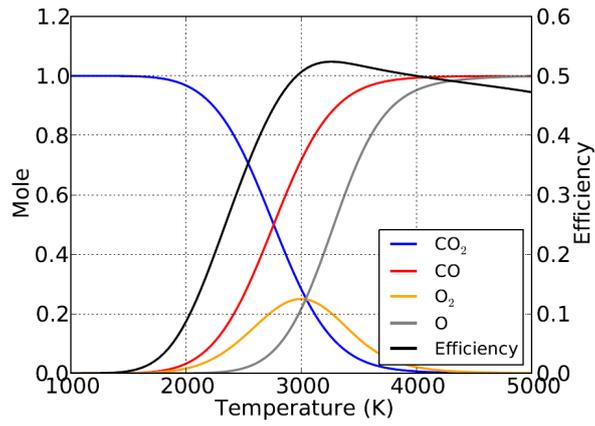


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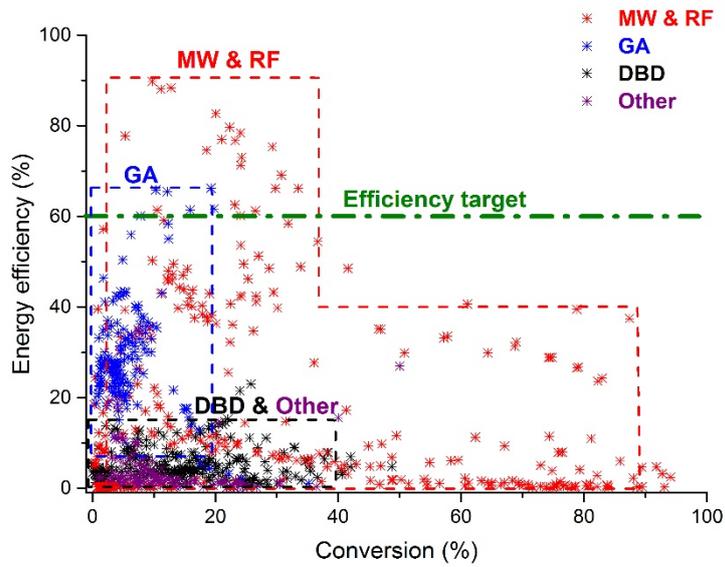


Fig 9

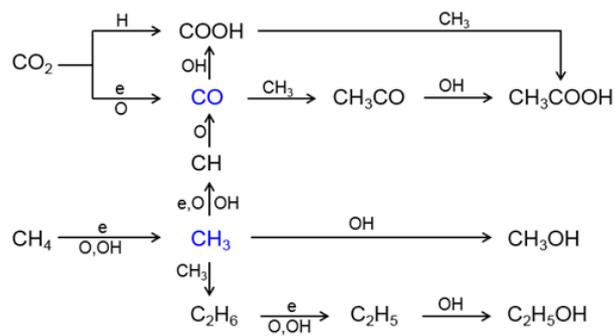
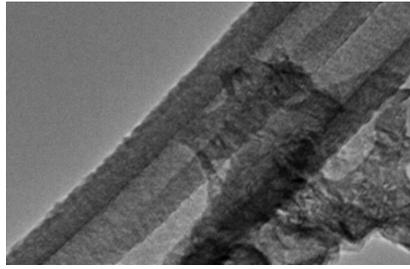
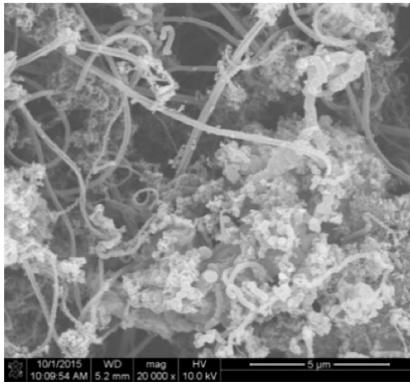


Fig. 10



(a)



(b)

Fig. 11

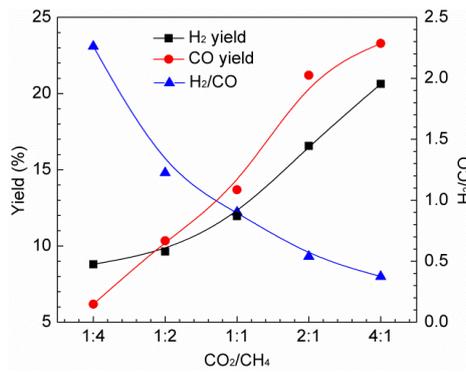


Fig. 12

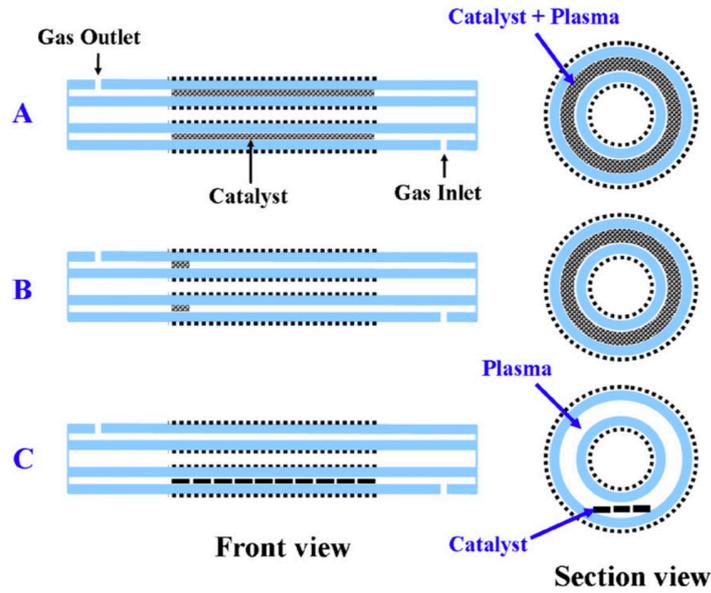


Fig. 13

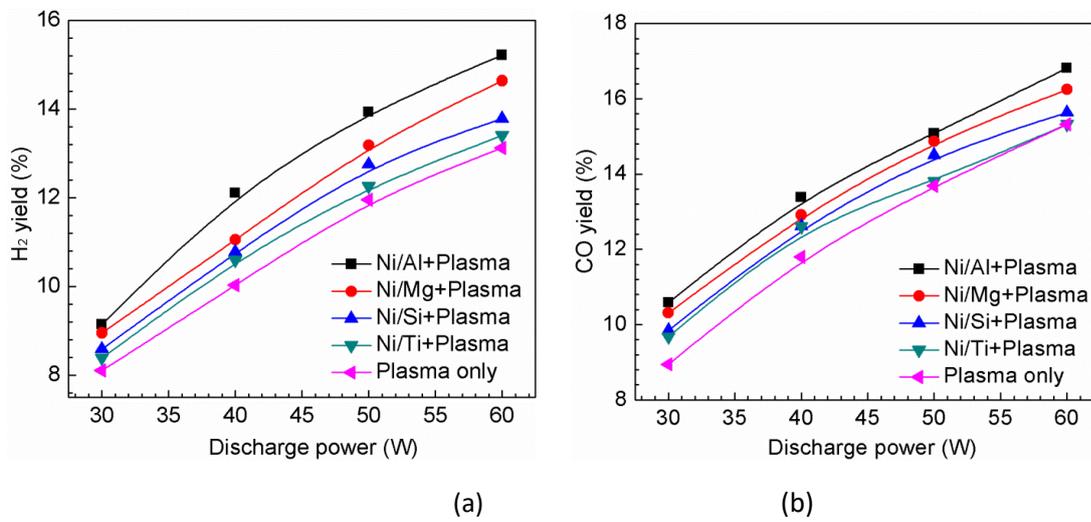


Fig. 14

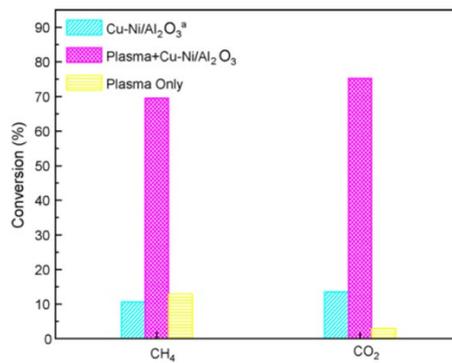


Fig. 15

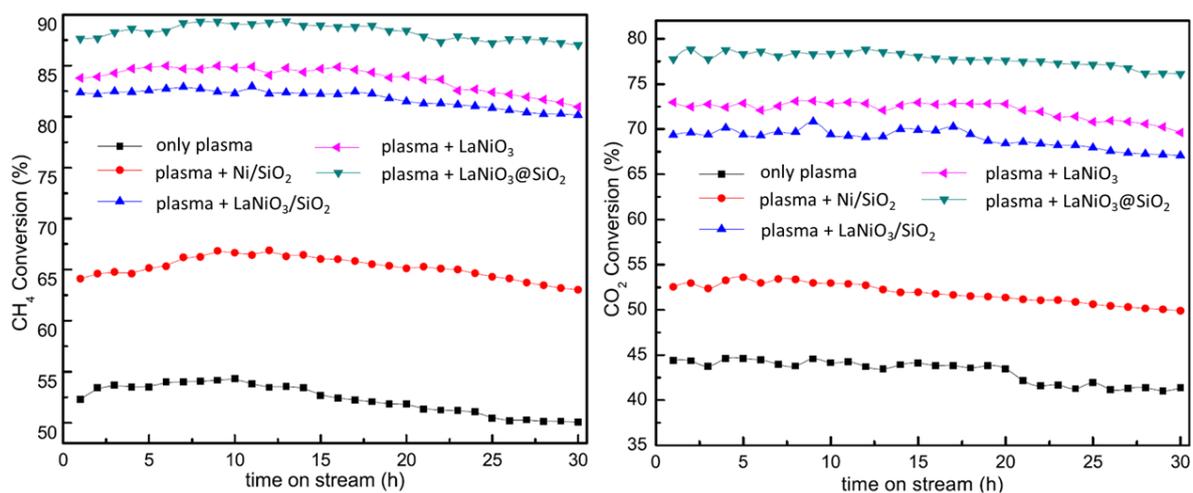
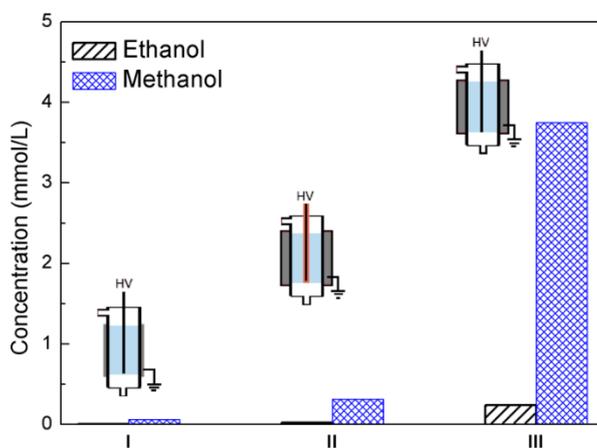
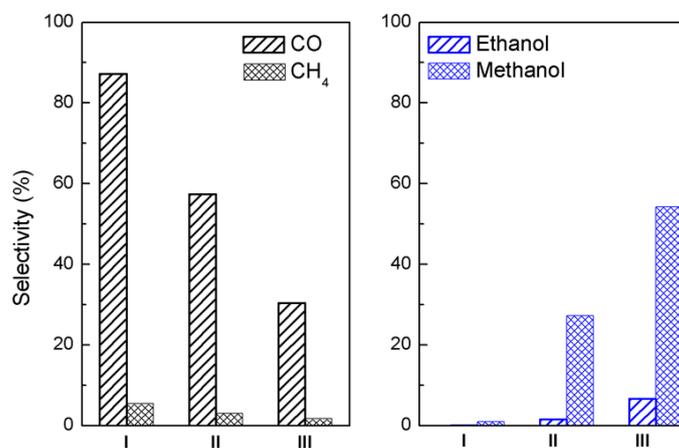


Fig. 16



(a)



(b)

Fig. 17

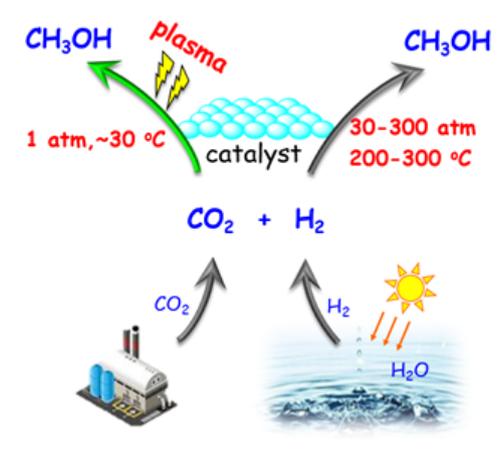
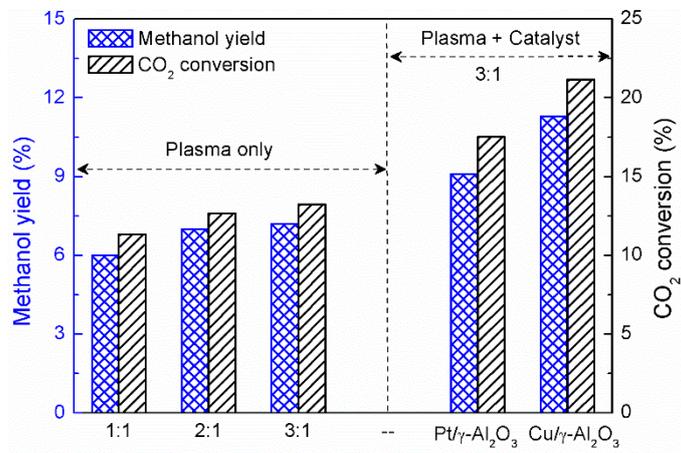
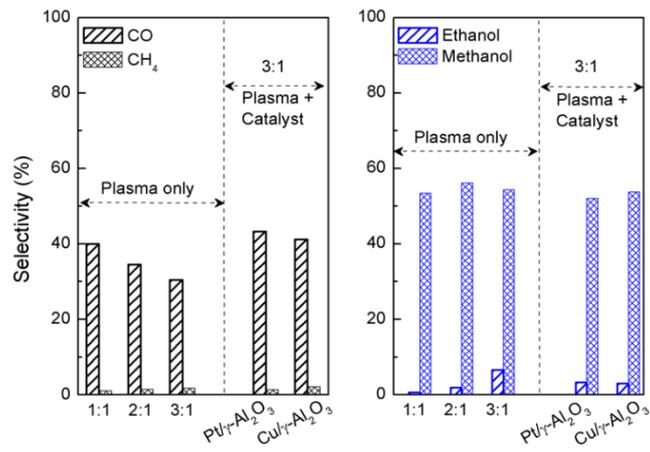


Fig. 18



(a)



(b)

Fig. 19

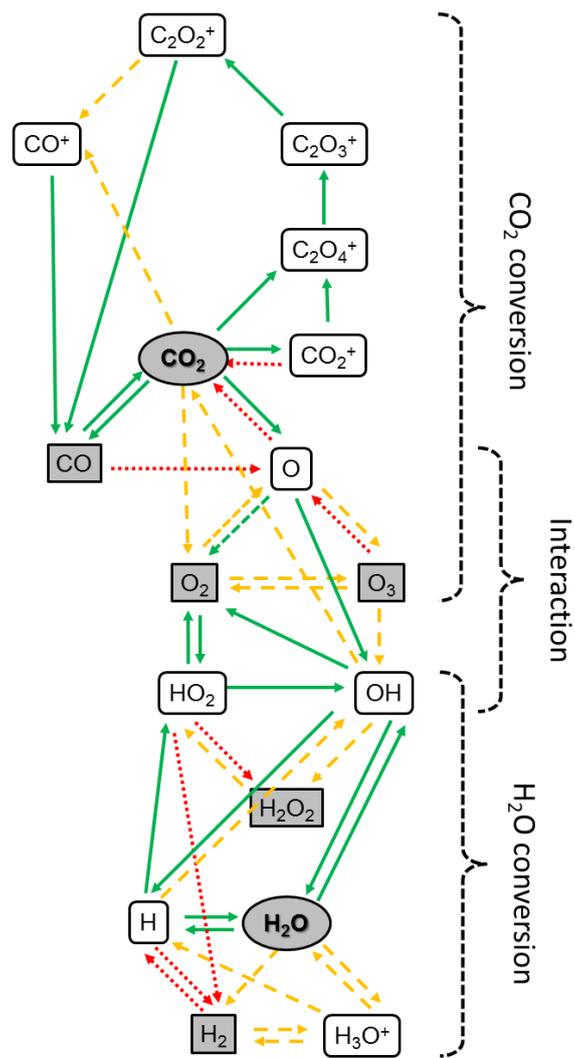


Fig. 20