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Introductory Chapter: Plasma Chemistry for Better CO₂ Conversion

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1. Preface

The aim of this book is to cover recent advances in the field of plasma chemistry and, in particular, to explore the role of low-temperature discharges for efficient greenhouse gas conversion, synthesis of valuable chemicals, potential fuel production, and storage.

Low-temperature plasmas produced by electric discharges represent unique non-equilibrium state of matter where electrons possess much higher temperatures than neutrals and ions. This distinctive feature opens new possibilities for production of highly reactive species in a chemically rich environment close to the room temperature in the wide range of gas pressure, which may vary from mTorr range to a fraction of atmosphere. Moreover, the discharge conditions far from thermodynamic equilibrium may further intensify the “traditional” chemical processes, which normally happen without plasma.

Low-temperature discharges are deeply related to a large number of important technologies with extraordinary societal and environmental benefits. For example, since the second half of the nineteenth century, low-temperature plasma has been used to improve the microelectronics industry [1]. Indeed, these discharges are able to provide ion fluxes that are responsible for surface modifications by sputtering, etching, activation, and deposition, which are of a critical importance for the development of any micro device. Other domains in which low-temperature plasmas play an important role involve light sources [2], lasers [3], sterilization of biological samples [4], etc. All of these technologies make important contributions to the development of the modern society.

2. Historical remarks

The use of low-temperature plasmas for chemical conversion of the greenhouse gases has a rich history and can be traced back to the 1970s–1980s, namely, to the research related to CO₂ transformation into the valuable chemicals conducted in the former USSR (see [5] and therein). During this period the experimental and theoretical background on the plasma-chemical processes has been mainly understood (see [6] and therein). Interestingly, it was already estimated theoretically that the limit of the energy efficiency of CO₂ decomposition (term defined in the following chapters) in microwave discharges can reach about 43% in the equilibrium regime

and about 80% in the non-equilibrium regime [5]. The corresponding experimental results related to these efficiencies have shown excellent agreement with the estimates [5–7].

Nowadays the gamut of potential applications of plasma-chemical processes undergoes significant widening, covering in the case of CO₂ decomposition the areas from the treatment of power plants exhausts [6] to the potential fuel production on Mars [8]. Regarding the environmental concerns associated with consumption of the fossil fuels, this topic is now also receiving a special attention. Naturally, these concerns are related to the necessity of moving toward the usage of the renewable technologies that would give access to the green CO₂-based electricity. In this case, the non-equilibrium discharge can potentially act as a vehicle transforming electricity into the useful chemical reactions, being at the same time environmentally friendly. This paradigm is well recognized by the modern plasma research community due to its important social and economic footprints [1].

3. How does it work?

One particular plasma-chemical process, which is mainly covered in this book, as well as widely studied nowadays in general, is the plasma-based dissociation of CO₂ into CO and O. Such a dissociation process may be considered as a first step toward the production of fuels and chemical feedstock, for example, methanol. Under this scenario an efficient plasma-based CO₂ decomposition process can provide a suitable storage solution for renewable sources via the conversion of temporary electrical energy. This would permit fuel production using electrical power in remote locations where solar/wind energy availability is optimal, or even abundant, and to use the existing infrastructure for energy distribution to the end users [9]. From this point of view, CO₂ would no longer be considered as a pollutant but rather a raw material for further transformations using the plasma technology.

Motivated by the previously mentioned strategy, numerous research groups are currently focused on achieving the maximum conversion and energy efficiencies (defined in the following chapters) associated to the CO₂ decomposition via modeling [10, 11] as well as through the experimental studies [12–15]. In addition to the plasma itself, utilization of the pre-activated highly porous catalyst may also significantly increase the energy efficiency of the conversion process, as shown in the numerous literature sources [16, 17] and demonstrated in this book.

The main idea behind the mentioned research works is to take advantage of the non-equilibrium nature of low-temperature plasmas, with activation of the plasma at low-energy cost. Indeed, it is relatively easy to transfer energy to the CO₂ vibrational excitation using a plasma source possessing low electron temperature (~1 eV). Under this scenario, it is possible to benefit from the energy stored in the vibrational levels, that is, vibrational excitation of the molecule, which is known to be favorable for molecular decomposition in the case of CO₂ [6]. More specifically, if the electron energy is selectively channeled into the CO₂ asymmetric stretch mode of vibration, then the vibrational quanta can be pumped up through the so-called vibrational “ladder climbing” mechanism, offering a unique way to achieve efficient decomposition [10].

4. Achievements and challenges

As mentioned already, rather high-energy efficiency of CO₂ conversion had been reached in the past using the supersonic gas flow (for gas expansion and cooling) in

Figure 1.
 The optimized values of the CO₂ conversion efficiency and energy efficiency obtained in various low-temperature discharges. The arrows correspond to the efficiency gains achieved by using power modulation (green) and plasma catalysis (red). Reproduced with permission from Ref. [17].

a microwave plasma [7]. This result had a huge impact on the plasma research community, which nevertheless were not reproduced since then. Other types of plasma reactors including dielectric barrier discharges (DBD), gliding arc plasmatrons (GAP), and microwave plasmas have been used, together with plasma catalysis, having a goal of increasing the energy efficiency associated to the CO₂ conversion (see **Figure 1**). These studies have shown that such an increase in energy efficiency of the decomposition can be attained through the fine-tuning of different plasma parameters such as gas pressure, temperature, gas composition, molecule residence time, etc. More recent works have proven that using the plasma power interruption along with plasma catalysis also enhances the CO₂ conversion and energy efficiencies significantly, as illustrated in **Figure 1**.

Despite the relevance of the abovementioned works, the application of plasmas for large-scale fuel production is not yet viable [18]. Indeed, the issues related to the optimal plasma operation conditions (such as gas pressure, reactor geometry, degree of non-equilibrium, etc.) still provoke many questions, while the pathway of CO₂ dissociation is not yet completely understood to achieve its full control and optimization. In order to overcome these difficulties, the scientific research toward both modeling and diagnostic studies is mandatory for a deeper understanding of these processes.

From the modeling point of view, there are still many challenges ahead. Among these challenges, there is a lack of modeling studies related to calculation of the rate coefficients in which CO₂ ro-vibrational excitation is present. In this respect, many CO₂ chemical reaction rates are still poorly known. This needs further attention from the theoretical methods (e.g., based on quasi-classical trajectory simulations [19]) to calculate rate coefficients more accurately than those which are currently available in literature. These calculations are essential to simulate and predict the overall behavior of CO₂ discharges while guiding future experiments targeted at fuel production.

From the experimental point of view, careful verification of the role of electronic and vibrational states of CO and CO₂ molecules as well as the electronic states of O atoms during the CO₂ decomposition process under different degrees of discharge non-equilibrium may shade light on the valuable decomposition pathways pointing out to an optimum regime of plasma operation for maximization of the energy efficiency of decomposition and other critical parameters. In this case, the

implementation of the advanced (time- and space- resolved) laser diagnostics along with the discharge characterization by infrared absorption spectroscopy would be critical.

As a conclusion we can say that, the development of the low-temperature plasma sources operating at the elevated (virtually up to atmospheric) pressure is mandatory in order to scale up the laboratory processes and to match the industrial workflow in gas conversion. Thus, the experimental research related to production of valuable fuels and chemical feedstock (e.g., hydrocarbon-based fuels) through CO₂-containing discharges is mandatory. Besides this, the other approaches enabling reasonably high-energy efficiencies of conversion should be investigated as well.

The chapters gathered in this book are dedicated to the carbon dioxide (CO₂) and methane (CH₄) decomposition in non-equilibrium plasma discharges. These chapters represent the state-of-the-art modeling and experimental research studies in the field, paying special attention to the plasma catalyst and containing recent achievements in the field of greenhouse gas conversion in non-equilibrium discharges. The book can be considered as an addition to the more general book “Green Chemical Processing and Synthesis” (INTECH, DOI: 10.5772/65562) published recently.

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