NON-OXIDATIVE COUPLING OF METHANE TO C_2 HYDROCARBONS:

Integration of dielectric barrier discharge plasma
and catalyst packed bed

NON-OXIDATIVE COUPLING OF METHANE TO C_2 HYDROCARBONS

MOHAMMADREZA TAHERASLANI

Mohammadreza Taheraslani

ISBN: 978-90-365-4683-6

**Non-oxidative coupling of methane to C₂ hydrocarbons:
Integration of dielectric barrier discharge plasma
and catalyst packed bed**

Mohammadreza Taheraslani

**NON-OXIDATIVE COUPLING OF METHANE TO C₂
HYDROCARBONS:
INTEGRATION OF DIELECTRIC BARRIER DISCHARGE
PLASMA AND CATALYST PACKED BED**

DISSERTATION

To obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
Prof. dr. T. T. M. Palstra,
on account of the decision of graduation committee,
to be publicly defended on
Friday the 8th of February 2019 at 14:45 hrs.

by

Mohammadreza Taheraslani

This dissertation has been approved by the promotor (supervisor):

Prof. dr. J.G.E. Gardeniers

This Ph.D. study was carried out at the Faculty of Science and Technology (TNW) of the University of Twente, Enschede, The Netherlands.

Cover design: Mohammadreza Taheraslani- NetzoDruk

Printed by: NetzoDruk, Enschede, The Netherlands

Lay-out: Mohammadreza Taheraslani

ISBN: 978-90-365-4683-6

DOI: 10.3990/1.9789036546836

© 2018 Mohammadreza Taheraslani, Enschede, The Netherlands. All rights reserved. No parts of this thesis may be reproduced, stored in a retrieval system or transmitted in any form or by any means without permission of the author.

Graduation Committee:

Chairman/secretary: Prof. dr. ir. J.W.M. Hilgenkamp University of Twente

Supervisor: Prof. dr. J.G.E. Gardeniers University of Twente

Members:

Prof. dr. ir. K.P. de Jong Utrecht University

Prof. dr. S.R.A. Kersten University of Twente

Prof. dr. ing. A.J.M. Pemen Eindhoven University of Technology

Prof. dr. G. Mul University of Twente

Prof. dr. F. Reniers Free University of Brussels

Contents

Chapter 1: Introduction.....	1
1.1. Natural Gas Conversion.....	2
1.2. Methane Coupling.....	4
1.3. Non-Thermal Plasma (NTP)	7
1.4. Dielectric Barrier Discharge (DBD) Plasma.....	11
1.5. Packed-bed DBD plasma reactors (PBRs).....	12
1.6. Challenges in PBRs.....	14
1.7. Synergy of DBD Plasma and Catalyst for Methane Coupling.....	16
1.8. Plasma Catalysis Configuration.....	19
1.9. The scope of the present study.....	21
1.10. The outline of the dissertation.....	22
References.....	24
Chapter 2: The performance of the implemented DBD plasma reactor.....	29
2.1. Introduction.....	30
2.2. Experimental.....	32
2.3. Results and discussion.....	38
2.4. Conclusions.....	51
References.....	52
Chapter 3: The synergistic effect of Pd/γ-alumina catalyst and the DBD plasma reactor in the post-plasma catalysis configuration.....	54
3.1. Introduction.....	55
3.2. Experimental.....	57
3.3. Results and discussion.....	58
3.4. Conclusions.....	76
References.....	77
Chapter 4: The synergy of DBD plasma and Pd/γ-alumina catalyst integrated in the in-plasma catalysis configuration for non-oxidative coupling of methane.....	79
4.1. Introduction.....	80
4.2. Experimental.....	82
4.3. Results and discussion.....	83

4.4. Conclusions.....	135
References.....	136

Chapter 5: The effect of dielectric property of the packing materials on the performance of the packed-bed DBD plasma reactor for non-oxidative coupling of methane...138

5.1. Introduction.....	139
5.2. Experimental.....	141
5.3. Results and discussion.....	142
5.4. Conclusions.....	168
References.....	169

Chapter 6: The high resolution scanning electron microscopy (HRSEM) and energy dispersive X-ray spectroscopy (EDX) characterization of the deposits formed during the DBD plasma reaction for non-oxidative coupling of methane.....171

6.1. Introduction.....	172
6.2. Experimental.....	175
6.3. Results and discussion.....	177
6.4. Conclusions.....	197
References.....	198

Chapter 7: Conclusions.....199

Summary.....208

Samenvatting.....212

Chapter 1

Introduction

In this chapter, an introduction and background to the topic of the present study including the methane coupling, packed bed DBD plasma reactors (PBRs) as well as the synergy of plasma and catalyst for methane coupling are explained considering the existing literature. Furthermore, the scope and the outline of the dissertation with an overview of the chapters will be presented at the end.

1.1. Natural Gas Conversion

The availability of low-cost and domestically sourced natural gas is growing every year, which leads to an increasing demand for its utilization for a number of applications, as represented in Fig.1.

Fig.1. Natural gas utilizations in different sectors

Although natural gas is a mixture of small hydrocarbons (C_1 - C_4), methane (CH_4) is considered as the main component, which can be converted to value-added fuels and chemicals. It has been for decades that methane is extensively utilized as the main feedstock in petrochemical industries for large scale production of syngas (i.e., the mixture of H_2 and CO), which can be subsequently consumed for the production of methanol, ammonia and synthetic fuels (i.e., via Fischer-Tropsch process). These processes are known as “indirect route” for conversion of methane. Despite the high energy consumption, high capital investment as well as high production costs, syngas-intermediate route processes are currently operated for industrial scale conversion of methane to chemicals and fuels. Fig.2 shows the schematic routes for direct and indirect conversion of methane.

The direct conversion of methane has attracted increasing attention, as it has the potential to produce the chemicals and fuels via processes which are more environmentally favourable

owing to less emission of CO₂, as well as more economical due to the integration of a multistep process to a single step process [1]. Nevertheless, the direct processes are suffering from thermodynamically limited conversion of methane, low selectivity of catalysts to desired products as well as deactivation of catalysts due to deposition of carbon-containing solid products. These challenges have still remained to be overcome.

Fig.2. Direct and indirect routes for the conversion of methane

Among all processes for direct conversion of methane to chemicals, light paraffins (e.g., ethane) and olefins (e.g., ethylene and propylene) production processes have attracted worldwide interest, leading to numerous research studies for conversion of methane to C₂ hydrocarbons (ethane, ethylene, acetylene) via coupling reactions, aiming at the development of the process for a large scale production. For instance, the coupling of methane to ethylene can be an alternative for steam cracking of petroleum derivatives (e.g., LPG or naphtha), which currently is the dominant route for industrial-scale production of light olefins [2,3]. In addition, the conversion of methane to light alkanes (e.g., ethane, propane) is still considered as methane valorization, whereas the direct utilization of methane as fuel has practical issues like technical difficulties to deliver it to consumers, which therefore demands expensive and inefficient transport costs. In this case, even conversion of methane to ethane (i.e., via coupling reactions)

can be considered a feasible process compared with those applications consuming methane directly. Thus this has stimulated a growing number of research studies devoted to coupling of methane to C₂ hydrocarbons by conducting different chemical processes for the activation of methane and furthermore to the integration with catalysis for improving the selectivity of the desired products, which will be discussed in the next sections.

1.2. Methane Coupling

Since the 1980s, many works have been performed to convert methane, including direct oxidation to methanol and formaldehyde, oxidative coupling of methane (OCM), and non-oxidative coupling of methane. The main focus has been to overcome the difficulty of breaking the C–H bond and to form the desired C–C and C–O bonds from the perspectives of both chemistry and engineering [4, 5].

To prevail the thermodynamic barrier of C-H bond scission, co-feeding of oxygen (e.g., oxidative coupling of methane, OCM) has been extensively studied for the production of C₂ compounds, starting with the work of Keller et al. in 1982 [6]. The addition of oxygen for conversion of methane could further give the opportunity to potentially consider large scale production of oxygenates like methanol [7, 8].

In oxidative coupling reactions, CH₄ and O₂ react over a catalyst at temperatures higher than 700 °C to form C₂H₆, C₂H₄ as the desired products, however, both the C₂H₆ and the C₂H₄ can also be largely converted to CO_x, which is undesired. This therefore results in a significantly lower yield of C₂ products (i.e., C₂H₄ and C₂H₆), limited to about 25% as reported by Lunsford [9].

Various catalysts have been utilized to improve the yield of C₂ products for oxidative coupling of methane such as SrO/La₂O₃ [10], Mn/Na₂WO₄/SiO₂ [11] and Li/MgO [6,12], which are considered promising catalysts for OCM processes, where the C₂ yield was promoted to about 30 %.

Almost, half of the C₂ hydrocarbons obtained via OCM is C₂H₄ and the rest is C₂H₆, while the C₂H₄/C₂H₆ ratio can be enhanced by using a second catalyst, which can proceed the dehydrogenation of C₂H₆ towards C₂H₄ [9,10].

The chemical reactions involved in OCM process are highly exothermic, which release a large amount of heat to the reaction zone. This can increase the temperature of the catalyst bed to be 150-300 °C hotter than the external temperature [13]. Thus, heat management is considered a serious engineering issue for OCM to be tackled. Furthermore, the undesirable CO_x by-products is still an obstacle for an efficient scale-up of this process [11].

Considering the issues of the OCM process, as mentioned above, which is mainly due to the presence of O₂, several studies have attempted to convert methane at the absence of oxygen, notably circumventing the production of CO_x by-products [14-16]. Unlike OCM reactions, almost all reactions involved in non-oxidative conversion of methane to C₂ products are endothermic reactions as represented below:

As can be seen from these reactions, H₂ is also generated as a reaction product in non-oxidative conversion of methane, where in OCM some of the generated H₂ can be further oxidized to form H₂O.

In addition, H₂ can be generated via direct dehydrogenation of CH₄ to form solid carbon (C) and H₂: $\text{CH}_4 \longleftrightarrow \text{C} + 2\text{H}_2 \quad \Delta H^\circ = + 75 \text{ kJ/mol}$, which is known as pyrolysis process [17]. This is the main challenge in non-oxidative conversion of methane, where coke formation severely impacts the performance and the stability of the catalyst and consequently leads to a rapid deactivation of the catalyst, by which the conversion of methane as well as the yield of desired products significantly declines [18-20]. For a better comparison, the temperature

dependence of methane conversion to C_2H_6 and C_2H_4 as well as to C and H_2 is represented in Fig.3.

Fig.3. Equilibrium conversion of methane under non-oxidative conditions versus applied temperature ($^{\circ}C$)

Although the decomposition reaction of methane to C and H_2 is not favourable, thermodynamically this reaction is more likely to take place at moderate temperatures ($\sim 500^{\circ}C$) rather than coupling reactions, where a notably higher temperature ($\geq 800^{\circ}C$) is practically needed to couple CH_4 to form C_2H_4 and C_2H_6 [21], as can be seen in Fig.3. Furthermore, at high temperatures, some of the formed C_2 usually goes through further chemical reactions to form aromatics (e.g., benzene). The yield for the formation of C_2 hydrocarbons as well as aromatics is highly dependent on the choice of the catalyst. Thus, depending on the target product, the formation of C_2 products or aromatics can be optimized using a selective catalyst. For instance, Fe/SiO_2 for coupling of methane to a major production of ethylene [16], $Mo/HZSM-5$ for dehydroaromatization of methane to benzene [22] and $Pt-Bi/HZSM-5$ for coupling of methane to ethane and ethylene [23], have been reported.

Despite circumventing the formation of CO_x by-products in non-oxidative coupling of methane, this process is still facing with a high thermodynamic barrier for activation of methane (434 kJ/mol) [24], which limits the equilibrium conversion of methane under non-oxidative conditions to below 10% even at high temperatures ($700-800^{\circ}C$).

In recent years, non-thermal plasma has been exploited for activation of methane, where the electrical energy of highly energetic electrons (i.e., generated by the formation of plasma) is converted to chemical energy by breaking the C-H bond of CH_4 via electron impact dissociation. In this case, the activation of methane is taking place via collisions of high energy electrons with methane molecules, going beyond the thermodynamic barrier of methane activation, which is a different pathway than the conventional thermal activation of methane. This will be further explained in the next section.

1.3. Non-Thermal Plasma (NTP)

Plasma is defined as the fourth state of matter, which constitutes from charged species (i.e., ions and electrons) and neutral species (i.e., radicals, excited atoms/molecules). Plasma is usually created by exposing a neutral gas or a mixture of gases to a strong electromagnetic field, by applying a sufficiently high voltage in the range of thousands of Volts, which can electrically break down the neutral gas and then ionize it to form plasma. This ionization takes place by stripping electrons from an atom/molecule, which consequently leaves positive charges on the ionized species, as shown in Fig.4. In this case, the gas environment becomes electrically conductive, exhibiting behaviours unlike those of the other states (i.e., solid, liquid and gas) of matter.

Fig.4. The creation of plasma discharges by ionization of neutral gas

Plasma generation can be accompanied by heating up the plasma environment due to the power absorbed inside the discharges, which can increase the temperature of all plasma species

including electrons, ions and neutral particles. Considering the relative temperatures of the electrons, ions and neutrals, plasmas are classified as “thermal” or “non-thermal”.

In thermal plasmas (also called equilibrium plasma or hot plasma), all plasma species including electrons, ions and neutral particles are at the same temperature. In other words, all species are in thermal equilibrium with each other. High temperatures are required to form thermal plasmas, typically ranging from 4,000 K to 20,000 K [25]. Under such conditions, the plasma activated species are mainly generated by electron collisions or thermal activation. Arc discharge plasma is a characteristic form of thermal plasmas, which can be applied for high temperature applications. For instance, thermal arc discharges were employed for direct conversion of methane to acetylene, hydrogen and carbon black via a process known as Hüls process [26].

In non-thermal plasma (also called non-equilibrium plasma or cold plasma), plasma species are not in thermal equilibrium, which means that they are at different temperatures. By definition, under non-equilibrium conditions, only electrons are thermalized, where heavy particles (i.e., ions and neutral species) have substantially lower temperatures, which can be even close to room temperature [27]. Dielectric Barrier Discharges (DBD), corona and nanosecond pulsed discharges are the conventional forms of non-thermal plasma.

It should be noted that in some forms of plasma the bulk temperature of the plasma (i.e., the temperature of neutral species) can be as high as 1000 K. It was found that this type of discharges do not entirely match with the definitions and models demonstrating non-thermal plasma discharges. On the other hand, as there is still a temperature difference between electrons and other heavy particles (e.g., ions, excited atoms and molecules), plasma species are not in thermal equilibrium with each other. Therefore, these plasmas like microwave, radio frequency, glow and spark discharges have been classified in another group called “warm plasma” [28].

Non-thermal plasmas have been extensively utilized in several applications such as food industry, medicine, power generation, aerospace and for chemical reaction processes. Similar to other applications, in recent decades, atmospheric pressure non-thermal plasma has attracted attention to be employed for promoting chemical reactions, in particular for those which are thermodynamically limited due to their high activation energy barrier. In non-thermal plasmas, dissociation reactions can take place via collisions between hot electrons, with sufficient energy (1-10 eV corresponding to temperatures ranged from 10,000 to 100,000K [27]) and cold gas molecules, subsequently leading to the formation of radicals, which are considered essential intermediates for chemical reactions to proceed. The main advantage of non-thermal plasma for promoting chemical reactions is that the bulk temperature is quite low, where still a high conversion can be achieved via the energy provided by hot electrons. Furthermore, non-thermal plasma can be conjugated by catalyst surfaces to further enhance the chemical conversion of reactants and/or to influence the selectivity of the final products.

Up to now, non-thermal plasma has been studied in combination with catalysis for different processes such as ozone generation [29], pollution abatement [30], VOCs removal [31] and CO₂ conversion [32]. In addition, the conversion of hydrocarbons by plasma as well as its integration with catalysis, in particular conversion of methane to syngas via dry reforming [33], partial oxidation of methane to methanol [34,35] and coupling of methane to C₂ hydrocarbons [36] have been pursued to be considered as alternatives for existing indirect processes.

The non-thermal plasma reaction usually occurs via a free radical mechanism which is unfavorable for controlling the selectivity of products [37–39]. The randomness of interactions amongst radicals occurs rapidly in the range of nanoseconds to milliseconds. In this case, radicals recombine or de-excite to their ground state level of energy in exceptionally short time [40]. Integration of a catalyst with the plasma can give the opportunity to create an alternative

medium, where the randomness of interactions of plasma components (e.g., radicals) can be influenced by the surface activity of the catalyst (e.g., adsorption), which can result in tuning the interactions towards desired products [27].

Intensive efforts have been devoted to a hybrid plasma-heterogeneous catalyst system by using various types of non-thermal plasma such as dielectric barrier discharge (DBD), corona and glow discharge [41–44]. The characteristics of non-thermal discharges are described in the Table 1.

Table 1. Characteristic of non-thermal plasma discharges. [45]

Parameter	Glow discharge	Corona discharge	Barrier discharge
Pressure (bar)	$< 10^{-2}$	1	1
Electric field (kV cm^{-1})	0.01	0.5–50, variable	0.1–100
Electron energy (eV)	0.5–2	5, variable	1–10
Electron temperature (K)	5000–20,000	50,000	10,000–100,000
Electron density (cm^{-3})	10^8 – 10^{11}	10^{13} , variable	10^{14}
Degree of ionization	10^{-6} – 10^{-5}	Small, variable	10^{-4}

Considering the characteristics of different non-thermal plasmas, DBD and corona plasmas can be used at atmospheric pressure and have higher electron density compared to other non-thermal plasmas. The energy of free electrons with a suitable design of discharge reactor as well as a proper catalyst can be an effective approach in order to selectively convert methane to specific products (e.g., ethane and ethylene). Among different plasma approaches for activation of methane, dielectric barrier discharge (DBD) is one of the plasma techniques that has attracted attention for its versatility in combination with catalyst surfaces [45]. DBD plasma reactors have been numerously utilized in combination with catalysis for its simplicity and flexibility in combination with catalyst packed-bed in different configurations.

1.4. Dielectric Barrier Discharge (DBD) Plasma

Dielectric barrier discharge (DBD), which is also called silent discharge, is a non-thermal (non-equilibrium and cold) plasma which can be operated at atmospheric pressures as well as gives high reactor volumes for the generation of plasma, which makes it suitable for chemical processes. Fig.5 shows typical configurations of dielectric barrier discharge plasma. The typical DBD configurations are classified in two groups: planar and cylindrical in such a way that at least one electrode is covered by a dielectric material such as glass, quartz and ceramics [46].

Fig.5. Dielectric barrier discharge (DBD) plasma configurations [46].

The dielectric, being an insulator, cannot pass a current. Its dielectric constant and thickness determine the amount of displacement current that can be passed through the dielectric. In most applications, the dielectric limits the average current density transferring across the gas space. The dielectric can also be placed between the electrodes to separate two gas layers. The roles of the dielectric are not only limited by the amount of charge and energy conveyed to an individual microdischarge, but it also distributes the microdischarges over the

entire electrode area. Furthermore, the dielectric can prevent the formation of unwanted spark or arc discharges which can interfere with the expansion of typical filamentary discharges of the DBD plasma. The total charge transferred in a microdischarge as well as discharge characteristics like the density and the energy level of plasma species (e.g., electrons, ions, radicals) inside the discharges substantially depend on the properties and the composition of the gas or the mixture of the utilized gases for the generation of DBD plasma, which can be further influenced by the discharge gap spacing and also by the properties of the dielectric [37,47].

DBD plasma has a long and proven background for industrial-scale production of ozone (O_3), whereas its fundamentals have also been well established in both aspects of physical and chemical properties [37]. Ozone generators are utilized in waste water treatment, water purification, pulp industry as well as food processing. This further demonstrates that DBD can be considered as a scalable technology for treatment of gases in large quantities. In addition, DBD reactors show great flexibility in terms of electrodes and reactor configurations, which can be readily adapted for different applications or to be integrated with other systems, for instance, with catalytic packed bed reactors [48,49].

1.5. Packed-bed DBD plasma reactors (PBRs)

The utilization of packed bed DBD reactors (PBRs) is growing as a promising approach for environmental gas treatment as well as for energy-related chemical processes, as it benefits from the integration of both plasma and catalysis technologies together [50]. Due to the vicinity of the contact points of catalyst particles, the strength of the electric field can become significantly greater than the mean value of the field between the high voltage and the ground electrode, depending on the dielectric properties as well as other parameters of the packing (e.g., shape, particle size) [51]. The Fig.6 shows the scheme of a typical packed-bed DBD reactor for performing chemical processes.

Fig.6. Scheme of a typical packed-bed DBD plasma reactor (PBR) [55].

The properties of the packing material have a dominant impact on the mechanism of plasma formation, its propagation across the packed bed as well as the strength of the created electric field. This therefore can change the properties of the generated electrons (i.e., density and temperature) by plasma which can, in turn, change the involved chemistry. As a result, the presence of catalyst particles inside the discharge gap can influence both the conversion of reactants by modifying the electric field as well as the distribution of products by interaction of plasma species with the catalyst surface, creating new reaction pathways towards specific products [52,53].

It should be mentioned that the plasma-catalyst hybrid system makes the discharge characteristic rather complex, due to the presence of solid particles. The reason is that the

discharge structure varies due to changing the electrical parameters (i.e., electric field strength and current density). In addition, the catalytic activity of the catalyst can be affected by changing the surface properties of the catalyst, when it is exposed to plasma. This mutual impact therefore can create a complex medium for understanding the mechanism of the plasma discharge formation as well as the catalytic behaviour of the catalyst [54].

1.6. Challenges in PBRs

One of the main challenges in scaling up of DBD reactors is the energy efficiency of the process which is quite low. The reason is attributed to the input power which is spent for ionization of gas ($\geq 12\text{eV}$) to sustain the plasma as well as to generate sufficiently hot electrons in order to overcome thermodynamic barrier of bond activation. Earlier, it was found in a study by Nozaki et al. [49] that the power absorbed by DBD plasma discharges is mainly dissipated into the dielectric surface (more than 60%), by propagation of filamentary discharge channels in the form of surface discharges on the surface of the dielectric, as illustrated in Fig.7.

Fig.7. The propagation of a microdischarge on the surface of the dielectric in DBD plasma [56].

To prevail the challenge of energy efficiency in DBD reactors, many researchers have attempted to combine non-thermal plasma, in particular DBD plasma, with heterogeneous catalysis which is known as “plasma catalysis”[57]. There are numerous research studies which have reported that the integration of plasma discharges with catalyst surfaces can enhance the

performance of the process in terms of conversion, selectivity as well as the energy efficiency [51]. This has created the synergistic effect of plasma catalysis, where it is stated that the cumulative effect of plasma and catalyst together leads to a better overall performance than that of obtained via either the plasma process or the conventional catalytic process alone. The initial idea of merging these two methods was to place catalyst particles in the vicinity of plasma discharges, where in such a medium a longer retention time can be achieved for reactive plasma species to interact with catalyst surface via the adsorption of reactive plasma species, followed by surface reactions to form desired products, which was mainly studied for VOCs removal in PBRs [58,59].

High reactivity of plasma species as well as the possibility of their generation in a low temperature plasma process are the substantial advantages that have led to the scientific and technical development of plasma-induced technologies as a promising approach for performing chemical processes. These can furthermore be coupled with catalysis, to be able to tune the selectivity of desired products, as well as to consume the input power in a more efficient way, taking advantage of the dielectric properties of the solid catalysts.

One point to be noted is that catalysts which are actively used in conventional thermal processes are usually operated in comparably higher temperature than the temperature of DBD plasma reactors. In this case, those catalysts active in conventional methods may not be necessarily active when they are in a low temperature plasma, giving poor conversion and/or yielding unwanted products. On the other hand, in thermal catalytic processes, the type of the species (e.g., molecules, radicals), which are interacting with the catalyst, as well as their distributions are different than the species generated by plasma discharges. This therefore can influence the interactions as well as the surface activities (e.g., adsorption, surface reactions) of the catalyst in a hybrid plasma-catalyst system.

Moreover, the presence of catalyst inside the plasma influences the formation of discharges as well as the distribution of electric field, which results in a different performance of the plasma reactor. Thus, both plasma and catalyst has mutual impacts on each other, which both can substantially modify the performance of each other. This indicates that the choice of a suitable catalyst for a hybrid plasma-catalyst system needs to be studied for each specific chemical process in order to find those catalysts which are still active in low temperatures (i.e., even close to room temperature) and exhibit synergy in interactions with plasma activated species as it is essential for achieving a higher energy efficiency of a plasma-driven chemical process.

In addition, the selected catalysts should possess adequate physicochemical properties such as conductivity, dielectric constant, surface area and porosity for optimal integration with plasma. Thus, in order to design an efficient plasma-catalyst system for a specific chemical reaction, all above-mentioned parameters should be carefully considered in both cases of PBRs using only the support dielectric materials (i.e., without the presence of metal active sites like Ni, Pt), as well as those using metal supported catalysts (e.g., Ni/ γ -alumina) as the packing.

1.7. Synergy of DBD Plasma and Catalyst for Methane Coupling

Several catalysts have been utilized for conversion of methane in packed bed DBD plasma reactors for the production of different compounds (e.g., syngas, methanol, C₂ hydrocarbons) via oxidative (using CO₂, O₂ and H₂O) and non-oxidative routes.

The oxidative conversion of methane in PBRs has been mainly studied for dry reforming (i.e., methane is mixed with CO₂) to syngas and partial oxidation to produce oxygenates like methanol as well as oxidative coupling of methane (OCM). Although C₂ hydrocarbons can be produced via the oxidative route (OCM), most of these studies have reported the deep oxidation of carbonaceous intermediates to CO_x, which leads to a low yield of C₂ products [60-63]. Recently, Lee et al. [64] attempted to perform oxidative coupling of methane with Ag/SiO₂

catalyst packed bed in combination with DBD discharges. Around 10% yield of C_{2+} (mainly C_2 and C_3) was obtained by applying almost 400 °C temperature using a furnace, as the plasma-induced temperature process was giving a quite low yield of C_{2+} (less than 2%). Furthermore, it was reported that, despite the presence of oxygen, still coke formation occurs, which led to the deactivation of catalyst and as a consequence both the conversion and the C_{2+} selectivity showed a decreasing trend during the reaction time.

Methane dry reforming has been extensively studied for production of syngas in packed bed DBD plasma reactors [33, 65-69]. Mostly Ni/alumina catalyst has been used as packing, while other metals like Cu, Co, and Mn have also been evaluated by Zeng et al. [67] and Brune et al. [69], where all these metals demonstrated rather similar activity to Ni for dry reforming in PBRs. In particular, Cu and Mn showed a better performance compared to Co-supported alumina. Partial oxidation of methane to oxygenates like methanol have been also pursued using PBRs. Catalysts such as Pt, Fe_2O_3 , CeO_2 supported on ceramic [35], Fe_2O_3 -CuO/ γ - Al_2O_3 [70] and Mn_2O_3 -coated glass bead [71] showed a synergistic effect between DBD plasma and catalyst in improving the selectivity, for the formation of methanol as the target product.

Non-oxidative coupling of methane with PBRs has been studied by integration of DBD plasma and metal supported catalysts (e.g., Cu, Pt, Ni, Ru supported with alumina) [72-74] as well as using only support dielectric materials (e.g., alumina, silica, titania) [40,56,75], although compared to the oxidative route a comparably smaller number of studies have been dedicated to investigate non-oxidative coupling of methane in PBRs. The main attempt in most of these studies has been to explore the synergistic effect of plasma and catalyst in enhancing the conversion of methane towards a high yield of C_2 products [76].

Different parameters have been considered in order to study the mutual effect of plasma and catalyst on each other. Among all these parameters, the plasma characteristics such as the distribution of electric field, the mechanism of plasma formation, the propagation of discharges

in PBRs [51] as well as the physicochemical properties of the catalyst such as the particle size, particle shape and packing density have been investigated in packed bed DBD plasma reactors [56,77]. These results indicate that the packing conditions can substantially influence the strength of the electric field by influencing the electron density and the electron energy, in particular at contact points of the particles, where it was explained to have a higher intensity of the electric field compared to the gas gap between the particles.

In addition to macro-scale packing properties (e.g., packing density), it was discovered that the micro-scale properties (e.g., the structure and morphology) of the catalyst can influence the methane conversion as well as the reaction pathways, shifting the distribution of final products. In a recent study, Park et al. [78] investigated the conversion of methane in a combination of a thermal and a packed bed DBD reactor at a moderate temperature (~ 300 °C). NiO and MgO were used as the catalysts supported by meso-porous silica. It was found that the conversion of methane at the presence of bare silica is higher than that obtained for NiO and MgO doped silica catalysts. This was attributed to the high surface area of bare silica, which enhances the interaction of vibrationally excited methane molecules with the surface for a longer contact time. This was also in line with a higher polarization of chemical bonds on bare silica, which could therefore intensify the dissociation of methane on the surface. The lower conversion for NiO and MgO silica catalysts was therefore attributed to a significantly lower surface area of the meso-porous silica after being impregnated with NiO and MgO by 20 wt%, which decreases the efficiency of interactions between vibrationally excited methane molecules and the catalyst surface, causing a lower conversion of methane as well as a lower yield of C_{2+} .

1.8. Plasma Catalysis Configuration

In general, a catalyst packed bed can be integrated with DBD plasma discharges by two forms of configuration, depending on the position of the catalyst: post-plasma catalysis (i.e., catalyst packed downstream of the plasma; PPC) and in-plasma catalysis (i.e., catalyst packed inside the plasma; IPC), as shown in Fig.8.

Fig.8. Plasma catalysis configurations in PBRs.

In PPC most short-lived active species (e.g., vibrationally excited species and radicals) generated in the plasma return to their ground state level of energy before they reach the catalyst and thus are not as reactive as they were, once generated inside the plasma zone. In such a configuration, plasma mainly plays the role to change the gas composition fed into the downstream catalyst. However, the long-lived activated species (i.e., exited from the plasma) can be still reactive enough to participate in surface reactions by interacting with catalyst packed bed downstream of the plasma at quite low temperatures, due to that part, or even all of the energy barrier has been paved by the earlier activation in the plasma zone [41,79].

On the contrary, in IPC, the catalyst particles are in direct contact with plasma discharges, whereas both short and long-lived plasma species are generated in the vicinity of the catalyst surface; this then allows more efficient interactions of plasma reactive species and the catalyst packed bed. However, the mutual effect of plasma and catalyst on each other can influence the behaviour of the plasma and its characteristics differently than when no packing is used. Additionally, the physicochemical properties of the catalyst surface can also be altered due to the exposure of the catalyst to plasma environment, which thus changes the function of the surface, showing different catalytic properties [46,67,80]. Considering that each chemical process needs its own optimized process conditions as well as specific types of materials (i.e., catalytic or non-catalytic materials to be used as packing), this mutual effect should be separately investigated for each chemical process.

1.9. The scope of the present study

This dissertation aims at studying the synergistic effect of plasma and catalyst in a hybrid plasma-catalyst system to be implemented for coupling of methane to C₂ products (ethane, ethylene, acetylene) using a packed bed DBD plasma reactor operating at ambient conditions. This will be investigated in both configurations of “post-plasma catalysis” as well as “in-plasma catalysis”, focusing on the interaction of plasma activated species with a catalyst packed bed by applying different process conditions. Taking into account the lifetime of the plasma species, these two configurations can remarkably influence the efficiency of the interactions between plasma activated species and the catalyst surface and thus will impact the conversion and the selectivity of the final products.

Therefore, the following research questions have been considered for investigation in this dissertation:

- What is the effect of the reactor configuration (post-plasma or in-plasma catalysis) in creating a synergy between the plasma and the catalyst packed bed, aiming at enhancing the C₂ production and reducing the formation of deposits?
- Which surfaces should be employed in combination with the DBD plasma discharges? Catalyst support (e.g., γ -alumina) or metal supported catalyst (Pd/ γ -alumina)? What are their influences on the conversion and the selectivity of the final products?
- How do the process conditions such as discharge power, residence time, methane concentration and the volume of plasma reactor influence the conversion of methane and the distribution of C₂ products (C₂H₂, C₂H₄ and C₂H₆)?
- What is the effect of the dielectric constant on the conversion and selectivity of products? In other words, how is the performance of the packed bed DBD plasma reactor influenced when materials with different dielectric constants are utilized as packing inside the discharge gap?

1.10. The outline of the dissertation

This dissertation contains 7 chapters. Chapter 1 is the introduction chapter, which gives a background for the topic under study as well as an overview of the existing literature (i.e., the current chapter).

In chapter 2, the design of the implemented packed bed DBD plasma reactor is discussed and its performance is evaluated in different process conditions. Furthermore, plasma activated species inside and downstream of the plasma are identified with UV-Vis spectroscopy. Several packing materials with different physicochemical properties are packed downstream of the plasma in order to explore the interaction of long-lived activated species and to evaluate their impacts in altering the distribution of final products.

In chapter 3, the integration of Pd/ γ -alumina downstream of the DBD plasma (PPC) and their synergy via the interaction of long-lived plasma species and the Pd active sites are discussed and evaluated in different process conditions. Furthermore, the effect of distance downstream of the plasma and the existence of interactions between long-lived plasma species exited from the plasma zone with the catalyst packed bed downstream is elaborated in detail. At the end of the chapter, the reaction pathways and the involved radical chemistry are elucidated, considering the obtained experimental results.

In chapter 4, methane coupling is investigated in in-plasma catalysis (IPC) configuration using γ -alumina as well as Pd/ γ -alumina with different loadings of Pd. The synergy between plasma and catalyst is discussed in terms of methane conversion, selectivity/yield of C₂ compounds as well as selectivity/yield of deposits. Furthermore, the energy efficiency of the implemented DBD plasma reactor is calculated in order to compare the performance of the plasma reactor at the presence and the absence of the catalyst. The effect of the presence of the catalyst on the reaction pathways in comparison with a non-packed plasma reactor and

furthermore the synergy of plasma and catalyst in IPC configuration and the consequent shifting of the selectivity towards desired products are discussed in detail.

In chapter 5, the effect of the dielectric constant is studied by packing different materials including γ -alumina, silica-SBA-15, ZrO_2 , $\text{MgO}/\text{Al}_2\text{O}_3$, α -alumina in comparison with a high dielectric packed bed of BaTiO_3 . Results will be presented in terms of the conversion of methane and the selectivity/yield of the products, focusing on the effect of the dielectric constant of the tested materials. Furthermore, the effect of the discharge power is evaluated for BaTiO_3 (i.e., a high dielectric material) packed-bed reactor in comparison with γ -alumina (i.e., a low dielectric material) packed-bed reactor and the blank reactor. The energy efficiency is also analysed in terms of the amount of converted methane, the amount of energy input as well as the heat value of the gas-phase products.

In chapter 6, the deposits formed during the plasma reaction for both the blank reactor as well as for the catalysts used in in-plasma catalysis configuration are characterized using high resolution scanning electron microscopy (HR-SEM), in order to study the structural changes of the catalyst samples after being exposed to CH_4/Ar DBD plasma discharges. In addition, energy dispersive X-ray spectroscopy (EDX) is utilized to analyze the elemental composition of the deposits formed on the inner surface of the dielectric quartz tube as well as on the catalyst samples.

Finally, in chapter 7, the main conclusions of this dissertation will be given based on the findings, discussed in previous chapters.

References

- [1] C. Karakaya, R. J. Kee, *Progress in Energy and Combustion Science*, 55 (2016) 60–97.
- [2] T. Ren, M. Patel, K. Blok, *Energy*, 31 (2006) 425-451.
- [3] R. Horn, R. Schlögl, *Catt Lett.*, 145 (2015) 23-39.
- [4] A. Holmen, *Catal Today*, 142 (2009) 2–8.
- [5] J.R. Rostrup-Nielsen, *Catal Today*, 18 (1993) 305–324.
- [6] G.E. Keller, M.M. Bhasin, *J Catal*, 73 (1982) 9-19.
- [7] Z. Qijian Z., H. Dehua, Z. Qiming, *Natural Gas Chemistry*, 17 (2008) 24-28.
- [8] K. Otsuka, Y. Wang, *Applied Catalysis A*, 222 (2001) 145-161.
- [9] J.H. Lunsford, *Catal. Today*, 63 (2000) 165-174.
- [10] H. Mimoun, A. Robine, S. Bonnaudet, C.J. Cameron, *Appl. Catal. A: Gen.*, 58 (1990) 269-280.
- [11] L. Chou, Y. Cai, B. Zhang, J. Niu, Sh. Ji, Sh. Li, *Journal of Natural Gas Chemistry*, 11 (2002) 131–136.
- [12] S.J. Korf, J.A. Roos, L.J. Veltman, J.G. Van Ommen, J.G., J.R.H. Ross, *Applied Catalysis*, 56 (1989) 119–135.
- [13] D. Schweer, L. Mleczko, M. Baerns, *Catal. Today*, 21 (1994) 357-369.
- [14] J.M. Fox, *Catal. Rev. Sci. Eng.*, 35 (1993) 169-212.
- [15] N.D. Parkyns, C.I. Warburton, J.D. Wilson, *Catal. Today*, 18 (1993) 385-442.
- [16] X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, Ch. Ma, X. Wu, D. Deng, M. Wei, D. Tan, R. Si, Sh. Zhang, J. Li, L. Sun, Z. Tang, X. Pan, X. Bao, *Science*, 344 (2014) 616-619.
- [17] Ch. Guéret, M. Daroux, F. Billaud, *Chemical Engineering Science.*, 52 (1997) 815-827.
- [18] H. Ma, R. Kojima, S. Kikuchi, M. Ichikawa, *Catal. Lett.*, 104 (2005) 63-66.

- [19] Y. Song, Y. Xu, Y. Suzuki, N. Nakagome, Z.G. Zhang, *Appl Catal A Gen.*, 482 (2014) 387-396.
- [20] Y. Song, Y. Xu, Y. Suzuki, N. Nakagome, Z.G. Zhang, *J Catal.*, 330 (2015) 261–272.
- [21] O. Garnier, J. Shu, B.P.A. Grandjean, *Ind Eng Chem Res.*, 36 (1997) 553-558.
- [22] L.Q. Huang, Y.Z. Yuan, H.B. Zhang, Z.T. Xiong, J.L. Zeng, G.D. Lin. *Stud Surf Sci Catal*, 147 (2004) 565-570.
- [23] Y. Xiao, A. Varma, *ACS Catal.*, 8 (2018) 2735–2740.
- [24] F.P. Larkins, A.Z. Khan, *Aust J Chem.*, 42 (1989) 1655-1670.
- [25] A. Bogaerts, E. Neyts, R. Gijbels, J. van der Mullen, *Spectrochim. Acta B.*, 57 (2002) 609-658.
- [26] J. R. Fincke, R. P. Anderson, T. Hyde, B. A. Detering, R. Wright, R. L. Bewley, D. C. Haggard, W. D. Swank, *Plasma Chemistry and Plasma Processing.*, 22 (2002) 105-136.
- [27] H.L. Chen, H.M. Lee, S.H. Chen, Y. Chao, M.B. Chang, *Applied Catalysis B: Environmental.*, 85 (2008) 1-9.
- [28] A. Gutsol, *Handbook of Combustion*, Wiley-VCH, (2010).
- [29] B. Eliasson, M. Hirth, U. Kogelschatz, *Journal of Physics D: Applied Physics.*, 20 (1987) 1421–1437.
- [30] J.Sh. Chang, *Science and Technology of Advanced Materials.*, 2 (2001) 571–576.
- [31] M.F. Mustafa, X. Fu, Y. Liu, Y. Abbas, H. Wang, W. Lu, *Journal of Hazardous Materials.*, 347 (2018) 317-324.
- [32] B. Ashford, X. Tu, *Current Opinion in Green and Sustainable Chemistry.*, 3 (2017) 45–49.
- [33] A. H. Khoja, M. Tahir, N. A. S. Amin, *Energy Conversion and Management.*, 144 (2017) 262–274.
- [34] L. Chen L, X. Zhang, L. Huang, L. Lei, *Chem. Eng. Technol.*, 33 (2010) 2073–2081.

- [35] L. Chen L, X. Zhang, L. Huang, L. Lei, *Chemical Engineering and Processing*, 48 (2009) 1333–1340.
- [36] A. Górská, K. Krawczyk, S.Jodzis, K. Schmidt-Szałowski, *Fuel*, 90 (2011) 1946-1952.
- [37]. U. Kogelschatz, *Plasma Chem Plasma Process*, 23 (2003) 1-46.
- [38]. S. Kado, Y. Sekine, K. Fujimoto, *Chem Commun*, 24 (1999) 2485–2486.
- [39]. M.C. Alvarez-Galvan, N. Mota, M. Ojeda, S. Rojas, R.M. Navarro, J.L.G. Fierro, *Catal Today*, 171 (2011) 15–23.
- [40] X.S. Li, A.M. Zhu, K.J. Wang, Y.Xu, Z.M. Song, *Catal Today*, 98 (2004) 617-624.
- [41] M. Młotek M, J. Sentek, K. Krawczyk, K. Schmidt-Szałowski, *Appl Catal A Gen*, 366 (2009) 232–241.
- [42] C.J. Liu, R. Mallinson, L. Lobban, *J Catal*, 179 (1998) 326–334.
- [43] Z.J. Wang, Y. Zhao, L. Cui, H. Du, P. Yao, C.J. Liu, *Green Chem.*, 9 (2007) 554–559.
- [44] S.H. Kim, C.H. Jung, N. Sahu, D. Park, J.Y.Yun, H. Ha, J.Y. Park, *Appl Catal A Gen.*, 454 (2013) 53–58.
- [45] I. Istadi, N.A.S. Amin, *Fuel*, 85 (2006) 577–592.
- [46] G. Xiao, W. Xu, R. Wu, M. Ni, Ch. Du, X. Gao, Z. Luo, K. Cen, *Plasma Chem Plasma Process*, 34 (2014) 1033–1065.
- [47] M.A. Lieberman, A.J. Lichtenberg, *Principles of plasma discharges and materials processing*, Wiley (1994).
- [48] M.F. Mustafa, X. Fu, W. Lu a, Y. Liu, Y. Abbas, H. Wang, M. T. Arslan, *Journal of Cleaner Production*, 174 (2018) 670-677.
- [49] T. Nozakia, K. Okazaki, *Catalysis Today*, 211 (2013) 29-38.
- [50] H. Puliyalil, D. Jurkovi, V. D. B. C. Dasireddy, B. Likozar, *RSC Adv.*, 8 (2018) 27481-27508.

- [51] T. Butterworth, R.W.K. Allen, *Plasma Sources Sci. Technol.*, 26 (2017) 065008 (16pp).
- [52] E. C. Neyts, *Plasma Chem Plasma Proc.*, 36 (2016) 185–212.
- [53] E.C. Neyts, A. Bogaerts, *J. Phys. D: Appl. Phys.*, 47 (2014) 224010 (18pp).
- [54] P. Kasinathan, S. Park, W.C. Choi, Y.K. Hwang, J.S. Chang, Y.K. Park, *Plasma Chemistry and Plasma Processing.*, 34 (2014) 1317-1330.
- [55] I. Michielsens , Y. Uytendhouwen, J. Pype, B. Michielsens, J. Mertens, F. Reniers, V. Meynen, A. Bogaerts, *Chemical Engineering Journal.*, 326 (2017) 477–488.
- [56] M.A. Lindon, E.E. Scime, *Frontiers in Physics.*, 2 (2014) article 55.
- [57] J. C. Whitehead, *J. Phys. D: Appl. Phys.*, 49 (2016) 243001 (24pp).
- [58] Y.H. Song, S.J. Kim, K.I. Choi, T. Yamamoto, *Journal of Electrostatics.*, 55 (2002) 189-201.
- [59] A. M. Vandenbroucke, R. Morent, N. De Geyter, C. Leys, *Journal of Hazardous Materials.*, 195 (2011) 30-54.
- [60] C.J. Liu, R. Mallinson, L. Lobban, *Appl Catal A: Gen*, 178 (1999) 17-27.
- [61] H. Lee, D.H. Lee, Y.H. Song, W.C. Choi, Y.K. Park, D.H. Kim, *Chem Eng J.*, 259 (2015) 761-770.
- [62] K. Oshima, T. Shinagawa, Y. Sekine, *J Japan Pet Inst.*, 56 (2013) 11-21.
- [63] S. Delavari, N.A. S. Amin, H. Mazaheri, *React Kinet Mech Catal.*, 113 (2014) 557-573.
- [64] H. Lee, D. Lee, J. M. Ha, D. H. Kim, *Applied Catalysis A, General.*, 557 (2018) 39-45.
- [65] S. Kameshima, R. Mizukami, T. Yamazaki, L.A. Prananto, Tomohiro Nozaki, *J. Phys. D: Appl. Phys.*, 51 (2018) 114006 (8pp).
- [66] D. Yap, J.M. Tatibouët, C. Batiot-Dupeyrat, *Catalysis Today*, 299 (2018) 263-271.
- [67] Y. Zeng, X. Zhu, D. Mei, B. Ashford, X. Tu, *Catalysis Today.*, 256 (2015) 80-87.
- [68] H.J. Gallon, X. Tu, J. C. Whitehead, *Plasma Process. Polym.*, 9 (2012) 90-97.

- [69] L. Brune, A. Ozkan, E. Genty, T. Visart de Bocarmé, F. Reniers, J. Phys. D: Appl. Phys., 51 (2018) 234002 (14pp).
- [70] L. Chen, X. Zhang, L. Huang, L. Lei, J Nat Gas Chem., 19 (2010) 628-637.
- [71] H. Lee, D.H. Kim, Nature, Scientific Reports, 8 (2018) 9956.
- [72] A. Indarto, J.W.Choi, H. Lee, H. K. Song, Journal of Natural Gas Chemistry, 15 (2006) 87-92.
- [73] S. Kim, J. Choi, J. Kim, H. Lee, H.K. Song, J Ind Eng Chem, 11 (2005) 533-539.
- [74] S. Kim, B. Kwon, J. Kim, Catal Commun, 8 (2007) 2204-2208.
- [75] S. Jo, T. Kim, D.H. Lee, W.S. Kang, Y.H. Song, Plasma Chem Plasma Process, 34 (2014) 175–186.
- [76] M. Scapinello, E. Delikonstantis, G. D. Stefanidis, Chemical Engineering & Processing: Process Intensification, 117 (2017) 120-140.
- [77] S. Jo, D. H. Lee, W. S. Kang, Y.H. Song, Physics of plasmas, 20 (2013) 123507.
- [78] D. Park, J. Kim, T. Kim, Catalysis Today, 299 (2018) 86-92.
- [79] T. Nozaki, N. Muto, S. Kado, K. Okazaki, Catalysis Today, 89 (2004) 57-65.
- [80] J. Karuppiyah, Y. S. Mok, International Journal of Hydrogen Energy, 39 (2014) 16329-16338.

Chapter 2

The performance of the implemented DBD plasma reactor

In this chapter, the details of the design of the DBD plasma catalytic reactor set-up is elaborated. Furthermore, the integration of different catalyst supports downstream of the DBD plasma is evaluated in different process conditions. Result indicates that CH₄ can be activated to form C₂ and C₃ hydrocarbons and hydrogen as the major gas-phase products by DBD plasma discharges. The formation of solid products is mainly observed on the inner surface of the reactor wall, possessing a polymer-like structure due to a high content of H (60%at) in the content of the deposits, analyzed by CHN elemental analysis. UV-Vis spectroscopy was utilized to identify the plasma species inside and downstream of the plasma. The spectra indicate the de-excitation of most CH_x fragments upon leaving the plasma zone (i.e., in the afterglow of the DBD plasma). This shows consistency with the experiments performed with packing different materials downstream of the DBD plasma, where an efficient interaction of plasma species with downstream packing is not observed. Moreover, the effect of co-feeding of H₂ with methane is evaluated, where it can reduce the formation of deposits during the plasma reaction.

2.1. Introduction

Over recent decades, conversion of methane into value-added chemicals including alkanes and olefins has become a broad research topic, with the aim to identify alternative processes for steam cracking of petroleum derivatives (e.g. LPG or naphtha) [1,2]. On the other hand, utilization of methane as a feedstock for chemical industries effectively addresses the global concern for mitigation of greenhouse gas emissions, by exploring new synthesis routes of chemicals with less pollution [3]. However, an important issue is that the activation of methane is thermodynamically limited.

To prevail the thermodynamic barrier, co-feeding of oxygen (e.g. oxidative coupling of methane, OCM) has been extensively studied, starting with the work of Keller et al. in 1982 [4]. Despite achieving a high conversion of methane, the yield of C₂ hydrocarbons is drastically reduced, owing to deep oxidation towards CO and CO₂. As a result, the alternative, non-oxidative conversion of methane has become of special interest for direct synthesis of higher hydrocarbons, circumventing CO_x by-products. The drawback is that in the absence of oxygen, high temperatures ($T \geq 800$ °C) should be employed at the presence of a catalyst, to facilitate the activation of the C-H bond (434 kJ/mol) [5]. This has still remained as a challenge because high temperature processes require high amounts of energy and suffer from high selectivity to coke as the by-product as well as rapid deactivation of catalyst [6,7].

Non-thermal plasma processes can be considered as an alternative for high temperature processes, where methane is activated by interacting with highly energetic electrons. These interactions generate different reactive species such as radicals, ions and vibrationally excited molecules, far beyond thermodynamic limits and independently from the reaction temperature. Successive interactions of generated radicals (e.g. CH₃, CH₂, CH, C, C₂H₃, C₂H₅,...) proceed to form C₂, C₃ and higher hydrocarbons, by following radical chain reactions randomly [8].

The randomness of interactions amongst radicals occurs rapidly in the range of milliseconds to nanoseconds. In this case, radicals recombine or de-excite to their ground state level of energy in exceptionally short time [9]. Integration of a catalyst with the plasma can give the opportunity to create an alternative medium for interactions of plasma species with surfaces, which possibly results in gaining control over the distribution of desired products [10].

Integrations of catalyst and plasma are generally applied by two configurations, depending on the position of the catalyst: post-plasma catalysis (i.e., catalyst downstream of the plasma; PPC) and in-plasma catalysis (i.e., catalyst inside the plasma; IPC). The performance of both PPC and IPC reactor configurations depends on the lifetime of plasma activated species. Short-lived activated species can demonstrate synergy in integration with catalyst surfaces only in the IPC configuration where catalyst and plasma species are interacting *in situ* [11]. However, long-lived activated species (i.e., leaving the plasma zone) still can react with catalyst surfaces downstream of the plasma even at low temperatures, due to paving part, or even all of the energy barrier, as earlier activated in the DBD plasma zone [12-14].

In this chapter, the design of the implemented packed bed DBD plasma reactor is discussed and its performance is evaluated in different process conditions. The plasma activated species are identified by UV-Vis spectroscopy for inside and afterglow of DBD plasma discharges. Several packing materials with different physicochemical properties are packed downstream and evaluated in different process conditions. This will be elaborated in terms of conversion of methane, selectivity and the yield of final products.

2.2. Experimental

2.2.1. Materials and characterizations

The following materials were utilized as the packing materials: γ -alumina (Alfa Aesar, 234 m²/gr), α -alumina (Alfa Aesar, 0.82 m²/gr), silica-SBA-15 (Sigma Aldrich, 673 m²/gr), ZrO₂ (RC 100, Gimex, 97 m²/gr), MgO/Al₂O₃ (Sasol Company, 440 m²/gr), BaTiO₃ (Alfa Aesar, 18 m²/gr), quartz wool (VBGL, Nederland). The surface area of the samples, as given in the brackets above, was measured with nitrogen physisorption at 77 K with Surface area and Porosity Analyzer, TriStar, Micrometrics.

CHN elemental analysis (Organic Elemental Analyzer, Flash 2000, Thermo Fisher Scientific Inc.) was performed to identify the composition of the formed deposits on the inner surface of the quartz tube.

2.2.2. Experimental setup

Non-oxidative coupling of methane was carried out in a dielectric barrier discharge (DBD) plasma reactor at atmospheric pressure. The reactor was a quartz tube with an i.d. of 4 mm (inner diameter), an o.d. of 6 mm (outer diameter) and length of 30 cm, and also acts as the dielectric. A stainless steel rod with a diameter of 1.6 mm, acting as the high voltage electrode, was fixed at the centre of the quartz tube. The quartz tube was covered with a rigid stainless steel tube with a length of 10 cm, which acted as the ground electrode.

A home-made heater capable of applying temperatures up to 600 °C was utilized for those experiments used external heat source downstream of the plasma. Fig. 1 and Fig.2 show the scheme and the picture of the experimental setup as well as the high voltage (HV) electrode, which was built and utilized for all experiments during this study.

Fig.1.Scheme of the experimental setup

Fig.2.Picture of the experimental setup and the high voltage electrode

The gas discharges were initiated at room temperature without using an external heat source. The downstream temperature, where the materials were packed, was measured by a thermocouple to be 35 °C and 27 °C, respectively, for 1 and 5 cm gap distance between plasma zone and catalyst packed bed downstream of the plasma. The temperature of the outer surface of the ground electrode was monitored with a thermocouple. Temperature was raised with time for about 1hr, where it reached 52 °C and was stabilized around this level for the rest of the reaction time for the blank reactor, as shown in Fig.3. For all other experiments in which packing materials were used inside the plasma, a similar trend was observed by applying a discharge power within the range of 7-8 W.

Fig.3. The outer surface temperature profile of the DBD plasma reactor versus time, operated at atmospheric pressure, applying V=7-8kV and P=7-8W.

For those experiments that used packing downstream of the plasma, 100-300 mg of the catalyst sample, depending on the experiment, was sieved in the particle size range of 100-300 μm and packed downstream of the plasma supported with quartz wool at different distances (0, 1, and 5cm) from the tip of the high voltage electrode. The reaction was conducted with a total flow rate of 50 and 100 ml/min with 5 and 10% methane mixed with Ar as the carrier. The reaction products were analyzed with an online Varian 450 GC equipped with TCD and FID detectors. The GC was calibrated with a standard mixture of methane and products with a known concentration of each compound in the range of concentrations similar to those obtained in the performed experiments. The products were separated by Hayesep T&Q, Molsieve 13x and PoraBOND Q columns to analyze all C_2 and C_3 hydrocarbons and H_2 as the gas-phase products. All other gas-phase products (C_{4+}) with very small amount of each compound were detected and considered as one item specified as “other hydrocarbons” in the calculations of the selectivity.

The conversion of methane, selectivity of gas-phase products, selectivity of deposits and the hydrogen yield were calculated based on the following equations:

$$\text{Conversion of CH}_4 (\%) = \frac{\text{Moles of converted CH}_4}{\text{Moles of introduced CH}_4} \times 100$$

$$\text{Selectivity of C}_x\text{H}_y \text{ gas-phase product } (\%) = \frac{\text{Moles of C}_x\text{H}_y \text{ product} \times x}{\text{Moles of converted CH}_4} \times 100$$

$$\text{Selectivity of the formed deposits } (\%) = \frac{\text{Moles of converted CH}_4 - \text{Moles of CH}_4 \text{ consumed to form gas-phase products}}{\text{Moles of converted CH}_4} \times 100$$

$$\text{Hydrogen Yield } (\%) = \frac{\text{Moles of produced H}_2}{2 \times \text{Moles of introduced CH}_4} \times 100$$

2.2.3. Plasma generation and diagnostics

A plasma discharge was generated between the high voltage stainless steel rod and the stainless steel tube covering the dielectric quartz tube. A high voltage of 7-8 kV with a frequency of 23

kHz was applied using an AC power supply. Fig.4 presents the picture of the DBD plasma generated with a mixture of methane and argon.

Fig.4. Picture of the DBD plasma generated with a mixture of methane and argon

A high voltage probe (TESTEC TT-HVP15 HF), a probe for connecting the ground electrode (TESTEC TT-HV 250), a 3.9 nF capacitor and an oscilloscope (Pico Scope 2000 series) were used to measure the discharge power as depicted in Fig. 1. The discharge power was calculated from Q-V Lissajous figures according to the following equations (1 and 2):

$$P = Ef = \frac{f}{K} \sum_{k=1}^K \oint C_p V_p(t) dV \quad (1)$$

$$Q(t) = C_p V_p(t) \quad (2)$$

In this equation, P is the discharge power, E is the electric field created by DBD plasma, f is the frequency, K is the number of discharge cycles, C_p is the capacitance of the capacitor,

$V_p(t)$ is the voltage measured over the capacitor and $Q(t)$ is the instantaneous charge transferred through DBD plasma electrical circuit. The average discharge power during the reaction time was calculated to be 7-8 Watt, for all experiments. Fig.5 depicts the typical form of the Lissajous figure obtained from the implemented DBD plasma reactor.

Fig.5.Q-V pattern of the implemented DBD plasma reactor

UV-Vis spectroscopy was employed to identify the chemical composition of DBD plasma by using an optical emission spectrometer (HR 4000, Ocean Optics). Light was transmitted by the input optical fiber through the quartz tube via two small rectangular slits, placed at the end of the ground electrode. The response from the interaction of the light with the plasma environment was carried by the output optical fiber to the spectrometer. Both optical fibers were positioned above as well as below (2mm) the tip of the high voltage electrode to detect the plasma species, respectively, for inside and afterglow of the DBD plasma. The resulting spectra were collected from a PC connected to the spectrometer.

2.3. Results and discussion

2.3.1. The performance of the DBD plasma reactor

Fig. 6 shows the performance of the DBD plasma reactor without packing at ambient conditions. Methane was converted to C_2 and C_3 hydrocarbons and H_2 as the major gas-phase products, as well as to solid deposits formed on the high voltage electrode and on the inner surface of the dielectric quartz tube. Other gas-phase products (C_{4+}) with very small amount of each compound were detected and all included in one category specified as “other hydrocarbons”.

Fig.6. The performance of blank DBD plasma reactor versus time: (a) methane conversion and H_2 yield; (b) selectivity of gas-phase products. Total flow rate = 50 ml/min, CH_4 Concentration = 5 %, $V = 7-8$ kV, $f = 23$ kHz, $P = 7-8$ W.

The average selectivity to deposits was 47%, estimated based on the converted methane and the amount of methane transformed to gas-phase compounds, during 2.5 hr reaction time. The remaining 53% of the methane converted to a mixture of C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 and other hydrocarbons as depicted in Fig.6 (b). Hydrogen was also detected with a high concentration at the outlet of the reactor, corresponding with the formation of deposits, as depicted in Fig.6 (a). The average yield of hydrogen was calculated to be 17% during the reaction time.

From Fig.6 (a), a decreasing trend in the conversion of methane as well as the yield of hydrogen is observed. This can be attributed to the formation of deposits on the high voltage electrode and more densely on the inner surface of the dielectric quartz tube, as depicted in Fig.7.

Fig.7.The yellowish deposits formed on the dielectric quartz tube during the generation of DBD plasma with the mixture of methane and argon.

The gradual growth of the deposits layer and furthermore the presence of solid particles in the gas gap of the plasma zone can disturb the generation of the discharges, formed between the high voltage electrode and the dielectric quartz tube. The measurement of the conductivity of the deposits layer formed on the dielectric quartz tube using a multimeter, showed very poor conductivity for the formed deposits. This means that the formation of this non-conductive deposits layer gradually increases the thickness of the dielectric layer, which in turn it decreases the equivalent capacitance of the dielectric layer, thus causing a gradually weaker electric field across the discharge gap. This therefore influences the sustainability of the DBD plasma, resulting in a gradual decrease of the energy adsorbed inside the plasma zone. As a consequence, the energy intensity transferred for ionization and dissociation of methane gradually lowers, which leads to a gradual decrease for the conversion of methane and correspondingly for the yield of H_2 during the plasma reaction.

The formed deposits on the inner surface of the dielectric quartz tube were analysed with CHN elemental instrument. This elemental analysis determines the content of hydrogen and carbon and the molar ratio between them. On the other hand, the molar values of hydrogen and carbon, consumed for the formation of deposits, can be estimated from the hydrogen and carbon balance, calculated from the amount of methane converted to deposits. Table 1 shows the results obtained from CHN elemental analysis in comparison with the amount obtained from the molar ratio between the hydrogen and carbon consumed for the formation of deposits.

Table 1. The comparison between the hydrogen and carbon balance obtained from CHN elemental analysis and calculated from hydrogen and carbon mass balance.

	CHN elemental analysis	Calculated from hydrogen and carbon mass balance
H/C molar ratio	1.7±0.1	1.8±0.1

These results indicate that the mass balance-based H/C molar ratio is 1.8 ± 0.1 , consistent with the one obtained by the CHN elemental analysis (1.7 ± 0.1). In addition, the higher content of hydrogen compared to carbon in the formed solid deposits further indicates that the formed deposits are mainly polymeric materials, due to a high content of H in the chemical composition of the formed deposits (60 at%).

2.3.2. UV-Vis spectra of plasma species inside and in the afterglow of the DBD plasma

In order to identify the chemical composition of the DBD plasma, UV-Vis spectroscopy was carried out, as described in the experimental section 2.3. Fig.7 (a) and (b) depict the spectra measured inside and in the afterglow of the DBD plasma generated by the mixture of argon and methane.

Fig.8 (a) confirms the decomposition of methane into different fragments. CH electronic excitations (313, 392, 429, and 434 nm) and C₂ Swan band excitations (516 and 545 nm) [15-17] were detected in different modes of excitation. In addition, the transitions corresponding to

H radicals and molecular hydrogen were observed for both inside and afterglow of DBD plasma according to Fig.8 (a) and (b). The peaks observed at 298nm and 405nm are assigned to the emissions of triple carbon (C_3) [18]. Detection of these bands together indicates that methane is dissociated into CH_x fragments as well as atomic carbon and hydrogen, responsible for producing C_2 and C_3 hydrocarbons and hydrogen. However, the distribution of these radicals has changed in the afterglow of the plasma. The evolution of CH_x radicals is much less, whereas the number of observed peaks for CH_x fragments and their intensities have remarkably decreased.

Fig.8. Optical emission spectra for 50 ml/min flow of the mixture of 5% methane mixed with argon. Discharge power = 7-8 W; (a) Inside the plasma zone; (b) Afterglow of the plasma zone (2mm below the tip of the high voltage electrode).

In contrast, the emission intensity of C_2 radical excitation (at 545 nm) and the hydrogen molecule excitation (at 613 nm) show a notable increase. This indicates that the concentration of C_2 radicals is much higher than that of CH_x fragments in the afterglow of the DBD plasma. As a result, it can be inferred that C_2 radicals have a longer life time downstream of the DBD plasma, where they can react with hydrogen molecules, via $C_2 + H_2 \rightarrow C_2H + H$, in comparison with CH_x fragments which have shorter life time and recombine to their stable form upon leaving the plasma zone.

From the above explanation, it can be stated that a high concentration of long-lived C_2 and subsequently C_2H radicals hints at the possibility of exploiting the interaction of these radicals (i.e., as the precursors of deposits formation) with a catalyst bed positioned downstream of the DBD plasma, in order to influence the distribution of final products. It should also be noted that the above explanations are supported by the observation of carbon-containing deposits in the afterglow of the DBD plasma. Fig.9 depicts the afterglow of the DBD plasma as well as the formation of carbon-containing deposits downstream of the plasma.

Fig.9. (a). The afterglow of DBD plasma; (b). The formation of carbon-containing deposits on the tip and downstream of the DBD plasma.

Fig.8 (a) also exhibits a peak for the excitation of Ar at 700 nm. This peak has disappeared in the afterglow of the plasma, which can be explained by the role of Ar as an energy-transferring medium in which the formation of metastable Ar^* takes place easier than excitation of methane molecules [19,20]. In other words, the probability of collisions between Ar atoms and highly energetic electrons is higher than that of electron collisions with methane molecules. Subsequently, the metastable Ar^* collides with methane molecules, transferring a sufficient energy for excitation and ionization of methane. Thus, it can be inferred that the metastable species of Ar rapidly relax to their ground state level of energy, upon leaving the plasma zone.

2.3.3. The performance of catalytic materials downstream of the plasma

The performance of the DBD plasma reactor at ambient conditions was evaluated in combination with γ -alumina, α -alumina, silica-SBA-15, ZrO_2 , $\text{MgO}/\text{Al}_2\text{O}_3$, BaTiO_3 and quartz wool packed downstream of the plasma. Furthermore, the influence of the gap distance between the plasma zone and the entrance edge of the packed material was assessed by placing γ -alumina at different distances downstream of the plasma.

Table 2 exhibits the performance of a DBD plasma reactor packed with γ -alumina at 1 cm below the high voltage electrode after 1 hr reaction. The conversion of methane reached to 19% with 35% selectivity towards C_2 hydrocarbons, where the differences in conversion and selectivity between the blank and the packed reactor are small.

Table 2. The effect of packing of γ -alumina downstream of the DBD plasma reactor. Total flow rate=100 ml/min, methane concentration=10% vol CH_4 mixed 90% vol Ar, Voltage = 7-8 kV, $f = 23$ kHz, $P = 7-8$ W, ambient conditions for downstream of the plasma.

Configuration	CH_4 Conversion%	Selectivity%						
		C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	Other hydrocarbons	Deposits
Blank DBD plasma reactor	19.1	7.4	5.8	21.4	1.9	9.6	8.5	45.4
Packed DBD plasma reactor with γ -alumina 1 cm below high voltage electrode	18.1	7.9	6.7	20.7	1.9	8.9	8.3	45.6

Table 3 shows the results when temperatures up to 400 °C were applied downstream of the plasma zone. The conversion of methane and distribution of the products were not significantly affected at 200 and 300 °C, compared to the blank reactor. However, with increasing the temperature up to 400 °C, the selectivity to acetylene decreased from 8.5% to 1.6% at the similar level of 16% conversion of methane. This indicates that at high temperatures acetylene is converted into deposits on the surface of γ -alumina, due to the acidic properties of high surface area γ -alumina in interaction with unsaturated hydrocarbons.

As presented in Fig.10, additional experiments were performed in which α -alumina and quartz wool were packed downstream of the plasma zone, while a temperature of 400 °C was applied to these materials. Fig.10 shows that acetylene (C_2H_2) was the only compound that could be adsorbed on γ -alumina at 400 °C. Thus, it can be stated that γ -alumina causes a more severe formation of deposits via the interaction with C_2H_2 (i.e., the precursor for the formation of deposits on γ -alumina), while α -alumina and quartz wool did not show the same behaviour. This further supports the relation between the adsorption of acetylene and the acidity of γ -alumina at elevated temperatures.

Table 3. The effect of temperature on the performance of γ -alumina packed downstream of the DBD plasma reactor. Total flow rate=100 ml/min, methane concentration=10% vol CH_4 mixed 90% vol Ar, Voltage =7-8kV, f=23 kHz, P=7-8 W, T(downstream)=200-400 °C.

Temperature	CH ₄ Conversion%	Selectivity%						
		C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	Other hydrocarbons	Deposits
T=200 °C γ -alumina	17.0	7.7	6.2	20.2	2.1	10.0	8.1	45.7
T=300 °C γ -alumina	16.1	6.7	6.7	20.4	2.3	10.1	7.9	45.9
T=400 °C γ -alumina	15.6	1.6	6.8	20.3	2.5	10.4	8.0	50.4
T=400 °C , Blank reactor	16.3	8.5	7.4	19.5	2.6	9.0	7.7	45.3

Fig.10. Methane conversion and yield of products for DBD plasma reactor packed with quartz wool, α -alumina and γ -alumina; total flow rate = 100 ml/min, CH₄ concentration =10 %, V= 7-8 kV, f=23 kHz, P=7-8 W, T (downstream) = 400 °C.

A similar trend to the blank reactor and the one packed with γ -alumina downstream of the DBD plasma for the conversion of methane as well as the selectivity of products was observed for experiments performed by packing silica-SBA-15, ZrO₂, MgO/Al₂O₃, BaTiO₃ downstream of the plasma. Fig.11 shows the methane conversion and the selectivity of C₂ products for all materials evaluated downstream of the DBD plasma at ambient temperature and pressure.

Fig 11. The effect of packing different materials downstream of the DBD plasma reactor. (a) the conversion of methane; (b) the selectivity of acetylene; (c) the selectivity of ethylene; (d) the selectivity of ethane; Total flow rate=50 ml/min, methane concentration=5% vol CH₄, Voltage = 7-8kV, $f = 23$ kHz, $P = 7-8$ W, ambient conditions for downstream of the plasma.

These results indicate that packing different catalyst supports with different surface properties does not significantly influence the interaction of long-lived activated species. This may be attributed to two reasons. First is that most activated species have been already de-excited/recombined to their ground state level of energy and they are not reactive anymore. Second is that the surface of these catalyst supports is not sufficiently reactive at ambient temperature and therefore the interactions of long-lived species do not result in strong adsorption with the catalyst surface. Thus in order to stimulate the adsorption of long-lived plasma species exited from the plasma zone, metal supported catalysts can be used as the downstream packing, where the presence of metals such as Palladium on the surface of a dielectric support (e.g., γ -alumina) can create a medium, whereas stronger interactions between metal active sites and long-lived plasma activated species can be expected, even at ambient conditions. This will be discussed in detail in Chapter 3.

2.3.4. The effect of residence time and methane concentration

Further experiments were conducted to see the effect of residence time and methane concentration, while packing γ -alumina downstream of the DBD at the same level of input

energy and operating at ambient conditions. Table 4 depicts the details of the methane conversion and the yield of the products.

Table.4. Methane conversion and yield of products for DBD plasma reactor packed with γ -alumina packed downstream of the plasma. Total flow rate = 100 ml/min and 50 ml/min, CH_4 concentration = 10 % and 5%, $V=7-8$ kV, $f=23$ kHz, $P=7-8$ W, ambient conditions downstream of the plasma.

Total flow rate & CH_4 Concentration	CH_4 Conversion%	Yield%						
		C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	Other hydrocarbons	Deposits
Total Flow Rate : 100 ml/min CH_4 Concentration : 10 %	18.1	1.4	1.2	3.8	0.3	1.6	1.5	8.3
Total Flow Rate : 50 ml/min CH_4 Concentration : 10 %	31.1	1.8	1.3	5.9	0.5	2.8	2.5	16.3
Total Flow Rate : 100 ml/min , CH_4 Concentration : 5 %	35.0	2.0	1.6	6.4	0.6	3.1	2.9	18.4
Total Flow Rate : 50 ml/min , CH_4 Concentration : 5 %	45.8	2.3	1.7	7.2	0.8	3.5	3.3	27.0

The experiments were performed in two different total flow rates of 50 and 100 ml/min and two methane concentrations of 5 and 10%. Results proved that for a higher residence time the conversion of methane increased from 35% to 46% by decreasing the total flow rate from 100 ml/min to 50 ml/min at 5% methane concentration. This is due to increasing the specific energy input (power/total flow rate) from 4.5 kJ/L to 9 kJ/L, respectively, for total flow rates of 100 ml/min and 50 ml/min. This means that the mixture of CH_4 and Ar was exposed to a higher level of energy at total flow rates of 50 ml/min in comparison with the experiment performed with 100 ml/min total flow rate. Furthermore, the yield of the products was influenced by changing the total flow rate. At a lower total flow rate of 50 ml/min, the yield of deposits increased. On the other hand, the yield of gas-phase products ($\text{C}_2, \text{C}_3, \text{C}_4+$) also increased, independent of the concentration of methane. From this, it is concluded that a lower total flow rate (a longer residence time) is also favourable to achieve a higher yield of C_2 products.

The increase in the methane concentration from 5% to 10% decreased the conversion of methane from 46% to 31% at the same level of energy input at a total flow rate of 50 ml/min. In addition, increasing the methane concentration from 5% to 10% at a total flow rate of 100 ml/min decreases the selectivity of the solid deposits from 53% to 46%, while the methane conversion lowers from 35% to 18%. However, at a higher concentration of methane, the selectivity of gas-phase products also decreased. Therefore, a lower concentration of methane is favourable for achieving a higher yield of C₂ products as well as a higher conversion of methane.

2.3.5. The effect of the addition of hydrogen

Fig.12 shows the changes in the yield of products by the addition of hydrogen to the mixture of methane and argon, where the hydrogen was mixed by methane with molar ratio of $\text{CH}_4/\text{H}_2=1$ and then fed to the DBD plasma reactor.

Fig 12. The yield of products affected by the addition of hydrogen to the mixture of methane and argon. γ -alumina packed downstream of the DBD plasma. Total flow rate=50 ml/min, $\text{CH}_4=2.5$ ml/min, $\text{H}_2=2.5$ ml/min mixed with argon, Voltage = 7-8kV, $f = 23$ kHz, $P = 7-8$ W, T (downstream of the plasma) = 400 °C.

According to Fig.12, the conversion of methane decreases from 38.1% to 31.0% by the addition of hydrogen. This is due to the presence of hydrogen molecules, which can be easily reduced to hydrogen radicals, which in turn increases the concentration of H radicals in the plasma zone, higher than what is obtained by the dissociation of methane to CH_x fragments ($\text{CH}_4 \leftrightarrow \text{CH}_x + (4-x) \text{H}$). As a consequence, considering Le Chatelier's principle, in order to counteract the excess generated H, the methane dissociation reaction follows the backward reaction (i.e., recombination of H with CH_x fragments) to re-form methane, which therefore

reduces the rate of methane dissociation. Although the addition of hydrogen can decrease the conversion of methane, in contrast, the addition of hydrogen has a positive effect in reducing the deposits yield from 18.8% to 11.3%. It should be mentioned that the addition of H_2 also facilitates hydrogenation reactions and therefore it influences the distribution of C_2 and C_3 products. In this case, a lower amount of unsaturated compounds such as ethylene and propylene is obtained, as they are very likely to go through hydrogenation reactions to form alkanes such as ethane and propane, as can be seen in Fig.12.

2.4. Conclusions

Methane was converted to C_2 , C_3 and hydrogen as the major gas-phase products by activation with a home-made DBD plasma reactor built during this study, operated at ambient temperature and atmospheric pressure. The formation of deposits was mainly observed on the inner surface of the dielectric quartz tube. The composition of the formed deposits was identified to possess a 1.8 molar H/C ratio, where it indicated that the formed deposits have a polymeric nature, as the content of hydrogen (60 at%) is remarkably higher than the content of carbon. In addition, UV-Vis spectroscopy revealed that most CH_x radicals de-excite to their ground state level of energy, upon leaving the plasma zone. Therefore the possibility of interactions of short-lived plasma activated species with the downstream packed bed becomes less, as the experimental results indicated that the presence of the catalyst supports packed bed downstream did not lead to a remarkable impact on the distribution of final products leaving the plasma zone. However, long-lived plasma species can still go through surface catalytic reactions downstream by interacting with a metal supported catalyst rather than a bare catalyst support, where the presence of metal can make the interactions between the long-lived plasma activated species and the catalyst stronger, leading to possible changes in the selectivity of the final products. The evaluation of process conditions such as residence time and methane concentration showed that a higher residence time and a lower concentration of methane are favourable for achieving a higher yield of C_2 products. It was also found that the addition of hydrogen has a positive effect in reducing deposits to a less amount, while it also changed the distribution of gas-phase products by promoting hydrogenation of unsaturated compounds like acetylene and ethylene towards a higher production of alkanes.

References

- [1] T. Ren, M. Patel, K. Blok, *Energy* 31 (2006) 425-451.
- [2] R. Horn, R. Schlögl, *Catal Lett*, 145 (2015) 23-39.
- [3] Intergovernmental Panel on Climate Change (2014), *Climate Change 2014, Synthesis Report*, Geneva.
- [4] G.E. Keller, M.M. Bhasin, *J Catal.*, 73 (1982) 9-19.
- [5] F.P. Larkins, A.Z. Khan, *Aust J Chem.*, 42 (1989) 1655-1670.
- [6] Y. Xu, X. Bao, L. Lin, *J Catal.*, 216 (2003) 386-395.
- [7] F. Papa, D. Gingasu, L. Patron, A. Miyazaki, I. Balint, *Appl Catal A: Gen.*, 375 (2010) 172-178.
- [8] T. Nozaki, K. Okazaki, *Catal Today.*, 211 (2013) 29-38.
- [9] X.S. Li, A.M. Zhu, K.J. Wang, Y. Xu, Z.M. Song, *Catal Today*, 98 (2004) 617-624.
- [10] H.L. Chen, H.M. Lee, S.H. Chen, Y. Chao, M.B. Chang, *Appl Catal B: Env.*, 85 (2008) 1-9.
- [11] P. Kasinathan, S. Park, W. Choi, Y. Hwang, J. Chang, Y. Park, *Plasma Chem Plasma Proc* 34 (2014) 1317-1330.
- [12] M. Młotek, J. Sentek, K. Krawczyk, K. Schmidt-Szałowski, *Appl Catal A: Gen.* 366 (2009) 232-241.
- [13] Y. Yang, *Plasma Chem Plasma Proc.*, 23 (2003) 283-296.
- [14] T. Nozaki, T. Hiroyuki, K. Okazaki, *Energy & Fuels.*, 20 (2006) 339-345.
- [15] M. Dors, T. Izdebski, M. Tański, J. Mizeraczyk, *Eur Chem Bull.*, 3 (2010) 798-804.
- [16] M. Yu, L.Y. Zhai, Q. Zhou, C.P. Li, X.L. Zhang, *Appl Catal A:Gen.*, 419-420 (2012) 53-57.
- [17] S.H. Kado, K. Urasaki, Y. Sekine, K. Fujimoto, T. Nozaki, K. Okazaki, *Fuel.*, 82 (2003) 2291-2297.

- [18] H. Zhou, J. Watanabe, M. Miyake, A. Ogino, M. Nagatsu, R. Zhan, *Diamond Rel Mater.*, 16 (2007) 675-678.
- [19] O. Khalifeh, H. Taghvaei, A. Mosallanejad, M.R. Rahimpour, A. Shariati, *Chem Eng J.*, 294 (2016) 132-145.
- [20] N. Rueangjitt, T. Sreethawong, S. Chavadej, H. Sekiguchi, *Plasma Chem Plasma Proc.*, 31 (2011) 517-534.

Chapter 3

The synergistic effect of Pd/ γ -alumina catalyst and the DBD plasma reactor in the post-plasma catalysis configuration

In this chapter, the integration of the DBD plasma reactor with Pd/ γ -alumina catalyst bed packed downstream of the plasma is discussed and evaluated in different process conditions. Methane is converted to C_2 and C_3 compounds as well as H_2 in the plasma zone. Subsequently, downstream of the plasma zone, all generated compounds as well as H_2 molecules interact with Pd/ γ -alumina at ambient conditions. Among all components generated in the plasma zone, unsaturated species such as C_2H_4 and C_2H_2 , which are still potentially reactive, as well as long-lived C_xH_y plasma species leaving the plasma can go through further chemical reactions by interacting with Pd active sites downstream. Results indicate that at the presence of Pd/ γ -alumina, the selectivity of C_2 and C_3 compounds is enhanced, which is accompanied with the reduction of deposits selectivity. It is found that the additional formation of C_2 and C_3 products are routed via the interaction of plasma activated species like C_2H_y and C_3H_z with the downstream catalyst, where the long-lived C_xH_y plasma species could live sufficiently long until they reach the catalyst and thus become hydrogenated by reacting with H_2 (i.e., earlier generated by methane decomposition in the plasma) on the surface of the Pd catalyst, resulting in a higher production of C_2 and C_3 hydrocarbons and therefore a lower formation of deposits. This will be further discussed by presenting the dominant reaction pathways for the possible routes for the extra production of C_2 and C_3 compounds via successive Pd-catalyzed hydrogenations of long-lived plasma species towards alkane production.

3.1. Introduction

The integration of catalyst and plasma is generally applied by two configurations, dependent on the position of the catalyst: *post-plasma catalysis* (i.e. catalyst downstream of the plasma; PPC) and *in-plasma catalysis* (i.e. catalyst inside the plasma; IPC). The performance of both PPC and IPC reactor configurations depends on the lifetime of plasma activated species. Short-lived activated species can demonstrate synergy in integration with catalyst surfaces only in the IPC configuration where catalyst and plasma species are interacting *in situ*. Long-lived activated species can still remain sufficiently reactive even when they exit the plasma zone. Thus these reactive species can be combined with a downstream catalyst to go through surface reactions even at low temperatures, due to paving part, or even all of the energy barrier via pre-activation in the plasma zone [1-3].

Conversion of methane with a post-plasma catalysis configuration has been addressed in some studies. Huu et al.[4,5] reported oxidative conversion of methane with Pd/ γ -alumina at elevated temperatures, which could show that the synergy between plasma and catalyst improves the overall conversion of methane. Their studies could demonstrate the advantage of utilizing a two-stage process for oxidative conversion of methane, where the sequential activation of methane by plasma and catalysts leads to a higher yield of products than using only the plasma activation or only the thermal catalytic activation. However, Huu et al. have not clearly discussed or proposed whether the synergy is due to the interaction of long-lived species with the catalyst.

Fe₂O₃-CuO catalyst has been packed downstream of a DBD plasma reactor to evaluate the oxidative conversion of methane to synthesize methanol, as reported in two studies [6,7]. These works demonstrate that most plasma activated species were short-lived and recombined to their stable forms upon leaving the plasma zone. Although authors explained that the

improvements are due to the synergy between the plasma and the catalyst, still the interaction of long-lived plasma components with catalyst was not specifically addressed in their reports.

In summary, in the existing literature, a limited number of works have studied the conversion of methane in a two-stage plasma catalyst system (i.e., post-plasma catalysis configuration). However, the importance and the involved mechanism for the interaction of long-lived plasma activated species and the downstream catalyst have not been fully addressed and therefore this topic merits further investigations.

In this chapter, the integration of Pd/ γ -alumina packed downstream of the DBD plasma and their synergy via the interaction of long-lived plasma species and the catalyst bed are discussed and evaluated in different process conditions. Furthermore, the reaction pathways for the activation of methane and the generation of hydrocarbons and deposits are elaborated in detail, considering the interactions of long-lived plasma species with the Pd catalyst downstream. It should be noted that most of the existing works have studied the conversion of methane via oxidative route for the integration of plasma and catalyst in the PPC configuration, but the present study focuses on the non-oxidative route for methane activation, for those reasons explained earlier in Chapter 2.

3.2. Experimental

3.2.1. Materials and characterizations

The γ -alumina (surface area: 234 m²/gr) and Pd (5wt%)/ γ -alumina (surface area: 157 m²/gr) were supplied from Alfa Acer. The surface area of the samples, mentioned inside the brackets for each material above, was measured with nitrogen physisorption at 77 K (Surface area and Porosity Analyzer, TriStar, Micrometrics).

3.2.2. Experimental setup

The experimental setup and the plasma generation and diagnostics have been explained in detail in Chapter 2. All experiments in this chapter were carried out close to room temperature, where the temperature rise above room temperature was caused by a small amount of heat generated in the plasma, as explained in Chapter 2.

3.3. Results and discussion

3.3.1. The effect of packing Pd/ γ -alumina at different distances downstream of the DBD plasma on the conversion and the selectivity

Fig.1 represents the performance of Pd/ γ -alumina catalyst packed at 1 and 5 cm downstream of the plasma. The results were compared with those obtained for the blank reactor and the experiment used bare γ -alumina packed downstream of the plasma to clarify the effect of the presence of the Palladium for Pd/ γ -alumina.

The results show that packing bare γ -alumina as well as Pd/ γ -alumina downstream of the plasma did not remarkably influence the conversion of CH₄. This is due to the configuration of post-plasma catalysis, in which the presence of a catalyst downstream of the plasma does not influence the plasma discharges, as they are processed in two distinct zones. In addition, the downstream catalyst is operated very close to room temperature, for which a catalytic methane conversion is not expected.

Fig.1. The performance of Pd/ γ -alumina packed at 1 cm and 5 cm downstream of the plasma zone as a function of time compared to the blank and the packed DBD plasma reactor packed with bare γ -alumina: (a) methane conversion; (b) ethane selectivity; (c) propane selectivity; (d) other hydrocarbons selectivity; (e) deposits selectivity. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, V = 7-8 kV, f = 23 kHz, P = 7-8 W, ambient conditions for the catalyst bed downstream of the plasma.

In contrast, according to Fig.1 (b) and (c), a notable increase was observed for the selectivity of ethane from 17% to 35% and propane from 9% to 16%. A part of the increase towards higher amounts of alkanes was sourced from hydrogenation of C₂ and C₃ unsaturated hydrocarbons in the presence of the Pd catalyst, as no C₂H₂, C₂H₄ and C₃H₆ were detected by the GC connected to the outlet of the reactor. The other part of the increase in the selectivity of

the gas-phase products has originated from the decrease in the selectivity of the non-volatile products (i.e., deposits), as can be seen in Fig.1 (e). Varying the distance from 1cm to 5cm between the plasma zone and the Pd catalyst bed shows a slight effect, where a shorter distance is beneficial for achieving a higher selectivity of gas-phase products including C₂, C₃ and C₄₊ products, correspondingly conforming with the decrease in the selectivity of deposits for 1 and 5cm distances. This will be further discussed below in detail to indicate the route for the increases in the selectivity of the gas-phase products, due to the presence of Pd active sites.

All changes in the distribution of products were observed merely in the presence of the Pd catalyst, whereas no change was observed for the reactor packed with bare γ -alumina downstream and the blank reactor. More in detail, a quantitative analysis was supplemented to elaborate the route for the increase of gas-phase products production, which is related to the reduction of deposits.

Fig.2. The comparison in the selectivity of C₂, C₃, other hydrocarbons (C₄₊) and deposits for the blank and the packed reactor with bare γ -alumina and Pd/ γ -alumina after 1 hour reaction at ambient conditions. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, V = 7-8 kV, f = 23 kHz, P = 7-8 W.

Fig. 2 shows a graphical comparison of the selectivity of C₂, C₃, other hydrocarbons (C₄+) and deposits for the blank and the reactor packed with bare γ -alumina and Pd/ γ -alumina after 1 hr reaction, all at a similar methane conversion of 40% for a better comparison. As depicted in Fig.2, results for the packed reactor with γ -alumina were similar to those obtained for the blank reactor, which therefore were merged in one section in Fig.2.

To specify in Fig.2, the summation of "C₂H₂, C₂H₄ and C₂H₆" compounds and the summation of "C₃H₆ and C₃H₈" compounds, respectively, are quantified as the selectivity of C₂ and C₃ hydrocarbons. For Pd/ γ -alumina, the quantities are based on the calculated selectivity of C₂H₆ and C₃H₈ as all C₂ and C₃ unsaturated hydrocarbons were hydrogenated with the Pd catalyst downstream of the plasma.

Fig.2 demonstrates that the selectivity of the deposits decreases from 50 $\pm$ 1% to 39 $\pm$ 2% for the DBD plasma reactor packed with the Pd catalyst, accompanied with an extra formation of C₂, C₃ and C₄+ compounds. The decrease in the formation of deposits corresponds with the increase in the selectivities of ethane (3% more), propane (5% more) and other hydrocarbons (4% more) for the packed reactor with the Pd catalyst.

It should be noted that in the case of no interaction between long-lived plasma species and the Pd catalyst, the C₂ and C₃ selectivity should be equal to the summation of all C₂ and C₃ species, produced for the blank experiment including the saturated and unsaturated compounds. The only change would be within the distribution of C₂ compounds (C₂H₂, C₂H₄, C₂H₆) as well as C₃ compounds (C₃H₆, C₃H₈), whereas all unsaturated compounds are hydrogenated by the Pd catalyst to form an extra amount of alkanes. In other words, in the case of no interaction, the C₂H₆ and C₃H₈ selectivity should not exceed from the summation of the selectivity of all saturated and unsaturated compounds, produced earlier in the plasma zone.

Surprisingly, the increase in the formation of C_2H_6 and C_3H_8 is more than what could result from complete hydrogenation of C_2H_2 , C_2H_4 and C_3H_6 (i.e., formed in the plasma) with the Pd catalyst, which is in line with the reduction of deposits formation. This indicates that the extra amount of gas-phase products are formed via the interaction of those radicals that are responsible for the formation of downstream deposits. In this case, these C_xH_y precursors which can be consumed for the formation of deposits, instead, interact with the Pd catalyst and proceed via hydrogenation reactions towards production of alkanes rather than becoming polymerized to form deposits. It can then be stated that the total increase in the formation of alkanes is attributed to the hydrogenation of alkenes and alkynes (C_2H_2 , C_2H_4 , and C_3H_6) plus hydrogenation of C_xH_y long-lived activated species, which results in an extra formation of alkanes.

To further explain this, deposits are formed via gaseous intermediates, so-called C_xH_y precursors. The additional alkanes, more than stoichiometric hydrogenation of unsaturated compounds, are formed via the hydrogenation of highly reactive intermediates (i.e., long-lived activated species such as C_2H_x , C_3H_y , etc.) on the surface of the Pd catalyst by reacting with dissociated molecular H_2 (i.e., earlier generated by methane decomposition in the plasma zone), opening new reaction pathways towards an extra formation of C_2 and C_3 hydrocarbons. The details of the reaction pathways for the hydrogenation of long-lived plasma species will be discussed in section 3.3.5 of this chapter.

To summarize the above discussion, it can be stated that the presence of the Pd catalyst downstream of the plasma has two functions: (i) the hydrogenation of unsaturated hydrocarbons (i.e., formed in the plasma), (ii) the reduction of deposits formation via hydrogenation of C_xH_y long-lived activated species, instead of being polymerized to deposits.

It should be noted that most hydrogen produced in the plasma zone exit in the form of hydrogen molecules, because H radicals (i.e., generated in the plasma by e.g., $CH_4 \rightarrow CH_3 +$

H) are very reactive and tend to recombine to H_2 molecules, upon exiting the plasma zone. This can also be seen in the spectra obtained from UV-Vis spectroscopy for inside and afterglow of the DBD plasma, as presented in chapter 2, Fig.8, where the absorption peak obtained for the molecular H_2 exhibited a higher intensity in the afterglow of the plasma compared to the peak observed for the molecular H_2 inside the plasma.

3.3.2. Analysis of the yield and the rate of deposits formation

Fig.3 (a) and (b) represents the yield as well as the rate of deposits formation versus time, calculated based on the amount of CH_4 consumed for the formation of deposits.

Fig.3. (a) The yield of deposits; (b) the rate of deposits formation for the packed reactor with bare γ -alumina and Pd/ γ -alumina. Total flow rate = 50 ml/min, CH_4 concentration = 5 %, V = 7-8 kV, f = 23 kHz, P = 7-8 W.

These results indicate that the yield (conversion $\times$ selectivity) as well as the rate of deposits reduce when Pd/ γ -alumina is utilized downstream of the DBD plasma. This reduction reaches to 20% lower than the amounts obtained for the blank reactor and the reactor used bare γ -alumina as the downstream packing. This further supports the interaction of long-lived activated species with palladium, which leads to a lower formation of deposits.

It should be noted that a slightly higher yield of deposits can be observed for the experiment with packing γ -alumina in comparison with the blank reactor in the beginning of the reaction time, however this slight difference is not stable with time and ultimately becomes similar to the values achieved for the blank reactor. This can be attributed to a slightly higher

conversion of methane which can therefore reflect in the yield of deposits. On the other hand, the surface of γ -alumina is not sufficiently reactive at room temperature in order to adsorb long-lived plasma activated species as well as to dissociate hydrogen molecules and thus the interaction of species with γ -alumina does not result in a shift within the distribution of products. This can be physically observed in Fig.4, where a very thin layer of deposits is formed at the beginning of the γ -alumina bed. Correspondingly it was discussed in chapter 2 that γ -alumina only adsorbs acetylene (C_2H_2), when elevated temperatures ($\geq 400^\circ C$) were applied; however, even applying high temperatures over the γ -alumina bed only results in the deposition of unsaturated compounds like C_2H_2 , where no enhancement in the formation of C_2 and C_3 gas-phase products can be obtained.

Fig.4. The formation of deposits downstream and on the beginning of γ -alumina bed downstream of the plasma

3.3.3. The effect of input power

In order to see the effect of different input powers on the interaction of plasma species with the Pd catalyst downstream of the DBD plasma, different discharge powers were applied. Fig.5 depicts the conversion and selectivity of products versus discharge power, varied from 3 to 16 W in the presence of Pd/ γ -alumina packed downstream of the plasma. The increase of the

discharge power from 3 to 16 W corresponds to the variation of specific energy density (energy input/total flow rate) from 3.6 to 19.2 kJ/L at a total flow rate of 50 ml/min.

Methane conversion increased from 28% to 51% following with an increase in the selectivity of deposits from 37% to 51% and a decrease in the selectivity of ethane from 40% to 26%, by increasing the discharge power from 3 to 16 W. No alkenes and alkynes were detected by varying the input power as they were hydrogenated on the Pd catalyst.

Fig.5. The methane conversion and the selectivity of products versus the discharge power for Pd/ γ -alumina packed at 1 cm downstream of the plasma. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, $f=23$ kHz, ambient conditions for downstream of the plasma.

In general, increasing the discharge power can generate a higher density of energetic electrons (i.e., obtained from ionization of CH₄) which can further accelerate the C-H bond activation in methane molecules; however, on the other hand, these energetic electrons can in turn change the distribution of primary CH_x radicals (i.e., obtained from the dissociation of CH₄), which are the precursors for the formation of C₂ products via recombination reactions.

This therefore changes the selectivity of C_2 products, as can be seen in Fig.5 for the selectivity of C_2H_6 which shows a decreasing trend by increasing the discharge power. From this, it can be stated that a higher concentration of energetic electrons can thus increase the probability of collisions between electrons and CH_3 radicals, accelerating hydrogen abstraction, which reduces CH_3 radicals to CH_2 and CH and C radicals and consequently a lower selectivity of C_2H_6 (i.e., obtained from recombination of CH_3 radicals) is achieved. In addition, increasing the input power simultaneously produces a higher concentration of H radicals, corresponding to a higher rate of methane dissociation. As a consequence, a higher concentration of H radicals further accelerates the interactions of H radicals with CH_x and C_2H_y radicals ($CH_x, C_2H_y + H \rightarrow CH_{x-1}, C_2H_{y-1} + 2H$), promoting dehydrogenation reactions.

To further elaborate this, C_2 plasma species (e.g., C_2H_5 , C_2H_3 , C_2H) can go through two reaction pathways at different level of discharge powers. One reaction pathway ends to the formation of C_2H_2 , C_2H_4 , C_2H_6 by recombination with one H radical, and thus it is expected to occur when moderate input powers are applied, which generates a medium with a lower concentration of H radicals. The other reaction pathway becomes dominant in a relatively higher discharge power, which consumes C_2 plasma species by the abstraction of H radicals as well as dehydrogenation of C_2 products. Considering the increasing trend of deposits selectivity, as shown in Fig.5, it can be stated that increasing the input power, a part from increasing the methane conversion, also leads to a greater possibility of dehydrogenation reactions by collision of energetic electrons as well as H radicals with C_1 and C_2 plasma species towards a larger production of those radicals, which are responsible for the formation of deposits.

Fig.6. The selectivity of C₂ gas-phase products and deposits versus the discharge power for Pd/γ-alumina packed at 1 cm downstream of the plasma. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, f = 23 kHz, ambient conditions for downstream of the plasma.

In order to see the effect of interaction of long-lived activated species at different plasma input energies, the selectivity of C₂ gas-phase products and the selectivity of deposits are compared with the blank reactor and the reactor packed with the Pd catalyst downstream of the plasma, as shown in Fig.6.

According to Fig.6, for all applied input powers, the C₂ selectivity for the experiment with the downstream catalyst is higher than in the experiment only operated with the DBD plasma. Correspondingly, a lower selectivity of deposits can be seen in comparison with the blank reactor. This would further support the existence of the interaction of C_xH_y long-lived activated species with the Pd catalyst, which gives rise to the reduction of deposits towards a higher formation of C₂ hydrocarbons.

3.3.4. The effect of residence time

The lifetime of plasma species is a key parameter in creating the possibility of efficient interactions between plasma species and catalyst surfaces, before they lose their reactivity or become de-excited to their ground state level of energy. In this case, the time which is spent by the flux of plasma activated species (i.e., generated in the plasma zone) to reach the catalyst bed downstream of the plasma highly impacts the possibility of efficient interactions of these species with the downstream catalyst. Different total flow rates (25, 50, 75, 100 ml/min) were applied in order to influence the residence time of plasma activated species that pass through the volume between the plasma zone and the catalyst bed packed at 1 cm downstream of the DBD plasma. Fig.7 shows the changes for the conversion of methane as well as for the selectivity of the products for different residence times.

Fig.7. The methane conversion and the selectivity of the products versus residence time. Pd/ γ -alumina packed at 1 cm downstream of plasma. CH₄ concentration = 5 %, V = 7-8 kV, f = 23 kHz, P = 7-8 W, ambient conditions for downstream of the plasma.

As can be seen in Fig.7, methane conversion increases from 23% to 65% by increasing the residence time from 75 millisecond to 300 millisecond. Therefore, at a higher residence time methane molecules collide with high energy electrons for a longer time, and as a result, a higher level of conversion can be obtained. Moreover, increasing the residence time significantly changes the selectivity of deposits and C_2H_6 . A considerable decrease is obtained for the selectivity of deposits from 61% to 31% with decreasing the residence time. In contrast, C_2H_6 selectivity increases from 21% to 41% by decreasing the residence time from 300 milliseconds to 75 milliseconds. The selectivity of C_3 and other hydrocarbons products are not influenced by the variation of the residence time.

These results indicate that the distribution of C_2 products and deposits can be largely manipulated by the variation of the residence time. All of the formed species inside the plasma, including primary radicals (e.g., CH_3 , CH_2 , CH) as well as secondary radicals (e.g., C_2H , C_2H_3 , C_2H_5), have the chance to collide with high energy electrons, when they are exposed to plasma environment for a longer time. These additional collisions among plasma components change the distribution of CH_x and C_2H_y radicals, whereas the interaction of high energy electrons with CH_x and C_2H_y radicals for a longer time enhance the abstraction of H radicals from these species before they go through recombination reactions to form stable C_2 products. This indicates that a higher residence time gives a lower concentration of CH_3 radicals, due to changing the distribution of CH_x radicals in such a way that CH_3 radicals can be converted to CH_2 and CH radicals, by hydrogen abstraction reactions. As a consequence, a lower concentration of CH_3 radicals leads to a lower formation of C_2H_6 molecules. Furthermore, even the formed unsaturated compounds, like C_2H_4 and C_2H_2 , are likely to be dehydrogenated via successive interactions with high energy electrons and with abundant H radicals (i.e., generated by dissociation of CH_4 molecules) to form radicals like C_2H_3 and C_2H . Thus, in addition to

C₂H₆, unsaturated compounds like C₂H₄ and C₂H₂ can be also consumed as the precursors for deposits formation.

3.3.5. Reaction pathways

In principle, methane activation in non-thermal plasma is initiated by collision of electrons with CH₄ molecules, upon applying high voltages and the generation of a strong electromagnetic field, where free electrons are accelerated by increasing their kinetic energy. The gained kinetic energy is transferred to CH₄ and taking into account the level of the energy gained by free electrons (low, medium or high), the activation of CH₄ can be initiated in different modes including vibrational excitation, electron impact ionization and electron impact dissociation.

Low energy electrons can vibrationally excite methane molecules by increasing the kinetic energy of CH₄ molecules, however this excitation energy is not sufficient to break C-H bonds. The threshold energy for vibrational excitation of CH₄ is lower than 1eV, which is much less than the energy required for electron impact dissociation of methane ($\geq 9\text{eV}$) in a non-thermal plasma [8]. High energy electrons with an input of 9-14 eV energy are required in order to be able to dissociate methane to CH_x fragments via collisions with CH₄ molecules. It should be noted that a limited number of high energy electrons also contribute to the ionization of CH₄ and Ar ($\geq 12\text{eV}$), which is substantial to sustain the plasma discharges. However, the adsorbed energy in a non-thermal plasma is mainly distributed into dissociation reactions rather than into ionization reactions.

In non-thermal plasma, the energy adsorbed by plasma discharges can highly influence the distribution of primary radicals generated by electron impact dissociation of methane (CH₃, CH₂, CH, C), considering the amount of energy transferred to methane molecules during the collisions. In this case, the distribution of final products can be also significantly affected, depending on the way the plasma discharges are generated as well as the energy per pulse of

the discharge. Commonly, in DBD plasma the energy per pulse of the discharge is below 0.1 mJ. Therefore, DBD discharges mainly generate electrons with an average energy within the range of 1-10 eV, which can provide sufficient energy for the dissociation of methane to a major production of CH₃ radicals [9,10]. Other fragments like CH₂ and CH are also produced, however, with a notably lower amount than CH₃ radicals.

In this study, DBD plasma was generated with a mixture of CH₄ and Ar. Generally, Ar atoms can adsorb the energy of free electrons easier than methane molecules within the plasma discharges, which also leads to a lower breakdown voltage, due to small recombination rates of metastable/ionized argon atoms (Ar*, Ar+) [11,12]. Subsequently, the received energy by Ar atoms can be transferred to CH₄ molecules by collisions with metastable Ar*. This occurs via Penning ionization reactions, which lead to the generation of excited and ionized CH₄ molecules as well as the dissociation of CH₄ to CH_x radicals. As a result, the addition of Ar can enhance average electron energy as well as electron density which results in a higher conversion of methane. Consequently a higher conversion of methane leads to a higher yield of products [17].

Dissociation of CH₄ molecules in dielectric barrier plasma discharges is initiated by simultaneous production of CH₃, CH₂, CH and C radicals, as shown in reactions 1-4 [13]. These radicals go through subsequent radical chain reactions by recombination to form C₂ compounds, following the reactions 5-8 [14,15], presented below:

Electron impact dissociation:

Recombination:

Further radical chain reactions occur inside the plasma discharges to form C₃ compounds via interactions of primary radicals (e.g., CH₃) and secondary radicals (e.g., C₂H₅), as specified in reactions 9 and 10:

Subsequently, interactions of primary radicals with C_2 and C_3 radicals in plasma discharges produce C_{4+} hydrocarbons. However, the main products are hydrogen, C_2 and C_3 products and the contribution of C_{4+} compounds in final products is very small. Further radical chemistry can be involved in the production of C_2 and C_3 products with rather complex reaction mechanisms [15]. However, those are not discussed here, as the present study aims at investigating the synergy of plasma and catalyst and thus the discussions are focused on the dominant reaction pathways, considering the experimental results obtained during the present study.

Experimental results indicated that C_2H_6 and C_3H_8 are the major hydrocarbon products in comparison with the unsaturated products, like C_2H_2 , C_2H_4 and C_3H_6 . In addition to the recombination reactions, the dehydrogenation of C_2H_6 and C_3H_8 may also contribute into a small production of unsaturated hydrocarbons (e.g., C_2H_2 , C_2H_4 , C_3H_6). However, dehydrogenation reactions demand a higher energy for H radical abstraction reactions. Increasing the energy input could be favourable for enhancing the abstraction of H radicals, however it may lead to the formation of the deposit-precursor radicals, like C_2H_3 , C_2H , leading to a higher production of deposits. Correspondingly, Fig.5 and Fig.7 in the previous sections indicated that exposing the methane and other components to plasma discharges with a higher energy input or for a longer time, results in shifting the distribution of radicals (e.g., CH_3 , C_2H_5) to a higher concentration of those radicals responsible for the formation of deposits (e.g., CH , C_2H_3 , C_2H), which are generated by consecutive H abstractions from CH_3 and C_2H_5 radicals. Accordingly, a lower concentration of CH_3 and C_2H_5 radicals leads to a lower production of alkanes like C_2H_6 and C_3H_8 and a higher formation of deposits.

The experimental results show that the formation of deposits takes place both inside as well as in the afterglow of the DBD plasma. As discussed in section 3.1, Fig.2, this study

proposes that the formation of solid products downstream of the plasma mainly occurs via the deposition of long-lived species such as C_2H_x , C_3H_y , etc. This is different than those precursors consumed to form the deposits layer inside the plasma zone, as CH_x fragments can also contribute in the formation of deposits layer. Consistently, UV-Vis spectra for inside and afterglow of the DBD plasma showed that the concentration of CH_x fragments is less in the afterglow of the DBD plasma compared with the number of the peaks detected for the excitation of CH bands inside the DBD plasma, as presented in Chapter 2, Fig.8, which is also in agreement with the decrease in the formation of deposits, when Pd/ γ -alumina was used as the downstream catalyst, as depicted in Fig.2 of this chapter.

Fig.8. The proposed reaction pathways for coupling of methane to C_2 and C_3 hydrocarbons in DBD plasma.

Fig.8 proposes the key reaction pathways for coupling of methane to C_2 and C_3 hydrocarbons as well as the possible route for the formation of deposits, downstream of the plasma. According to this scheme, the initial step is the evolution of CH_3 via dissociation of C-H bond of methane molecule. Subsequently CH_3 radicals dimerize to form C_2H_6 . At the same

time, interactions of high energy electrons with the formed species can further abstract H radical from C_2H_6 to generate C_2H_5 radicals. The radical propagations continue and C_3H_8 is produced by recombination of CH_3 and C_2H_5 radicals.

In addition to the dimerization of CH_2 and CH radicals to form C_2H_4 and C_2H_2 , dehydrogenation of C_2H_5 and C_2H_3 radicals and their interactions with CH_3 radicals are also considered as the possible intermediate steps in the formation of alkenes and alkynes including C_2H_4 , C_2H_2 and C_3H_6 . These formed alkenes and alkynes can be potentially consumed as the precursors (e.g., C_2H_x , C_3H_y), participating in the formation of the deposits downstream of the plasma. Thus, according to the pathways depicted in Fig.8, the C_xH_y gaseous intermediates like C_2H_3 , C_2H , C_3H_5 , C_3H_4 are considered as long-lived species (i.e., pre-formed in the plasma zone), which have the potential to form downstream deposits when no packing is utilized. It should be mentioned that CH_x radicals also contribute to the formation of deposits but mainly inside the plasma rather than to deposits formed downstream. This is attributed to their short lifetime in such a way that they are unable to stay reactive and thus recombine to their stable gaseous forms, upon exiting the plasma zone [14]. This was also discussed in a study by Nozaki et al. [16] where the lifetime of CH_x fragments was estimated to be within the range of nanoseconds to microseconds, which is substantially shorter than the lifetime of C_2 species which was proposed to lie within the range of microseconds to milliseconds.

According to the experimental results, the interaction of long-lived species with the catalyst bed becomes less when a longer distance of 5cm is used for the location of the downstream packing compared to the 1cm distance. To compare, the time that C_xH_y long-lived activated species pass through the gap between the tip of the HV electrode and the Pd catalyst bed is estimated for distances of 1cm and 5cm. The values are 150 milliseconds and 750 milliseconds, respectively, for distances of 1cm and 5cm downstream of the DBD plasma, for a total flow rate of 50 ml/min. Taking into account the existence of the interactions in both

distances, the present study also proposes that the lifetime of long-lived species lies within the range of milliseconds, consistent with the study of Nozaki et al.

After passing through the volume between the tip of the HV electrode and the packed bed, C_xH_y plasma species reach to Pd/ γ -alumina downstream of the plasma. Simultaneously, H_2 molecules, generated by methane decomposition in the plasma zone, interact with palladium active sites, leading to dissociation of H_2 to H radicals. This therefore creates a medium where the dissociated H_2 can react with long-lived C_xH_y species, via hydrogenation reactions. The existence of abundant H radicals attached to the surface of palladium catalyst can effectively proceed successive hydrogenations of these unsaturated species until they transform to saturated hydrocarbons such as C_2H_6 and C_3H_8 . For instance, a series of hydrogenation reactions can be initiated by hydrogenation of C_2H radicals with the H radicals adsorbed on the surface of the Pd catalyst, which results in the formation of C_2H_6 :

These interactions are responsible for an extra amount of alkane production, higher than complete hydrogenation of unsaturated compounds, accompanied with a decrease in the formation of deposits. In this case, C_xH_y long-lived activated species become hydrogenated by plasma-generated H_2 on palladium active sites, instead of being polymerized to form deposits. In other words, the downstream catalyst enhances the rate of recombination of C_xH_y long-lived species with H radicals, remarkably faster than the rate of their oligomerization to form deposits. Thus it can be stated that the synergy between the plasma and the downstream catalyst originates from the interaction of long-lived plasma species with Pd/ γ -alumina, as these species are sufficiently reactive in order to be catalysed by palladium at ambient conditions.

3.4. Conclusions

Pd/ γ -alumina was packed at different distances of 1cm and 5cm downstream of the DBD plasma reactor, and the products distribution was evaluated for different process conditions. The experimental results indicate that C_2H_x and C_3H_y plasma reactive species, responsible for the formation of deposits downstream of the plasma, are long-lived species that are able to interact with the Pd catalyst downstream of the plasma and react with H_2 molecules that previously were generated by the decomposition of CH_4 in the plasma zone and subsequently are dissociated to H radicals on the surface of the Pd catalyst. Successive hydrogenations of these long-lived species with dissociated H_2 resulted in an extra production of C_2 and C_3 hydrocarbons, higher than what would result from complete hydrogenations of olefins and acetylene, which were earlier formed in the plasma zone. This additional formation of alkanes corresponded with the reduction of the deposits. Therefore, it was concluded that a synergy exists between the plasma and the downstream Pd catalyst, whereas the presence of Pd catalyst enhances the hydrogenation of C_xH_y long-lived plasma species towards a higher formation of alkanes, instead of being consumed as the precursors for the formation of deposits, when no packing was utilized.

References

- [1] H.L. Chen, H.M. Lee, S.H. Chen, Y. Chao, M.B. Chang, *Appl Catal B: Env* 85 (2008) 1-9.
- [2] M. Młotek, J. Sentek, K. Krawczyk, K. Schmidt-Szałowski, *Appl Catal A: Gen.* 366 (2009) 232-241.
- [3] Y. Yang, *Plasma Chem Plasma Proc* 23 (2003) 283-296.
- [4] T. Pham Huu, L. Sivachandiran, P. Da Costa, A. Khacef, *Top Catal* 60 (2016) 326-332.
- [5] T. Pham Huu, S. Gil, P. Da Costa, A. Giroir-Fendler, A. Khacef, *Catalysis Today.*, 257 (2015) 86–92.
- [6] L. Chen, X. Zhang, L. Huang, L. Lei, *Chem. Eng. Technol.*, 33 (2010) 2073–2081.
- [7] L. Chen, X. Zhang, L. Huang, L. Lei, *Chemical Engineering and Processing*, 48 (2009) 1333–1340.
- [8] M. Scapinello, E. Delikonstantis, G. D. Stefanidis, *Chemical Engineering & Processing: Process Intensification*, 117 (2017) 120–140.
- [9] X.S. Li, A.M. Zhu, K.J. Wang, Y. Xu, Z.M. Song, *Catal Today.*, 98 (2004) 617-624.
- [10] Y. Yang Y, *Ind Eng Chem Res*, 41 (2002) 5918-5926.
- [11] O. Khalifeh, H. Taghvaei, A. Mosallanejad, M.R. Rahimpour, A. Shariati, *Chem Eng J.*, 294 (2016) 132-145.
- [12] N. Rueangjitt, T. Sreethawong, S. Chavadej, H. Sekiguchi, *Plasma Chem Plasma Proc.*, 31 (2011) 517-534.
- [13] S. Kado, K. Urasaki, Y. Sekine, K. Fujimoto, T. Nozaki, K. Okazaki, *Fuel.*, 82 (2003) 2291-2297.
- [14] R. Snoeckx, R. Aerts, X. Tu, A. Bogaerts, *J Phys Chem C.*, 117 (2013) 4957- 4970.
- [15] C. De Bie, B. Verheyde, T. Martens, J. van Dijk, S. Paulussen, A. Bogaerts, *Plasma Process Polym.*, 8 (2011) 1033-1058.
- [16] T. Nozaki, N. Muto, S. Kado, K. Okazaki, *Catalysis Today*, 89 (2004) 57-65.

[17] S. K. Jo, D.H. Lee, W. S. Kang, Y.H. Song, Physics of Plasma, 20 (2013) 083509.

Chapter 4

The synergy of DBD plasma and Pd/ γ -alumina catalyst integrated in the in-plasma catalysis configuration for non-oxidative coupling of methane

In this chapter, the coupling of methane is investigated using DBD plasma reactor with Pd/ γ -alumina catalyst packed inside the plasma discharges. The differences in the performance of bare γ -alumina packed DBD reactor in comparison with Pd/ γ -alumina packed DBD reactor for different loadings of Pd (0.5, 1, 5 wt%) are elaborated in detail. Different process conditions including input power, residence time, methane concentration and plasma volume are applied to evaluate the effect of each of them on the conversion and the distribution of the products. Results indicate that packing Pd/ γ -alumina inside the plasma discharges, even with low amounts of Pd (0.5 wt% and 1 wt%), creates a barrier against the formation of deposits, leading to a notable increase in the yield of C_2 compounds in comparison with the blank reactor as well as the packed reactor with γ -alumina. It is evidenced that low amounts of Pd are more favorable for a higher formation of unsaturated compounds like C_2H_4 . A higher loading of Pd leads to a higher formation of alkanes like C_2H_6 , as it enhances successive hydrogenations of unsaturated compounds like C_2H_4 and C_2H_2 to form C_2H_6 . It is presented that the distribution of C_2 products as well as the formation of deposits can be largely influenced by the variation of process conditions, showing optimum points for the yield of C_2H_4 , C_2H_6 as well as the yield of deposits. Moreover, it is found that the existing synergy of the DBD plasma and the catalyst improves the energy efficiency of the process by 48% compared to the blank reactor. Reaction pathways are discussed considering the differences obtained for the distribution of the products for the blank and for the packed reactor. At the end, the synergy of plasma and catalyst and their mutual impacts is elaborated considering the obtained experimental results.

4.1. Introduction

Non-thermal plasma techniques have been extensively employed for the production of value-added products including hydrogen, hydrocarbons, oxygenates (e.g., methanol) and aromatics at ambient conditions [1]. Operating at ambient conditions gives a unique opportunity in order to take advantage of non-thermal plasma to transfer electrical energy to chemical energy by using the energy of electrons to activate stable molecules, such as methane. However, the gas-phase plasma reactions occur via a free radical mechanism [2] and are not efficiently selective to desired products. The integration of reactive plasma species (e.g., radicals) with catalyst surfaces can result in gaining control over the selectivity of the desired products and consequently improving the efficiency of the process [3]. In other words, the plasma provides the required energy for activation of the stable molecule to form radicals. Subsequently, the catalyst can be a medium that is capable of controlling the interaction among these radicals, selectively conducting reaction pathways towards more value-added products.

Different types of plasma discharges have been utilized in integration with catalyst surfaces including corona, spark, gliding arc and dielectric barrier discharge (DBD) [4-10]. Among all these non-thermal plasma approaches for activation of methane, dielectric barrier discharge (DBD) is one of the plasma techniques that has attracted attention for its versatility in combination with catalyst surfaces. The catalyst particles can be adaptively incorporated into DBD plasma discharges in two common configurations: post-plasma catalysis (i.e., catalyst downstream of the plasma; PPC) and in-plasma catalysis (i.e., catalyst inside the plasma; IPC). The performance of both PPC and IPC reactor configurations depends on the lifetime of plasma activated species. Short-lived activated species can demonstrate synergy in integration with catalyst surfaces only with IPC configuration where catalyst and plasma species are interacting *in situ* [11]. Most plasma activated species by DBD plasma are short-lived [19], therefore in-

plasma catalysis configurations have been more extensively studied for the integration of catalyst and DBD plasma.

Catalyst supports, such as alumina, silica and titania [7,12,13] with or without metals, such as Pt, Ni, Cu, Ru, were utilized for coupling of methane via a non-oxidative route in combination with DBD plasma reactors [8,10,14-16]. Previous studies attempted to mainly investigate the influence of the synergy on the formation of C₂ species, however, the separate role of metal and support and their synergy with DBD plasma is not fully clarified. In addition, the formation of deposits has been reported in these studies, but it was not clearly discussed how the catalyst can influence the formation of deposits. Therefore, the mechanism needs to be further studied for a better understanding of the effect of catalyst on the performance of DBD plasma reactors. Commonly, DBD plasma reactors are operated at ambient conditions. On the other hand, catalysts usually need to be activated by applying a temperature comparatively higher than ambient temperature; however, among all metals, Pd has the capability to catalyze surface reactions even at ambient temperature [28]. Therefore, Pd was selected to be used as the metal catalyst for the present study with γ -alumina as the catalyst support.

In this chapter, the interaction of DBD plasma species with γ -alumina as well as with Pd/ γ -alumina in different loadings of Pd is evaluated. The synergy between plasma and catalyst is discussed in terms of methane conversion, selectivity of C₂ compounds as well as the selectivity of deposits. Different process conditions are applied to tune the distribution of products, in particular maximizing the formation of C₂ compounds, while minimizing the formation of deposits at the presence of the catalyst. The energy efficiency of the implemented DBD plasma reactor is calculated for comparison with the performance of the plasma reactor at the presence and absence of the catalyst. Moreover, reaction pathways are discussed and the

role of the catalyst in shifting the reaction pathways and its synergy with plasma is further elucidated.

4.2. Experimental

4.2.1. Materials and characterizations

The γ -alumina (surface area: 234 m²/gr), Pd (5wt%)/ γ -alumina (surface area: 157 m²/gr, dispersion 24.0%, 4.7 nm Pd particle size), Pd (1wt%)/ γ -alumina (surface area: 160 m²/gr, dispersion 27.7%, 4.1 nm Pd particle size) and Pd (0.5wt%)/ γ -alumina (surface area: 159 m²/gr, dispersion 25.3%, 4.4 nm Pd particle size) were obtained from Alfa Aesar. The surface area of the samples was measured with nitrogen physisorption at 77 K (Surface area and Porosity Analyzer, TriStar, Micrometrics). CO-chemisorption (ChemiSorb 2750, Micrometrics) was utilized to measure the metal dispersion and particle size of the Pd catalysts. The values for the surface area and Pd particle size are given above, inside the brackets for each catalyst.

4.2.2. Experimental setup

The experimental setup and the procedure of the experiments including the packing and the plasma generation and diagnostics have been explained in detail in Chapter 2. All experiments in this chapter have been performed at ambient conditions.

4.3. Results and discussion

4.3.1. The effect of packing on plasma electrical parameters

Results indicate that packing the discharge gap with catalyst particles influences the plasma electrical parameters such as applied voltage, discharge power and the characteristics of discharges, which can be seen in Lissajous figures.

Fig.1 shows the applied voltage and discharge power during the plasma conversion of methane with the blank reactor and the packed reactor with γ -alumina and Pd/ γ -alumina inside the plasma discharges. For all experiments, the average discharge power was kept in the range of 7-8 W, by applying a high voltage (7-9kV) generated by the power supply during the experiments, which was measured by the high voltage probe, as shown in Fig.1 (a).

Fig.1. The effect of packing on applied voltage and discharge power for the blank reactor and the packed reactor with γ -alumina and Pd/ γ -alumina with different loadings of Pd (0.5, 1, 5 wt%) on the DBD plasma reactor: (a) applied voltage (kV); (b) discharge power (W); Total flow rate = 50 ml/min, CH_4 concentration = 5 %, f = 23 kHz.

According to Fig.1 (a), a higher voltage (8.5-9 kV) is required when the plasma gap is packed with catalyst, instead of 7.6 kV for the blank reactor, in order to keep the level of the plasma power in the range of 7-8 W. It is known that solid materials possess a relatively higher dielectric constant than gas molecules. Therefore, packing materials inside the discharges will affect the plasma behaviour, as the presence of the solid particles changes the electrical parameters of the plasma, for instance the capacitance. Due to the presence of γ -alumina, the

capacitance of the electrical circuit is influenced, which consequently impacts the voltage across the packed bed [29].

In comparison with γ -alumina, the Pd γ -alumina packed bed reactor needs the same range of applied voltage as the bare γ -alumina packed reactor, as can be seen in Fig.1 (a). However, a different trend is observed for the values of discharge power, in particular for bare γ -alumina. According to Fig.1 (b), γ -alumina can generate a stronger electric field for plasma discharges at the start of the plasma reaction, thus giving rise to a greater discharge power in comparison with the blank and the packed reactor with the Pd catalysts up to 1 hr of the reaction time. However, after 1hr the discharge power for γ -alumina follows a descending trend, where still the same voltage is applied. This can be attributed to the formation of carbon-containing deposits on the surface of γ -alumina, in a remarkably higher amount than on the Pd catalyst. These deposits can disturb the formation of discharges in the case of γ -alumina. The other reason is related to the possible conductivity of the deposits, as also indicated in previous studies [13]. The presence of carbon in the deposits can influence the electrical impedance of the DBD reactor, by short-circuiting the electric field over the γ -alumina particles, leading to a relatively lower strength of the electric field. This can become a different case, when Pd particles are dispersed on γ -alumina. The presence of Pd conductive particles moderates the strength of the electric field and facilitates the expansion of plasma discharges as well as the charge transfer across the catalyst bed. Similarly the enhancement of the charge transfer was concluded in a study by Tu et al. [32] for the effect of the conductivity of Ni, on γ -alumina, after being reduced by H₂/Ar DBD discharges. In this way, it can be stated that the coverage of γ -alumina with Pd facilitates the transfer of the charges and therefore a more stable trend for the discharge power can be achieved during the reaction in comparison with the γ -alumina packed reactor. This is the case for all Pd/ γ -alumina catalysts with low to high loadings of Pd (0.5, 1, 5wt%).

Fig.2 depicts the comparison of Lissajous figures for the blank reactor and for the packed reactor with γ -alumina and the Pd catalysts. The shape of Lissajous figure changes from parallelogram form to an oval form, when the discharge gap is packed with the catalyst. This change for the Lissajous figure can be attributed to the change in the way that plasma discharges are formed. Typically, plasma discharges form following a filamentary pattern, when high voltages are applied to the gap between the high voltage electrode and the ground electrode. Packing this gap with catalyst particles changes the filamentary formation of discharges into a situation with more formation of surface discharges, as discharges pass through the catalyst particles (i.e., packed between the high voltage and the ground electrode) and not directly from the high voltage electrode to the ground electrode in the forms of filaments, which are typically observed in non-packed DBD reactors [17,34].

Fig.2.The effect of packing on Lissajous figures

In packed-bed DBD plasma reactors (PBRs), the discharge volume is occupied with catalyst particles and thus the space for the formation of filamentary discharges decreases. As a result, discharges are mainly generated over the catalyst surface and at contact points of catalyst particles, rather than the gap between particles. This change leads to different characteristics of plasma discharges such as a different value of the breakdown voltage and the shape of the Lissajous figures, as can be seen in Fig.2. These results indicate that packing γ -alumina inside the discharges can slightly decrease the breakdown voltage from 1.8 kV (i.e., obtained for the blank reactor) to 1.7 kV (i.e., for the packed reactor with γ -alumina).

Packing the discharge gap with solid materials can result in a lower breakdown voltage and furthermore a stronger electric field, which consequently influences the conversion and the selectivity; however, this highly depends on the dielectric property of the utilized materials as well [13,17,24]. This will be further elucidated in Chapter 5 as well.

According to Fig.2, the breakdown voltage increases when γ -alumina is loaded with Pd reaching to 2.1 kV, due to the conductivity of Pd particles which can induce a higher amount of charge to be transferred over the surface. On the other hand, it needs a higher threshold voltage to overcome the burning voltage of the PBR and as a result the strength of the electric field decreases compared to bare γ -alumina, causing a lower conversion of CH_4 for Pd/ γ -alumina packed reactor compared to the packed reactor with bare γ -alumina. This will be discussed in the following section in combination with the conversion and the selectivity of the products.

4.3.2. The effect of packing γ -alumina and Pd/ γ -alumina on the performance of the DBD plasma reactor

Fig.3 represents the conversion of methane and the selectivity of C_2 products for the DBD plasma reactor packed with γ -alumina and Pd/ γ -alumina with different loadings of Pd (0.5, 1, 5 wt%) inside the DBD plasma discharges.

Packing bare γ -alumina inside the plasma discharges improves the conversion of methane in comparison with the blank DBD plasma reactor. This occurs due to the accumulation of high energy electrons on the surface of the packing, in particular near contact points of the particles, where the gap spaces are smaller. In this way, the energy adsorbed in plasma discharges increases and consequently a higher amount of energy is transferred to methane molecules, which leads to a higher conversion of methane. However, this improvement changes with time as can be seen in Fig.3 (a), because of the formation of deposits on the surface of γ -alumina.

Fig.3. The effect of packing the DBD plasma reactor with γ -alumina and Pd/ γ -alumina with different loadings of Pd (0.5, 1, 5 wt%): (a) methane conversion; (b) acetylene selectivity; (c) ethylene selectivity; (d) ethane selectivity; Total flow rate = 50 ml/min, CH₄ concentration = 5 %, V = 7-9 kV, f = 23 kHz, P = 7-8 W.

Gadzhieva et al. [18] studied the dissociation of methane in a plasma induced medium, packed with γ -alumina using diffuse scattering IR spectroscopy. In agreement with the results of the present study, γ -alumina showed a positive effect in enhancing the conversion of

methane; however for a longer exposure of γ -alumina to methane plasma, the formation of deposits was observed, weakening the transmittance of the IR system. It was further explained that the exposure of γ -alumina to plasma discharges generates new active sites for the adsorption of excited methane molecules. These active sites are capable to store the energy of plasma components (e.g., electrons, radicals, ions) and consequently transfer it to methane molecules. Thus, methane is dissociated into CH_x fragments with a higher conversion in comparison with using only plasma activation. However, it should be noted that this explanation mainly shows the effect of γ -alumina as a dielectric material with capability of intensifying the electric field rather than as a catalyst, which can conduct the reaction pathways towards the formation of desired products. In other words, the effect of the dielectric property of γ -alumina is more dominant in influencing the conversion of methane than its catalytic activity.

Due to the presence of Pd, as discussed in the previous section, a relatively lower electric field is formed for the Pd/ γ -alumina packed bed DBD reactor, which then yields a relatively lower conversion of methane in comparison with the bare γ -alumina packed bed reactor. This can be further explained by considering that the conversion of methane can be proportionally influenced by manipulating the strength of the electric field in non-packed DBD reactors [15]. This becomes a different case for the PBR, where the conductivity of metal (e.g., palladium) on a dielectric support (e.g., γ -alumina) moderates the strength of the electric field to a relatively lower value, which results in a lower conversion of CH_4 .

As discussed in Chapter 2, the formation of carbonaceous solid materials on the high voltage electrode, inner surface of the dielectric quartz tube as well as on the catalyst surface (i.e., for those experiments that used a packing) gradually influences the intensity of the electric field formed by the discharges in such a way that it leads to a decreasing trend for the conversion of CH_4 , as shown in Fig.3. This can be further attributed to the increase of the

resistivity of the plasma electrical circuit, due to the formation of deposits that contain conductive carbon species, which causes short-circuiting the electric field over the γ -alumina packed bed [13].

Fig.3 (b), (c) and (d) depict the selectivity of C_2 compounds including C_2H_2 , C_2H_4 and C_2H_6 . It can be observed that the distribution of C_2 compounds is strongly influenced by the presence of the catalyst. In the case of packing with γ -alumina, the distribution of C_2 products shifts towards a higher formation of unsaturated compounds like C_2H_2 and C_2H_4 . The recombination reactions of CH_x radicals (i.e., generated by dissociation of methane) are the predominant routes for the production of C_2 compounds like C_2H_2 , C_2H_4 and C_2H_6 [19]. However, the distribution of CH_x fragments (CH_3 , CH_2 , CH , C) can be influenced by packing dielectric materials inside the discharges as well as by varying process conditions. The higher formation of C_2H_2 , C_2H_4 implies that higher concentrations of CH_2 and CH are generated at the presence of γ -alumina inside the discharges. This is different in comparison with the blank reactor, where CH_3 radicals possess the highest concentrations and thus C_2H_6 becomes the major gas-phase product for the blank reactor. This shows that the strength of electric field is enhanced by packing γ -alumina particles. On the other hand, the surface reactivity of γ -alumina can also be influenced by exposure to the plasma, which results in shifting the distribution of radicals to form a higher amount of CH_2 , CH and C radicals rather than CH_3 radicals. Consequently, this shift within the distribution of CH_x fragments appears in the selectivity of C_2 products as well as in the selectivity of the deposits and yield of hydrogen, as shown in Fig.5.

One point to mention here is that the increase of the energy of plasma discharges due to the presence of γ -alumina does not only influence the distribution of primary CH_x radicals, but also influences the distribution of secondary C_2H_y radicals, as formed upon recombination of CH_x radicals. In this case, it is likely that a part of the increase in the formation of C_2H_2 and

C_2H_4 originates from the successive abstractions of hydrogen from C_2H_6 compounds, enhancing dehydrogenation of C_2H_6 to form C_2H_4 and C_2H_2 products.

In contrast to a lower selectivity of C_2H_6 achieved by packing γ -alumina, at the presence of Pd even with a low amount of 0.5wt%, the selectivity of C_2H_6 considerably increases. This is accompanied by a lower selectivity of deposits, as shown in Fig.5 (a). Results indicate that this notable increase of C_2H_6 selectivity is sourced from two pathways. The first pathway is favourable for successive hydrogenations of unsaturated compounds like C_2H_4 and C_2H_2 . The second pathway originates from the decrease in the formation of deposits, where the precursors, which can be consumed for the formation of deposits, instead, are consumed via catalytic surface reactions to form gas-phase products, comparably faster than their polymerization to deposits. In other words, a substantial amount of those species which are responsible for the formation of deposits are hydrogenated on the surface of the catalyst. This can be attributed to the capability of Pd active sites in promoting hydrogenation reactions, where the progressive sequence of hydrogenation reactions are dependent on the amount of Pd loading. Considering that all the Pd-loaded catalysts have similar dispersions as well as similar range of Pd particle sizes, thus the only variable for comparing the selectivity of the products in the Pd-loaded γ -alumina packed reactors is the amount of Pd loading.

To further explain, in the case of loading with 1wt% and 5wt% of Palladium, no C_2H_2 is formed. This becomes a different case when the amount of Pd loading changes to a lower amount of 0.5wt%, resulting in a higher production of C_2H_2 . According to Fig.3 (c), the selectivity of C_2H_4 can also be improved by choosing low contents of Pd, as obtained for Pd loadings of 0.5 and 1 wt%. Increasing the amount of palladium loading to 5% provides more active sites for successive hydrogenation reactions. In this case, not only C_2H_2 compounds but also C_2H_4 compounds have the chance to go through hydrogenation reactions to form saturated products like, C_2H_6 .

Fig.4 shows the selectivity of C_3 and C_{4+} products, where the formation of C_3H_8 is reduced at the presence of bare γ -alumina. The higher production of C_3H_6 follows the same explanation as discussed for a higher formation of unsaturated C_2 hydrocarbons above. The generation of a higher electric field by packing γ -alumina shifts the selectivity towards the production of unsaturated compounds by promoting the abstraction of H from CH_x and C_2H_y radicals, leading to a higher production of radicals like CH, CH_2 , C_2H , C_2H_3 rather than radicals like CH_3 and C_2H_5 . As a consequence, the distribution of C_3 compounds, which can be formed via the interaction of CH_x and C_2H_y radicals, shifts to produce more C_3H_6 rather than C_3H_8 .

Fig.4. The effect of packing the DBD plasma reactor with γ -alumina and Pd/ γ -alumina with different loadings of Pd (0.5, 1, 5 wt%): (a) propylene selectivity; (b) propane selectivity; (c) other hydrocarbons selectivity; Total flow rate = 50 ml/min, CH_4 concentration = 5 %, V = 7-9 kV, f = 23 kHz, P = 7-8 W.

This trend changes when Pd is added to the surface of γ -alumina. This enhances hydrogenation reactions, as it can be seen for the selectivity of C_3H_8 , which is returned almost to the same level as in the blank reactor. Fig.4 (c) depicts the selectivity of higher hydrocarbons (C_{4+}). According to these results, a lower amount of C_{4+} is produced when γ -alumina and Pd/ γ -alumina are packed in the reactor. This lower formation of C_{4+} is in line with a higher formation of C_2 compounds. This can be explained by the effect of packing on the distribution of primary radicals (CH_3 , CH_2 and CH) as well as secondary radicals (C_2H , C_2H_3 , C_2H_5). The C_3 and C_{4+} products are formed by reactions between CH_x and C_2H_y radicals, which are influenced by the presence of the packing particles in such a way that it reduces the formation of C_{4+} products. This can be explained by two reasons. First, the surface reactivity of Pd/ γ -alumina conducts the interactions between CH_x and C_2H_y radicals towards pathways which produce mainly C_2 and C_3 compounds on the surface and they subsequently desorb to the gas-phase. In other words, most radical chain reactions terminate before they have the chance to go through further interactions between C_2 and C_3 species on the surface. This therefore decreases the possibility of the formation of C_{4+} . The second reason that can be considered is that C_{4+} species are reduced to C_2 species via cracking reactions, occurring on the catalyst surface.

Fig.5 presents the selectivity of deposits as well as the yield of hydrogen. A higher formation of deposits on γ -alumina is achieved, originating from a higher conversion of methane compared to the blank reactor, as also depicted in Fig.3 (a). Similarly, a higher yield of H_2 is achieved, corresponding with the dissociation of CH_4 to CH_x and H radicals. It should be noted that, as it can be concluded from Fig.5 (a), although a stronger electric field is formed by packing γ -alumina, the energy of this electric field is also consumed for a higher production of deposits, whereas the generated strong electric field is more favourable for the production of CH_2 , CH , C radicals rather than CH_3 radicals. This then results in a higher formation of

acetylene (C_2H_2) and olefins (C_2H_4 and C_3H_6), but also accelerates the formation of those radicals that are responsible for the formation of deposits.

Fig.5. The effect of packing the DBD plasma reactor with γ -alumina and Pd/ γ -alumina with different loadings of Pd (0.5, 1, 5 wt%) on the DBD plasma reactor: (a) deposits selectivity; (b) hydrogen yield; Total flow rate = 50 ml/min, CH_4 concentration = 5 %, V = 7-9 kV, f = 23 kHz, P = 7-8 W.

The selectivity of deposits remarkably decreases at the presence of Pd on γ -alumina, accompanied with a lower yield of H_2 for Pd/ γ -alumina catalysts, as can be seen in Fig.5 (a) and (b). The results indicate that even with a low amount of Pd, the formation of deposits can be noticeably reduced. The lowest selectivity of deposits was 15%, achieved for Pd/ γ -alumina with 5 wt% of Pd loading, significantly lower than the selectivity in the blank reactor (47%). However, it should be noted that, in the case of 5 wt% loading of Pd, the formation of unsaturated hydrocarbons like C_2H_2 and C_2H_4 is minimized.

In general, C_2H_4 is considered a more preferred product than C_2H_6 because of its higher reactivity, which makes it a better feedstock in the petrochemical industry for the large production of valuable chemical products. Results indicate that, in addition to the beneficial effect of Pd in the reduction of deposits, its amount of loading is also of paramount importance, as it can be controlled in order to optimize the formation of C_2H_4 . This can be the case, when Pd/ γ -alumina with 1 wt% of Pd loading is used as the catalyst, as depicted in Fig.3 (c). In this

way, the selectivity of C_2H_4 is greater than the one obtained in the blank reactor, while the selectivity of deposits is remarkably reduced by this catalyst from 47% to 20% almost to a similar level as obtained for loading of 5wt% of Pd. More importantly, C_2H_4 for a Pd content of 1wt% is still produced with a selectivity higher than in the blank reactor. This becomes a different case when loading of Pd is 5wt%, which can easily hydrogenate C_2H_4 to C_2H_6 . Thus it is concluded that the selectivity of C_2 products, in particular C_2H_4 , is strongly dependent on the amount of Pd loading, where according to the presented results, 1wt% Pd/ γ -alumina is considered as the optimum catalyst, due to its high selectivity to C_2H_4 and C_2H_6 as well as its resistance to the formation of deposits.

Fig.6 shows the dielectric quartz tube after the experiments performed in the blank and the packed reactors. For the blank reactor, the formation of deposits was mainly observed on the inner surface of the dielectric quartz tube, as can be seen in Fig.6 (a). The yellowish deposits were still formed when γ -alumina was packed inside the discharge gap, but not as uniformly as formed in the blank reactor, which indicates that a part of deposits is then formed on γ -alumina. For the catalysts containing palladium, the formation of the yellowish deposits was not observed. This is in line with the substantial decrease in the formation of deposits as obtained for Pd containing catalysts. Despite the decrease of the selectivity of deposits from 46% (i.e., for the blank reactor) to 15-25% (i.e., for the packed reactor with Pd containing catalysts), the formation of deposits still takes place; however, they mostly form on the catalyst surface rather than on the inner surface of the dielectric quartz tube, as can be seen in Fig.6.

Fig.6.The formation of deposits on the inner surface of the dielectric quartz tube after plasma reaction; (a) the blank reactor; (b) the packed reactor with γ -alumina; (c) the packed reactor with 0.5 wt% Pd/ γ -alumina; (d) the packed reactor with 1.0 wt% Pd/ γ -alumina; (e) the packed reactor with 5.0 wt% Pd/ γ -alumina.

4.3.3. The effect of process conditions

1wt% Pd/ γ -alumina was considered the optimum catalyst, giving the highest formation of C_2 products, in particular C_2H_4 and C_2H_6 , accompanied with notable resistance to the formation of deposits, as explained in the previous section. Thus 1wt% Pd/ γ -alumina is evaluated under different process conditions including discharge power, residence time, methane concentration and plasma volume in order to investigate their effect on the conversion and on the yield of products as well as to find the underlying reasons for the shifts in the distribution of the products, caused by changes in each process condition.

4.3.3.1. The effect of discharge power

In this section, the effect of discharge power and its effect on the conversion and the selectivity of products at the presence of Pd/ γ -alumina is discussed. These results will give further insight into the possible reaction pathways, as changing the discharge power directly influences the dissociation of methane and the distribution of plasma species, in particular radicals, which thus influences the selectivity of the final products.

Fig.7. The effect of discharge power on the conversion of methane and the selectivity of products. 1wt% Pd/ γ -alumina packed inside the plasma discharges. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, f=23 kHz.

Fig.7 shows the changes for the conversion of methane and the selectivity of products by varying discharge power from 1.6W to 11.1W. The conversion of methane increases from 13% to 58% by increasing discharge power from 1.6W to 8.6 W. However, applying a higher energy input, up to 11.1 W does not change the conversion of methane. This can be explained by considering the formation of deposits on the catalyst surface. In a high amount of discharge power, the distribution of CH_x fragments is influenced in such a way that it promotes hydrogen abstraction from CH_3 and CH_2 radicals, giving rise to a higher production of C and CH radical. These radicals (i.e., C and CH) have the chance to interact with the catalyst and contribute to the formation of deposits, which contains a higher amount of conductive carbon species, which therefore can form a deposit layer with a relatively higher C/H ratio, increasing the conductivity of the formed deposits [20]. Therefore, the additionally applied energy input, provided by increasing the discharge power from 8W to 11W, mainly dissipates through the catalyst packed bed and the dielectric quartz tube, instead of being stored and transferred to the plasma discharges [30]. In this case, the conversion of methane is slightly affected by increasing the discharge power.

According to Fig.7, the variation of input power mainly influences the selectivity of deposits and C_2H_6 . On the other hand, the selectivity of deposits decreases from 45% to 27%, while the selectivity of C_2H_6 increases from 35% to 47%. It can be seen in Fig.7 that the selectivity of C_2H_4 is also influenced by varying the discharge power, however, not with the same impact as was obtained for the selectivity of deposits and ethane.

In order to further explain the effect of discharge power and obtain a better understanding of the effect of the catalyst on the performance of the DBD plasma reactor, the yields (conversion $\times$ selectivity) of C_2 products and deposits for the blank reactor and the packed reactor, are depicted in Fig.8. This comparison shows that Pd/ γ -alumina improves the yield of C_2 and reduces the yield of deposits, compared to the blank reactor. For the packed reactor with

Pd/ γ -alumina, increasing discharge power from 2.6 W to 11.1 W shows a considerable influence on the yield of C_2 products, causing a rise from 12% to 31%.

Fig.8. The yield of C_2 (a) and the yield of deposits (b) for the blank and the packed reactor with 1 wt% Pd/ γ -alumina packed inside the plasma discharges. Total flow rate = 50 ml/min, CH_4 concentration = 5 %, $f=23$ kHz.

In contrast, in the case of the blank reactor, the yield of C_2 remains almost unchanged, around $12 \pm 0.5\%$. On the other hand, the yield of deposits noticeably increases from 19% to 31%, by increasing the discharge power from 4.5W to 10.5W. From this, it can be concluded that increasing the discharge power, on one hand, can dissociate a larger number of CH_4 molecules to CH_x fragments, on the other hand it influences the distribution of CH_x fragments in the way that, by applying a very high discharge power, most of the extra converted CH_4 molecules mainly dissociate to CH_2 , CH and C radicals rather than CH_3 radicals. This therefore leads to a larger generation of C_2H and C_2H_3 radicals, which have a high potential to be consumed in the formation of deposits.

In other words, a higher conversion of methane can generate a greater number of energetic electrons as well as H radicals (i.e., obtained from the decomposition of methane). The interaction of these energetic electrons and H radicals accelerates the abstraction of H from C_2H_y radicals, which results in a higher production of C_2H_3 and C_2H radicals rather than C_2H_5 which can contribute in the formation of deposits. Thus it can be stated that in the case of the blank reactor, the extra energy input not only influences the distribution of CH_x fragments but

also accelerates the oligomerization of C_2H_y radicals to form deposits rather than their recombination with H radicals to form C_2 products.

This becomes a different case when the reactor is packed with Pd/ γ -alumina, as shown in Fig.8 (b). It can be clearly seen that Pd/ γ -alumina substantially reduces the yield of deposits. Particularly, at a high level of discharge power (11W), the yield of deposits decreases from 30% for the blank reactor to 16% for the packed reactor. This is accompanied with a substantial increase in the C_2 yield from 12% to 32%, which evidently shows the synergy between the plasma and the catalyst in all ranges of the applied discharge power.

Moreover, the yield of deposits for the packed reactor shows a maximum at a discharge power of 6W. This can be explained by two effects. First, increasing the power strengthens the effect of the plasma on the catalyst, by a direct plasma treatment that regenerates the activity of the catalyst in order to enhance hydrogenation and recombination reactions, towards promoting the formation of C_2 products rather than the formation of deposits. In this case, the plasma effect on the catalytic activity of the surface also accelerates the desorption of C_2 species into the gas-phase, before they become polymerized on the surface to form deposits. Second, increasing the power promotes the activity of Pd particles as well as modifies the catalyst surface in such a way that it can more actively reduce the formation of deposits. It was reported in a study by Cho et al. [33] that a proper formation of carbon-containing solid material on the catalyst surface can improve the catalytic activity. In that study, Pd-NiO/ Al_2O_3 in combination with a microwave plasma was evaluated for conversion of methane under vacuum conditions.

Fig.9. The yield of ethylene for the blank reactor and the packed reactor with 1 wt% Pd/γ-alumina packed inside the plasma discharges. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, f = 23 kHz.

The yield of C₂H₄ versus discharge power is depicted in Fig.9 for a further comparison. As discussed above, the selectivity of C₂ compounds did not considerably alter by varying the discharge power for the blank reactor, as depicted in Fig.8 (a). Following a similar trend for the blank reactor, the yield of C₂H₄ does not show a noticeable change by increasing the discharge power, according to Fig.9. However, in the case of the packed reactor, it can be seen that C₂H₄ yield shows a minimum, corresponding with a maximum for deposits yield, as depicted in Fig.8 (b). This can further indicate that C₂H₄ is one of the possible precursors for the formation of deposits, where its formation depends on the surface reactivity of the catalyst.

To explain this, Fig.10 depicts the rate of deposits formation for the blank reactor as well as for the packed reactor, for different discharge powers. The rate of deposits formation is lower for the packed reactor and follows a similar trend as the deposits yield, where the difference between the rates of deposits formation for the blank and the packed reactor increases by increasing the discharge power. As can be seen in Fig.10, when the discharge power reaches 11W, the rate of deposits formation becomes 22.5 mg/hr for the blank reactor, which is significantly higher than the value of 12.8 mg/hr obtained for the packed reactor.

Fig.10.The rate of deposits formation (mg/hr) for the blank reactor and the packed reactor with 1wt% Pd/γ-alumina packed inside the plasma discharges. Total flow rate = 50 ml/min, CH₄ concentration =5 %, f=23 kHz.

These results further indicate that the surface of the catalyst exhibits different catalytic and dielectric properties when it is covered with deposited materials. In addition, the amount of energy input influences the catalytic activity of Pd/γ-alumina, which alters the selectivity of the final products. This can be explained by considering the effect of the deposits on the conductivity of the catalyst surface, which can therefore enhance the charges transferred through the catalyst bed due to the formation of carbonaceous species on the surface, however, the formation of deposits, particularly in a high amount of discharge power, interrupts the stable formation of discharges as well as the efficient transfer of energy to methane molecules and other plasma components (e.g., CH_x, C₂H_y), therewith causing a gradually lower conversion of methane. In addition, the presence of deposits can affect the catalytic activity of the catalyst surface in the way that the mechanism of adsorption, surface reactions and desorption of the plasma species can be influenced, opening new reaction pathways, which therefore leads to a different distribution of the final products.

4.3.3.2. The effect of residence time

In this section, the effect of residence time is evaluated by applying different total flow rates of the mixture of methane and argon passing through the plasma zone. In general, the residence time indicates the time that methane and other plasma components (e.g., electrons, ions, radicals) are exposed to high energy electrons and reactive H radicals (i.e., generated by the dissociation of methane molecules) upon exposure to the plasma discharges.

The lifetime of plasma species plays a key role in determining the distribution of CH_x and C_2H_y radicals and consequently the selectivity of C_2 and C_3 products as well as the selectivity of deposits. In particular, the dissociation of methane is highly influenced by the residence time, as in the case of a shorter or longer exposure to the plasma zone, the formed products, like C_2 and C_3 compounds, can also go through additional interactions (e.g., via cracking reactions for a longer exposure) to form radicals, which can be further consumed as the precursors for the formation of deposits.

Particularly, C_2 hydrocarbons (C_2H_2 , C_2H_4 , C_2H_6) have a large tendency for polymerization to deposits [21]. The residence time can largely influence the interactions among C_2 species and as a consequence can change the selectivity of C_2 products. In other words, a longer exposure of C_2 compounds to high energy electrons and H reactive radicals can notably increase the chance of successive dehydrogenation reactions. This is due to a low activation energy of C_2 dehydrogenation reactions (1-2eV) [31], which can be provided by electrons or H radicals via interactions with C_2 species. However, it should be noted that the development of dehydrogenation reactions can lead to a higher concentration of C_2H_y radicals, like, C_2H_3 , C_2H which have a high potential to be consumed as the precursors for the formation of deposits. This can be depicted in a cascade manner as follows:

Thus it can be stated that all C_2 species can go through hydrogenation and/or dehydrogenation reactions reversibly. Therefore, the selectivity of C_2 products can be affected, where it is likely to control the formation of unsaturated hydrocarbons like C_2H_2 and C_2H_4 by finding the effect of residence time on the yield of products. In this way, with an optimum residence time, most C_2 species exit from the plasma zone before reducing to the precursors that can form deposits. Moreover, the presence of the catalyst can influence the way in which the residence time affects the selectivity of products. In other words, when the plasma discharges are packed with catalyst, the residence time can impact both the time that plasma species are exposed to the electric field, as well as the time that plasma species are interacting with the catalyst.

Fig. 11 shows the variation of methane conversion and the selectivity of products in 25, 50, 75 and 100 ml/min total flow rates, respectively, corresponding with residence times of 2.64, 1.32, 0.88, 0.66 s as well as specific energy inputs (power/total flow rate) of 18, 9, 6, 4.5 kJ/L for the packed reactor with Pd/ γ -alumina.

Fig.11. The methane conversion and the selectivity of the products versus total flow rates of 25, 50, 75 and 100 ml/min for 1wt% Pd/ γ -alumina packed inside the plasma. CH₄ concentration = 5 %, V = 8-9 kV, f = 23 kHz, P = 7-8 W.

By increasing the total flow rate from 25 to 100 ml/min, the conversion of methane remarkably declines from 53% to 19%. This is due to a shorter exposure of methane molecules to the plasma zone (i.e., a lower specific energy input) which dissociates a lower amount of methane to CH_x fragments. On the other hand, the selectivity of the products changes by the variation of the residence time. Specially, the selectivity of C₂ products as well as the selectivity of deposits were profoundly influenced. It can be clearly seen that changing the total flow rate from 25 ml/min (i.e., residence time of 2.64 s) to 100 ml/min (i.e., residence time of 0.66 s), results in a considerable increase for the selectivity of C₂H₆ from 24% to 53% and of the selectivity of C₂H₄ from 1% to 15%, corresponding with a notable decrease for the selectivity of deposits from 68% to 7%. The formation of other products (C₃ and C₄₊) were slightly

influenced by the variation of residence time, but much less than what was observed for the selectivity of C₂ products and the deposits.

This further indicates that a shorter residence time is favourable for the reduction of deposits, but on the other hand, at a shorter residence time, the conversion of methane drastically declines, which also influences the yield of C₂ products. For a better comparison, the yields of C₂ and deposits are plotted versus residence time in Fig.12.

Fig.12. The yield of C₂ and deposits versus residence time 1wt% Pd/ γ -alumina packed inside the plasma. CH₄ concentration =5 %, V= 8-9 kV, f=23 kHz, P=7-8 W.

According to Fig.12, by increasing the residence time from 0.66 s to 2.64 s, the yield of deposits increases from 1.3% to 35.9%. Interestingly, the yield of C₂ shows a different trend and reaches an optimum of 19.0% at a residence time of 1.32 s (i.e., total flow rate of 50 ml/min). This can be explained by the fact that the catalyst strongly influences the selectivity of the products, via adsorption of CH_x and C₂H_y plasma species as well as H reactive radicals on the surface. The abundance of H adsorbed on the surface increases the probability of recombination of H radicals with other adsorbed species. This intensifies the rate of

recombination reactions and reduces the rate of polymerization of CH_x and C_2H_y radicals on the surface.

From this, it can be implied that, at the optimum residence time, the ratio between “the rate of dissociation of methane to form C_2 products” to “the rate of overall conversion of methane to form all products” is maximum, whereas the formed C_2 products desorb from the surface and subsequently exit from the plasma zone, timely, before going through additional reduction reactions to form deposits.

4.3.3.3. The effect of methane concentration

The concentration of CH_4 in the feed entering the inlet of the DBD plasma reactor is one of the important parameters, affecting the overall performance of the process. It is known that the addition of a noble gas (i.e., argon for the present study) for activation of methane with DBD plasma discharges has a positive effect which can enhance energy transfer to methane molecules via an excited form of the noble gas (Ar^*). In addition, mixing methane with Ar in a high concentration can lower the breakdown voltage for the ignition of the plasma, in comparison with pure methane as the discharge gas. This is due to a low recombination rate of excited states of Ar, which leads to the activation of methane via Penning ionization reactions by collisions of metastable/ionized argon atoms (Ar^* , Ar^+) with methane molecules [22].

For these reasons, argon has been used as an additive gas for its positive role in activation of methane in DBD plasma in the present study. In addition, it should be noted that plasma activation of methane in pure methane or in a gas mixture with a high concentration of methane has the drawback of forming a drastic amount of carbon-containing deposits. In this case, the deposition of solid products inside the plasma zone can seriously disturb the formation of plasma discharges, which can consequently lead to a rapid extinguishing of the plasma as well. In addition, in case of the integration of DBD plasma discharges with catalyst particles, the formation of deposits in a large amount can notably influence the activity of the catalyst as well

as the sustainability of the plasma discharges, due to quenching of ionized and excited species on the surface of the catalyst [19]. As a result, from the application point of view of this process, the formation of deposits is not favourable, as it does not allow a long-term operation of the reaction.

The effect of CH_4 concentration on the conversion and the selectivity of the products was studied by applying different concentrations of 2.5%, 5%, 10% and 20% of CH_4 , mixed with Ar, at a similar amount of energy input, as shown in Fig.13.

Fig.13. The methane conversion and the selectivity of the products versus methane concentration of 2.5%, 5%, 10% and 20% for 1wt% Pd/ γ -alumina packed inside the plasma. Total flow rate= 50 ml/min, $V = 8-9$ kV, $f = 23$ kHz, $P = 7-8$ W.

The conversion of methane is strongly influenced by the variation of the CH_4 concentration. A dramatic decrease for the conversion of methane is observed from 55% to 9%, when the concentration of CH_4 in the input gas stream increases from 2.5% to 20%. It should be noted that the same amount of energy input was provided for all applied

concentrations of CH_4 . For this reason, at a higher concentration of methane, a smaller number of methane molecules was able to gain sufficient energy for scission of the C-H bond, leading to a drastically lower conversion. The selectivity of the products is affected by the variation of CH_4 concentration. Particularly, the selectivity of C_2H_6 shows a tendency to increase from 44% to 64%, when the concentration of CH_4 rises from 2.5% to 20%.

Fig.14. The yield of C_2 compounds and deposits versus methane concentration of 2.5%, 5%, 10% and 20% for 1wt% Pd/ γ -alumina packed inside the plasma. Total flow rate= 50 ml/min, $V= 8-9$ kV, $f=23$ kHz, $P=7-8$ W.

In contrast, the selectivity of deposits tends to decrease from 25% to 12% by increasing the CH_4 concentration from 2.5% to 20%. The selectivity of other products exhibits rather low changes. It should be noted that the selectivity of deposits can be reduced at higher concentrations of CH_4 , but the conversion of methane also lowers, as explained above. This leads, therefore, to a low yield of C_2 products for both C_2H_4 as well as C_2H_6 , which from an application perspective is not desirable. To further elucidate this, the yield of C_2 products and deposits are depicted versus the variation of CH_4 concentration in Fig.14.

According to Fig.14, by increasing the CH₄ concentration from 2.5% to 20%, the yield of C₂ products decreases from 29% to 6%. Similarly, the yield of deposits tends to decrease from 14% to 1%. However, the rate of the decrease in the yield of C₂ products is notably greater than the decrease of the yield of deposits. Thus the CH₄ concentration influences the yield of C₂ products with a relatively higher impact than the yield of deposits. On the other hand, a higher concentration of methane induces a lower electric field and consequently a lower dissociation of methane molecules, causing a lower generation of H radicals in the plasma zone. As a result, at a lower concentration of H radicals, the probability of reduction reactions for C₂ species ($C_2H_y + H = C_2H_{y-1} + H_2$) becomes smaller, owing to a smaller number of collisions between H radicals and C₂ species. For this reason, a lower amount of C₂ species is consumed as the precursors for the formation of deposits, leading to a lower yield of deposits. Therefore, the results indicate that it is preferred to activate methane in a mixture of CH₄ and Ar, where the concentration of methane can be kept low, as it is favourable to achieve a higher yield of desired C₂ products.

4.3.3.4. The effect of plasma volume

The performance of DBD plasma reactors can be highly influenced by their geometry including the diameter of the high voltage electrode, the discharge gap between the high voltage electrode and the dielectric quartz tube and the length of the ground electrode. Among all these parameters, the length of the ground electrode can be of paramount importance, as it determines the effective volume of the plasma, where the microdischarges are established. This can further influence the breakdown voltage as well as the strength of the electric field.

In addition, the contact time between high energy electrons and CH₄ molecules can be affected by varying the length of the ground electrodes, although in the case of a packed bed DBD reactor, this also influences the contact time between plasma activated species and the catalyst surface, which can therefore have an impact on the conversion of CH₄ molecules as

well. In addition to the effect of plasma volume in the propagation of plasma discharges across the catalysts bed, the selectivity of the products is also influenced considering that a shorter or a longer contact time influences the number of collisions among plasma-induced species like CH_x radicals as well as the formed products such as C_2 compounds (i.e., C_2H_2 , C_2H_4 , C_2H_6), which therefore increases the probability of changing the composition of radicals, leading to a different distribution of products. For instance, the formed C_2 products inside the plasma zone can go through further chemical reactions, reducing the C_2 products to radicals like C_2H , C_2H_3 , C_2H_5 [23], which can be potentially consumed for the generation of deposits. This therefore changes the composition of the plasma species which are interacting with the catalyst surface.

In order to investigate the influence of the plasma volume, the dielectric quartz tube was covered with three rigid stainless steel tubes, acting as the ground electrode, with different lengths of 2cm, 5cm and 10cm, which correspond, respectively, with different plasma volumes of 0.22mL, 0.55mL and 1.1mL as well as different residence times of 0.264 s, 0.66 s, 1.32 s, at a total flow rate of 50ml/min. These experiments were performed at the presence Pd/ γ -alumina, packed inside the discharge gap.

Fig.15. The applied voltage measured for three different lengths of 2cm, 5cm and 10cm used as the ground electrode for experiments with the blank reactor and the packed reactor with 1 wt% Pd/ γ -alumina. Total flow rate= 50 ml/min, $f=23$ kHz, $P=7-8$ W.

In order to compare the conversion and the selectivity of products at a similar level of energy input, the discharge power was kept in the range of 7-8 W for all three ground electrode lengths. According to Fig.15, for both the blank reactor as well as for the packed reactor, at a shorter length of the ground electrode, and therefore a smaller volume of the plasma, a higher voltage between the high voltage electrode and the ground electrode is needed in order to keep the same level of power input constant.

In addition, it should be noted that, independent of the volume of the plasma, the voltage induced between the high voltage electrode and the ground electrode is greater, when the discharge gap is filled with catalyst particles. The higher dielectric constant of the catalyst compared to a discharge gap filled with a gas increases the capacitance of the electric circuit of the plasma, which changes the breakdown voltage as well as the formation of discharges in the plasma region. The influence of the catalyst on the induced voltage becomes even greater, when a larger plasma volume is used. This can be seen in Fig.15, as the difference becomes larger at 10cm length of the ground electrode for the applied voltage of the blank reactor (7.6 kV) compared to the applied voltage for the packed reactor (9.0 kV).

The performance of the DBD plasma reactor in combination with Pd/ γ -alumina is shown for three different lengths of the ground electrode in Fig.16. The conversion of methane intensifies from 39% to 46%, when the length changes from 2cm to 10cm. This can be explained by the fact that a longer length of the ground electrode corresponds to a longer residence time. As a consequence, a larger number of methane molecules can be dissociated via collisions with high energy electrons and thus the conversion of methane intensifies.

Fig.16. The conversion of methane and the selectivity of products for three different lengths of 2cm, 5cm and 10cm used as the ground electrode for the packed reactor with 1wt% Pd/ γ -alumina. Total flow rate= 50 ml/min, f =23 kHz, P =7-8 W.

It should be noted that a larger volume of the plasma may limit the development of the discharges into the whole available free spaces of the plasma volume, where some spaces are not occupied by discharges. This is known as “partial discharging” in packed bed DBD plasma reactors (PBRs) [34], which can weaken the strength of the electric field and consequently decreases the conversion of methane. Partial discharging can be inhibited by applying a voltage sufficiently higher than the breakdown voltage in order to have the discharges fully covering the plasma volume. This will be further discussed in Chapter 5.

Therefore, it can be concluded that increasing the length has an overall positive effect on the conversion of methane, where a longer length of the ground electrode is favourable for achieving a higher conversion of methane.

Fig.17. The yield of C₂ compounds; (a) C₂H₂ yield; (b) C₂H₄ yield; (c) C₂H₆ yield for three different lengths of 2cm, 5cm and 10cm used as the ground electrode for the blank reactor and the packed reactor with 1wt% Pd/γ-alumina. Total flow rate= 50 ml/min, f=23 kHz, P=7-8 W.

The length of the ground electrode also influences the selectivity of the products. The selectivity of C₂ compounds as well as deposits is highly affected by the length of the ground electrode. As explained earlier in this chapter, C₂H₂ can be easily hydrogenated with Pd active sites to C₂H₄, even at a low amount of Pd (0.5wt%). Therefore, the main C₂ products are C₂H₄ and C₂H₆ in the case of the packed reactor with Pd/γ-alumina, which is different than the blank reactor, where in addition to C₂H₄ and C₂H₆, the amount of C₂H₂ is still considerable in the composition of the final products. Fig.17 shows the yield of each C₂ compound obtained for the blank and for the packed reactor.

From Fig.17 (a), it can be clearly seen that C₂H₂ is produced with an amount higher than C₂H₄, in the case of the blank reactor, and tends to increase by increasing the volume of the

plasma. In contrast, C_2H_2 yield remarkably decreases, when the reactor is packed with the catalyst, due to Pd-catalyzed hydrogenation of C_2H_2 to form compounds such as C_2H_4 and C_2H_6 . In addition, at a longer length, which implies a longer residence time for the interaction of plasma species with the catalyst, C_2H_2 is entirely consumed via hydrogenation reactions, resulting in no production of C_2H_2 .

Similar to C_2H_2 , the yields of C_2H_4 and C_2H_6 show an increasing trend in the case of the blank reactor, where at all lengths of the ground electrode, the yield of C_2H_6 is higher than unsaturated C_2 compounds, reaching to 8% at the length of 10cm. In the case of the packed reactor, the C_2H_6 yield increases to 20%, due to the presence of the catalyst.

Fig.18. The yield of C_2 compounds (a) and the yield of deposits (b) for three different lengths of 2cm, 5cm and 10cm used as the ground electrode for the blank reactor and the packed reactor with 1wt% Pd/γ-alumina. Total flow rate= 50 ml/min, $f=23$ kHz, $P=7-8$ W.

Although the yield of C_2H_6 becomes greater by packing Pd/γ-alumina inside the discharge gap, the yield of C_2H_6 exhibits a different trend, where there is a maximum C_2H_6 yield of 25% for a length of 5cm, in contrast with the results obtained for the blank reactor. Correspondingly, there is a minimum yield of C_2H_4 , where it reaches to 1% for a length of 5cm.

In order to clarify this, the summation of the yield of all C_2 compounds and deposits is shown in Fig.18. The results indicate that the formation of C_2 products as well as deposits

increases by enlarging the length of the ground electrode, where the C_2 and deposits yields reach 13% and 25%, respectively, at the length of 10cm, in the case of the blank reactor.

As Fig.18 shows, the C_2 yield increases to 22% at the presence of Pd/ γ -alumina, significantly greater than the 13% achieved for the blank reactor at 10cm length. Comparison of the results of Fig.17 and Fig.18 exhibits that the increase in the yield of C_2 originates mainly from the decline of the deposits yield. This decline is due to the presence of Pd, which enhances the recombination of C_2 species, like C_2H_3 and C_2H_5 with H radicals, before they are reduced to form deposits.

Similar to the trend observed for the yield of C_2H_4 , the deposits yield for the packed reactor also shows a minimum of 9% at the length of 5cm of the ground electrode. In this case, it can be stated that when the length of the ground electrode enlarges from 2cm to 5cm, which implies a longer residence time, a larger number of C_2H_4 molecules interact with the catalyst. In this case, the probability of the consumption of C_2H_4 via hydrogenation reactions increases, resulting in a higher amount of C_2H_6 . However, when the length of the ground electrode increases to 10cm, the values for the yield of C_2H_4 as well as the yield of deposits again rise, in an opposite manner to the decrease obtained for the yield of C_2H_6 at 10cm length.

From this, it can be stated that the surface reactions are reversible, where C_2H_6 which can be formed via hydrogenation of C_2H_4 as well as via hydrogenation of radicals such as, C_2H_3 and C_2H_5 (i.e., the precursors of deposits formation), can be also dehydrogenated to form C_2H_4 or other unsaturated species. By increasing the length of the ground electrode from 5cm to 10cm, which gives rise to a longer time for C_2H_6 molecules to reside in the plasma zone, it is likely that backward reactions proceed in such a way that C_2H_6 is reduced to form C_2H_4 as well as to form those radicals like C_2H_5 , C_2H_3 and C_2H , that are responsible for the formation of deposits. This means that employing a smaller or a larger volume of discharges can be used to manipulate the distribution of C_2 products, where they can be transformed into each other via

successive hydrogenation/dehydrogenation reactions and/or can be consumed (e.g., via reduction reactions). In other words, the rate of the hydrogenation reactions of C_2H_y species ($y \leq 5$) to form C_2H_6 on the catalyst surface can be manipulated in competition with the rate of the dehydrogenation reactions of C_2H_6 to form C_2H_y ($y \leq 5$), by varying the length of the ground electrode.

Among all C_2H_y ($y \leq 5$) species, it is strongly proposed that C_2H_4 is one of the key molecular intermediates that can be either consumed via Pd-catalyzed hydrogenation reactions to form C_2H_6 or can be produced via Pd-catalyzed dehydrogenation reaction of C_2H_6 . Furthermore, the catalytic activity of Pd particles on the surface of γ -alumina in combination with the DBD plasma discharges can provide a route to promote the production of C_2 products as well as the reduction of the deposits formation by establishing efficient interactions of plasma reactive species with the catalyst.

4.3.4 The energy consumption analysis

4.3.4.1. The effect of specific energy input (SEI)

In this section, an energy consumption analysis is discussed for the performance of the DBD plasma reactor with and without packing the catalyst. In order to compare the performance of the blank and the packed reactor, the conversion of methane as well as the yield of C₂ and deposits are shown in Fig.19 for different specific energy inputs. The specific energy input (SEI) is defined as the discharge power in the plasma divided by the total flow rate of the gas stream passing through the plasma.

Fig.19. The conversion of methane (a); the yield of C₂ compounds (b); the yield of deposits (c) versus specific energy input for the blank reactor and the packed reactor with γ -alumina and 1wt% Pd/ γ -alumina. Total flow rate= 50 ml/min, f=23 kHz.

According to Fig.19 (a), the conversion of methane increases for the blank reactor as well as for the packed reactor, by increasing the specific energy input (SEI). It can be observed from Fig.19 (a) that for a SEI below 4 kJ/L, the conversion of methane for the packed reactor, in particular for γ -alumina is lower than that in the blank reactor. The reason is attributed to “partial discharging” [34] which occurs when a low amount of energy input, which corresponds to a low voltage across the gap, is applied. In this case, plasma discharges do not entirely develop through all the discharge gap spaces and some spaces remain unfilled. Consequently a lower amount of charges are transferred across the gap for the packed bed reactor in comparison with the blank reactor. As a result, a weaker electric field forms for the packed reactor, which results in a lower amount of discharge power, causing a lower conversion of methane.

In contrast, the results indicate that a positive effect of the packing on the conversion of methane can be achieved, when SEI is more than 8 kJ/L. This effect can be explained by the fact that applying a higher voltage (8-9kV), which is significantly higher than the breakdown voltage (1.7kV), facilitates the propagation of plasma discharges throughout the catalyst bed, which can fill the entire space of the discharge gap. On the other hand, a complete establishment of the discharges in the whole plasma volume increases the capacitance of the DBD plasma reactor, which therefore generates a stronger electric field, particularly near contact points of the catalyst particles [15]. Furthermore, by increasing the specific energy input to greater values than 12 kJ/L, the conversion of methane for the packed reactor reaches 70% for γ -alumina and 58% for Pd/ γ -alumina, which is higher than the conversion of 53% obtained for the blank reactor. In this case, it can be stated that the synergistic effect of plasma and catalyst intensifies more profoundly in a higher specific energy input than in a lower one.

The results indicate that a stronger electric field can be formed when γ -alumina is packed inside the discharge gap, achieving a higher conversion of methane in comparison with Pd-

loaded catalyst. This can be attributed to the surface conductivity of the packed material. The surface of γ -alumina becomes conductive by loading Pd particles, leading to a relatively lower strength of the electric field for the Pd/ γ -alumina packed bed reactor. This has been also reported in previous studies, where the presence of conductive metals such as Pt [15] and Ni [25] moderates the strength of the electric field, yielding to a lower conversion of methane in comparison with the value obtained for the conversion of methane on the bare catalyst support (e.g., γ -alumina) packed bed DBD reactor.

The results for the yields of C_2 and deposits are shown in Fig.19 (b) and (c). The yield of C_2 exhibits a different trend for the reactor packed with Pd/ γ -alumina compared to the reactor packed with γ -alumina and the blank reactor. For Pd/ γ -alumina, C_2 yield increases by increasing SEI, where it reaches to 31% for SEI of 13 kJ/L. In contrast, in the case of the blank reactor as well as the packed reactor with γ -alumina, C_2 yield shows slight changes by increasing SEI. This can be seen in Fig.19 (b), whereas C_2 yield varies within a narrow range of 10-14%, when SEI increases more than two times, from 6 kJ/L to 13 kJ/L.

The results indicate that a significant improvement of C_2 yield for Pd/ γ -alumina, can be evidently attributed to the presence of Pd. Furthermore, the improvement of C_2 yield leads to a much lower yield of deposits, as shown in Fig.19 (c). It can be observed that the deposits yield for the Pd/ γ -alumina packed reactor tends to increase, when SEI increases to 7 kJ/L. Interestingly, applying a SEI of more than 7 kJ/L results in a much higher C_2 yield (31%), while the deposits yield remains almost constant at 16%. In contrast, the deposits yield for the blank reactor as well as for the packed reactor with γ -alumina shows a continuously ascending trend by increasing SEI, nearly proportional to the trend of methane conversion.

In addition, it should be noted that the deposits yield becomes higher in the case of packing γ -alumina, where it reaches 42% in a 13 kJ/L of SEI. This value is higher than the 30% obtained for the blank reactor in a similar level of SEI. This indicates that the dielectric property

of γ -alumina improves the strength of the electric field and consequently the conversion of methane, however, the surface of γ -alumina changes the distribution of CH_x as well as C_2H_y in such a way that it mostly intensifies the generation of radicals such as CH_2 , CH , C_2H , C_2H_3 rather than CH_3 and C_2H_5 radicals, which leads to a higher production of deposits. To conclude, the presence of Pd positively modifies the conductivity of the surface as well as the catalytic activity of the surface, whereas it drastically reduces the formation of deposits and correspondingly enhances the formation of C_2 products to a notably greater extent in comparison with the blank reactor.

4.3.4.2. The energy efficiency

The energy efficiency versus different specific energy inputs (SEI) is shown in Fig.20. These values were calculated by considering the high heat value (HHV) of the products and methane as well as the discharge power applied for the performed experiments, according to the following equation:

$$\text{Energy Efficiency \%} = \frac{\sum_{i=\text{product}}^n \text{HHV}(i) \times \text{molar flow rate}(i)}{\text{HHV of CH}_4 \times \text{molar flow rate of reacted CH}_4 + \text{Discharge Power}} \times 100$$

- i = product

-HHV(i) = High Heat Value of i (J/mol)

-Molar flow rate of i (mol/s)

-Discharge power (Watt)

For both the cases of the blank reactor and the packed reactor, energy efficiency tends to decrease by increasing SEI. In a low SEI of 2 kJ/L, the energy efficiency of the blank reactor is 13% which is higher than the one obtained for the packed reactor (8%). However, in a low SEI, the values for the conversion of methane as well as the yield of C_2 products are also very low, as presented in the previous section in Fig.19, which is not favourable for the productivity

of the process. Increasing SEI to higher values (≥ 4 kJ/L) causes a remarkable drop in the energy efficiency of the blank reactor, where it reaches 5% in a SEI of 13 kJ/L.

Fig.20. The energy efficiency versus specific energy input for the blank reactor and the packed reactor with γ -alumina and 1 wt% Pd/ γ -alumina. Total flow rate= 50 ml/min, $f=23$ kHz.

Packing the blank reactor shows a positive effect on the energy efficiency, at high values of SEI (≥ 4 kJ/L), for both packing with γ -alumina as well as Pd/ γ -alumina. However, this positive effect is considerably greater for Pd/ γ -alumina, due to the presence of Pd, which not only improves the yield of C_2 products and reduces the formation of deposits but also enhances the energy efficiency of the plasma reaction. In addition, the energy efficiency shows less variations by increasing SEI for the packed reactor. In the case of the packed reactor with γ -alumina, the energy efficiency lowers from 7.5% to 5.6%, when SEI increases from 6 kJ/L to 13 kJ/L. In a similar range of SEI, the energy efficiency for Pd/ γ -alumina changes from 9.7% to 6.9%. In comparison with the blank reactor, the energy efficiency was enhanced by 38% in the case of the packed reactor with Pd/ γ -alumina, where 4-14 kJ/L of SEI is applied. From this, it can be concluded that, in addition to the synergy between plasma and catalyst in improving the yield of the desired products, the integration of plasma and the catalyst can also lead to a

higher energy efficiency compared to using only DBD plasma for coupling of methane to C₂ hydrocarbons.

4.3.4.3. The comparison of the present study with the most promising literature results

In order to discuss the performance of the DBD plasma reactor for the present study, a comparison has been made with those studies, which are known as the most promising results for coupling of methane with DBD plasma reactors. In order to make this comparison, a recent review by Scapinello et al. [25] has been considered, which presents the performance of DBD plasma reactors for studies used a non-packed DBD reactor as well as for those used a packed DBD reactor for conversion of methane.

In general, it is difficult to compare the performance of DBD plasma reactors, considering that these reactors were designed in different configurations and the results were reported for operations under different applied process conditions. Various parameters such as applied voltage, flow rate, concentration, plasma volume and even the method of the measurements can effectively influence the comparison. Nevertheless, the cited review presents a number of research studies that utilized DBD reactors for non-oxidative coupling of methane to C₂ compounds, where authors attempted to give a fair overview of the existing literature.

Among all cited works in the review of Scapinello et al., three of these studies, which were able to obtain the highest values for the conversion of methane as well as the selectivity of the products, are considered for a comparison with the results obtained for the present study. Additionally, for a better understanding of the differences, more details about the applied process conditions of each study are included, as shown in Table 1.

Table 1 exhibits the comparison of the present study with the most promising ones, covering the range of the reported values for the conversion of methane, applied power, C₂ selectivity, carbon balance as well as the employed process conditions. The formation of

deposits has been reported for coupling of methane with DBD plasma in most existing works. Despite this fact, almost all studies in the literature have reported the selectivity based on only the gas-phase products and have not considered the formation of deposits within the calculation of the selectivity. This can be seen in the results for the carbon balance in Table 1, which is notably less than 100%, indicating that a part of the carbon, originating from the conversion of CH₄, is consumed in the formation of solid products.

Table 1. The performance of the DBD plasma reactor in the present study in comparison with the most promising results for non-oxidative conversion of methane in DBD plasma reactors in literature.

Study	CH ₄ Conversion%	Applied power	C ₂ selectivity%	Carbon balance %	Applied process conditions
Lu et al. [26]	20-47%	30-100 W	30-40% calculated based on only the gas-phase products	Not reported.	Total flow rate: 20-40 ml/min CH ₄ concentration: pure methane Plasma volume: 6.6 ml Residence time: 10.0-20.0 S Catalyst: no packing
Jo et al. [2]	11-14%	10.0-14.0 W	Only reported in applied power 14W: 45% calculated only based on the gas-phase products	Only reported in applied power 14W: 72%	Total flow rate: 336 ml/min CH ₄ concentration: 10% mixed with Ar Plasma volume: 4.0 ml Residence time: 0.71 S Catalyst: no packing
Kasinathan et al. [7]	9-23%	3.0-4.0 W	77-86% calculated only based on the gas-phase products	71-82%	Total flow rate: 200 ml/min CH ₄ concentration: 10% mixed with Ar Plasma volume: 6.6 ml Residence time: 10.0-20.0 S Catalyst: MgO/Al ₂ O ₃
The present study	13-58%	1.6-11.1 W	43-53% calculated including the gas-phase products and deposits	82-95%	Total flow rate: 25-100 ml/min CH ₄ concentration: 2.5-20% mixed with Ar Plasma volume: 0.22-1.1 ml Residence time: 0.26-2.64 S Catalyst: Pd/ γ -alumina

Lu et al. [26] reported the conversion of methane using a DBD plasma, where pure methane, without mixing with a noble gas such as Ar, was fed to the inlet of the reactor. It can be seen that quite a high amount of power (30-100 W) is needed to achieve rather low to medium values for the conversion of methane (20-47%). This is a different case when the flow of methane is mixed with Ar, enhancing an efficient transfer of energy to methane molecules, which therefore results in a lower input power for the activation of methane, as cited in Table 1 for the studies by Jo et al. [2] and Kasinathan et al. [7] as well as the present study.

The exhibited comparison indicates that the present study achieves a high conversion of methane at a relatively low amount of energy input. In addition, the introduction of the catalyst inside the discharge gap significantly improves the carbon balance to values within the range of 82-95%, which is higher than the carbon balance reported in studies by Jo et al. [2] and Kasinathan et al. [7]. C₂ selectivity is quite high (77-86%) in the work by Kasinathan et al., which can be attributed to the high total flow rate of 200 ml/min, which is favourable for achieving a higher selectivity of C₂ products. However, as was explained in section 4.3.2.2 of this chapter, at a higher total flow rate the conversion of methane also drops, leading to a lower yield of C₂ products.

It can be clearly seen that the performance of a DBD plasma reactor is highly influenced by the applied process conditions. As mentioned earlier, it is difficult to compare the present results with previously reported values, considering for instance, the differences in reactor configuration. Nevertheless, a relative comparison with the studies cited as the most promising ones, shows that the present study demonstrates a competitive performance in terms of conversion, C₂ yield as well as the energy efficiency where the integration of DBD plasma and catalyst improves the yield of desired products as well as reduces the formation of deposits, leading also to a higher energy efficiency of the process.

4.3.5. Reaction pathways

The possible reaction pathways for coupling of methane with DBD plasma will be discussed in this section. In addition, the interaction of plasma species with the catalyst surface is considered, based on the obtained experimental results and the changes within the distribution of the products, in the presence of the catalyst. First, the mechanism of methane activation with non-thermal plasma will be discussed and later the discussed mechanism will be coupled with the presence of the catalyst and the synergy between plasma and catalyst.

In principle, methane activation in non-thermal plasma is initiated by collision of electrons with CH₄ molecules, upon applying high voltages, which can generate a strong electric field. As a result, free electrons are accelerated and consequently their kinetic energy increases. Their gained kinetic energy is transferred to CH₄ molecules via collisions. Taking into account the level of the energy gained by free electrons (low, medium or high), the activation of CH₄ can be initiated in different modes, including vibrational excitation, electron impact dissociation and ionization.

Low energy electrons can vibrationally excite methane molecules by increasing the kinetic energy of CH₄ molecules, however, this level of energy is not sufficient to break a C-H bond. Commonly, the threshold energy for vibrational excitation of CH₄ is lower than 1eV or less which is much lower than the energy required for electron impact dissociation of methane ($\geq 9\text{eV}$) in non-thermal plasma [25]. CH₄ can only be dissociated by interactions with high energy electrons (9-14 eV) which are capable to provide sufficient energy to overcome thermodynamic barriers of dissociation reactions. It should be noted that a limited number of high energy electrons contribute to the ionization of CH₄ and Ar ($\geq 12\text{eV}$), which is substantial to sustain the plasma discharges. However, the adsorbed energy in non-thermal plasma is mainly distributed into dissociation reactions rather than ionization reactions.

In non-thermal plasma, the energy adsorbed by plasma discharges can highly influence the distribution of primary radicals (CH_3 , CH_2 , CH , C), considering the amount of energy transferred to methane molecules during the collisions. In this case, the distribution of final products can be significantly affected, depending on the way the plasma discharges are generated as well as on the energy per pulse of the discharge. Commonly, in DBD plasma the energy per pulse of the discharge is below 0.1 mJ. Therefore, DBD discharges mainly generate electrons with an average energy within the range of 1-10 eV, which can provide sufficient energy for the dissociation of methane to a major production of CH_3 radicals [12]. Other fragments like CH_2 and CH are also produced, however, with a relatively lower amount than CH_3 radicals.

In this study, DBD plasma was generated with a mixture of CH_4 and Ar. The mechanism of energy transfer to methane molecules can be changed by the addition of Ar [2]. As earlier explained in section 4.3.3.3, Ar atoms can adsorb the energy of free electrons easier than methane molecules within the plasma discharges, which also leads to a lower breakdown voltage, due to a small recombination rate of metastable/ionized argon atoms [5,22].

On the other hand, in a high concentration of Ar, the concentration of CH_x fragments as well as H radicals and consequently the concentration of high energy electrons (i.e., generated by dissociation of CH_4) remains low in the gas flow. This therefore can decrease the probability of the additional collisions among plasma species, in particular extra interactions of high CH_x primary radicals as well as C_2H_y secondary radicals with high energy electrons. In this case, the probability of the decomposition/reduction of CH_x and C_2H_y becomes smaller, which can lead to a higher yield of C_2 products, instead of their reduction to solid products. In other words, a lower concentration of methane is more favourable for increasing the probability of recombination reactions rather than decomposition/reduction reactions (e.g., dehydrogenation

of C₂H₅ to C₂H₃ and to C₂H radicals). This was also concluded from the results obtained for the effect of methane concentration, presented in section 4.3.3.3 of this chapter.

Dissociation of CH₄ molecules in dielectric barrier plasma discharges is initiated by simultaneous production of CH₃, CH₂, CH and C radicals, as shown in reactions 1-4 [27]. CH_x radicals go through radical chain reactions by recombination to produce C₂ compounds, following the reactions 5-8 [23], presented below:

Electron impact dissociation:

Recombination:

Further radical chain reactions occur inside the plasma discharges to form C₃ compounds via interactions of primary radicals (e.g. CH₃) and secondary radicals (e.g. C₂H₅) as specified in reactions 9 and 10:

Subsequently, interactions of primary radicals with C₂ and C₃ radicals in plasma discharges produce C₄₊ hydrocarbons. However, the main gas-phase products are hydrogen and C₂ compounds. The contribution of C₃ and C₄₊ compounds in final products is smaller than that of C₂ products. Further radical chemistry can be involved in the production of products with rather complex reaction mechanisms [23]. In the present study, the focus is mainly on the predominant reaction pathways which can explain the formation of products, considering the obtained experimental results. According to the results of the present study, the predominant products, of which their production is also sensitive to the variation of process conditions, are C₂ compounds and solid products. Thus the discussion for the reaction pathways is devoted to those which are possible routes for the formation and consumption of C₂ compounds as well as deposits.

- Dissociation
- Recombination/dimerization
- Hydrogen abstraction
- Dehydrogenation
- Polymerization/oligomerization

Fig.21. The proposed reaction pathways and radical reactions in coupling of methane to C_2 and deposits in the implemented DBD plasma reactor.

The dominant reaction pathways in the formation of C_2 products and deposits are shown in Fig.21. Different types of reactions can be involved in the formation of products. Each colour in Fig.21 represents the type of the reaction which occurs within the pool of the radicals, where they interact and ultimately form the final products. It should be emphasized that all involved reactions for the production of CH_x and C_2H_y species can be reversible, as shown in Fig.21 by the double headed arrows. In this case, all formed species can be consumed and again reformed, depending on the applied process conditions such as input power, residence time, methane concentration and plasma volume. This was concluded based on the experimental results, discussed for the effect of the variation of process conditions previously in this chapter. It should be mentioned that the interaction among radicals, for instance, for CH_x radicals like $CH_3 + CH_2 \rightarrow C_2H_5$, is also possible, however, only those important intermediate steps, which

have the highest contribution in the formation of C_2 compounds [23], are considered in the discussion of the reaction pathways.

Different types of plasma species (e.g., radicals, ions, atoms) are generated when methane is activated by plasma. Among all generated species, radicals have a key role in determining the reaction pathways and the distribution of products. The activation of methane starts with electron impact dissociation to generate CH_x fragments, depicted in red colour in Fig.21. As earlier stated above, in DBD plasma discharges, considering the limited energy of electrons (1-10 eV), CH_3 radicals are more abundant radicals than other fragments like CH_2 , CH , C . However, increasing the specific energy input can change this distribution, via the additional decomposition of methane and/or via the abstraction of H from generated CH_3 radicals, leading to a higher concentration of CH_2 , CH and C radicals. This therefore changes the distribution of C_2 products as well.

All of the CH_x fragments have the chance to go through recombination/dimerization reactions, which produce C_2H_6 , C_2H_4 , C_2H_2 products. In addition to the dimerization of CH_2 and CH radicals to form C_2H_4 and C_2H_2 , successive dehydrogenation reactions of C_2H_6 are also considered as possible intermediate steps in the formation of C_2H_4 and C_2H_2 . On the other hand, C_2H_4 and C_2H_2 are unsaturated hydrocarbons that can be potentially consumed as the precursors for the formation of deposits. This takes place via the H abstraction from C_2H_4 and C_2H_2 , generating C_2H_3 and C_2H intermediates, which subsequently contributes in the formation of deposits via polymerization/oligomerization reactions, as depicted in black colour in Fig.21.

At the presence of the catalyst, the properties of the plasma discharges are influenced. The catalyst particles change the strength of the electric field and consequently the distribution of energy transferred to plasma species, causing a remarkable shift in the distribution of CH_x fragments, where the concentration of CH_3 , CH_2 and CH radicals is highly influenced by the presence of the catalyst. As a result of this shift, the selectivity of C_2H_y species, which are

formed via recombination/dimerization reactions of CH_x fragments, also changes consequently. This was the case at the presence of γ -alumina, where the selectivity of C_2H_2 and C_2H_4 showed higher values than in the blank reactor. It was earlier explained in this chapter that the formation of a stronger electric field at the presence of γ -alumina provides a higher amount of energy, sufficient to directly dissociate CH_4 molecules to a higher production of CH_2 and CH radicals rather than CH_3 radicals, thus forming a higher amount of C_2H_4 and C_2H_2 . On the other hand, increasing the intensity of the electric field by packing γ -alumina increases the conversion of methane molecules, which are dissociated by collisions with excited Ar via Penning ionization reactions, which in turn increases the concentration of high energy electrons (i.e., generated by a higher degree of ionization reactions). As a consequence, a higher concentration of energetic electrons further increases the probability of the reduction of C_2H_2 and C_2H_4 , which results in a higher selectivity of deposits, as it was obtained for the packed reactor with γ -alumina.

For Pd-loaded γ -alumina, the formation of deposits was substantially reduced, accompanied with a notable increase in the yield of C_2 products. This can be explained by considering the catalytic activity of Pd in promoting hydrogenation reactions at ambient conditions. The active sites of Pd can easily adsorb H_2 and unsaturated species like C_2H_4 , C_2H_2 as well as the intermediates like C_2H_5 , C_2H_3 and C_2H and H radicals. Furthermore, the exposure of the Pd catalyst to the plasma electric field intensifies the adsorption of H radicals, forming strong palladium-hydrogen bonds, as also previously reported by Tomaszewska et al. [35]. In this way, most intermediate species (e.g., C_2H_5 , C_2H_3 and C_2H) react with the adsorbed H radicals, following hydrogenation reactions on the surface, which is faster than their oligomerization to deposits. Additionally, it is very likely that unsaturated compounds like C_2H_2 become further hydrogenated to form C_2H_4 , where C_2H_4 molecules can also go through further hydrogenation reactions, which will produce C_2H_6 . This depends on the amount of Pd

loading, which can influence the progress of hydrogenation reactions. This was concluded from the results discussed in section 4.3.1 for different loadings of Pd (0.5wt%, 1wt% and 5wt%) on γ -alumina, where a higher amount of Pd (5wt%) is favourable for a higher degree of hydrogenation reactions, as it consumes a greater amount of unsaturated C_2 compounds to form C_2H_6 . These results indicate that hydrogenation reactions follow a cascade trend, by which C_2H_2 is first consumed to form C_2H_4 and subsequently C_2H_4 can be hydrogenated to C_2H_6 . This implies that C_2H_4 is a key intermediate in determining the distribution of C_2 products, which can be generated by hydrogenation of C_2H_2 as well as can be also consumed via hydrogenation reactions to form C_2H_6 . In other words, in a higher amount of Pd loading (5wt%), a higher number of interactions occur with Pd active sites, which are accessible in the vicinity of each other. This therefore increases the possibility for successive hydrogenations of C_2H_y intermediates (e.g., C_2H) as well as molecules (e.g., C_2H_4) on the catalyst surface to form C_2H_6 , before they desorb from the surface.

In order to explain the synergy between the plasma and the catalyst, the mechanism of the generation and interaction of CH_x and C_2H_y species with the catalyst surface is shown in Fig.22. This mechanism is initiated by plasma activation of CH_4 molecules, which generates CH_x radicals, following with their recombination to C_2H_y species. Subsequently the generated CH_x and C_2H_y radicals interact with the catalyst. The interactions are expected to include the adsorption of CH_x and C_2H_y plasma species on the surface, following with surface reactions (e.g., recombination and/or hydrogenation) and subsequently desorption of reacted species to the gas-phase. In the case of the deposits formation, the precursors like C_2H and C_2H_3 strongly adsorb on the catalyst surface, following by oligomerization/polymerization reactions, which then leads to the formation of deposits on the surface. In this case, the desorption step does not take place for those species contributing in the formation of deposits on the surface. This means that surface reactions can be competitive, in the way that the rate of hydrogenation and

recombination of CH_x , C_2H_y radicals as well as potentially reactive molecules (i.e., C_2H_2 and C_2H_4) on the catalyst surface is competing with the rate of their oligomerization/polymerization reactions to form deposits. Results indicate that Pd has a positive effect in enhancing the rate of hydrogenation/recombination reactions, while reducing the rate of oligomerization/polymerization reactions.

The attachment of hydrogen radicals to adsorbed CH_x forms CH_{x+1} , resulting in a higher concentration of CH_3 and CH_2 rather than CH , which results in a higher production of C_2H_6 and C_2H_4 rather than C_2H_2 . Similarly, C_2H_y intermediates like C_2H , C_2H_3 and C_2H_5 also become hydrogenated to form C_2H_{y+1} . The attachment of hydrogen to C_2H_y intermediates further takes place successively on the surface until they form stable compounds like C_2H_6 and C_2H_4 . Ultimately, these compounds desorb to the gas-phase and exit from the plasma zone as the final products.

(a) The generation of CH_x and their recombination to C_2H_y

(b) The adsorption of plasma species on Pd active site

(c) The surface reactions on Pd active site

(d) The attachment of H to $\text{CH}_x(\text{ads})$ and $\text{C}_2\text{H}_y(\text{ads})$ on Pd/ γ -alumina

(e) The desorption to gas-phase

Fig.22. (a-e).The mechanism of the catalytic coupling of methane to form C_2 products by interaction of DBD plasma species with the surface of Pd/ γ -alumina.

4.3.6. The synergy of plasma and Pd/ γ -alumina

Table 2 summarizes the effect of the synergy between the plasma and the catalyst in relation to the performance of the implemented packed bed DBD plasma reactor for the present study.

Table 2. The effect of packing on the performance of DBD plasma reactor for the present study, performed in a similar range of specific energy input (10-12 kJ/L).

Experiment	CH ₄ Conversion %	C ₂ yield %	Deposits yield %	Energy efficiency%
Blank	48%	12.4%	25.5%	5.8%
Packed with γ -alumina	62%	11.3%	42.9%	6.0%
Packed with Pd/ γ -alumina	57%	29.6%	16.5%	8.6%

In addition to the changes obtained for the parameters presented in Table 2, it was found that the presence of a packing inside the discharge gap influences the plasma characteristics (e.g., breakdown voltage) as well as the mechanism of the plasma discharges formation, shifting from filamentary discharges to surface discharges, based on the obtained Lissajous figures. This was also accompanied with the enhancement of the electric field, which was more profound for a non-conductive packed bed (i.e., γ -alumina), boosting the conversion of methane to a higher value than that obtained for the blank reactor as well as the packed reactor with a conductive packed bed (i.e., Pd/ γ -alumina). However, it was revealed that the conductivity of the packing can influence the formation and expansion of plasma discharges, where the presence of Pd conductive particles on the surface of dielectric γ -alumina positively moderated the electric field, which yielded in a drastically lower amount of deposits than that obtained for the bare γ -alumina packed bed reactor, while achieving a higher yield of C₂.

4.4. Conclusions

The coupling of methane was investigated by the hybridization of a DBD plasma reactor and a Pd/ γ -alumina catalyst packed bed. The amount of metal loading of Pd showed a notable effect on the distribution of C₂ products, where low amounts of Pd (0.5 and 1wt%) were favourable for a higher production of unsaturated compounds like C₂H₄. Process conditions such as discharge power, total flow rate, methane concentration and plasma volume exhibited a strong influence on the overall performance of the DBD plasma reactor, where a different trend for the distribution of C₂ products and the yield of deposits was observed for the blank reactor in comparison with that obtained for the packed reactor. It was found that Pd/ γ -alumina is resistant to the formation of deposits, due to the catalytic property of Pd active sites, which strongly promotes hydrogenation reactions, in the way that the rates of hydrogenation reactions of CH_x and C₂H_y with H radicals on the surface become faster than the rates of their oligomerization/polymerization reactions towards the formation of deposits. The positive effect of Pd was also demonstrated by a higher energy efficiency of the process, where an increase of 48% was obtained for the packed reactor with Pd/ γ -alumina. The performance of the implemented DBD plasma reactor in the present study was competitive with the most promising literature studies. Results indicated that the presence of a metal like Pd on the surface of a dielectric material like γ -alumina enhances the synergistic effect of the plasma and the catalyst by two main positive effects. First, the presence of Pd modifies the strength of the electric field to generate less amount of those species which have high potential to form deposits. Second, considering the strong adsorption of H radicals on Pd active sites, the coverage of the surface with H radicals promotes the surface hydrogenation reactions. Consequently, this creates a stronger resistance of the surface against the formation of deposits, which leads to a higher yield of C₂ products as well.

References

- [1] H.H. Kim, Y. Teramoto, N. Negishi, A. Ogata, *Catalysis Today*, 256 (2015) 13–22.
- [2] S. Jo, D. H. Lee, Y.H. Song, *Chemical Engineering Science*, 130 (2015) 101–108.
- [3] E. C. Neyts, *Plasma Chem Plasma Process*, 36 (2016) 185–212.
- [4] S. Delavari, N. A. S. Amin, H. Mazaheri, *Reac Kinet Mech Cat.*, 113 (2014) 557–573.
- [5] N. Rueangjitt, T. Sreethawong, S. Chavadej, H. Sekiguchi, *Plasma Chem Plasma Proc.*, 31 (2011) 517–534.
- [6] B. Wang, H. M. Guan, *Catal Lett.*, 146 (2016) 2193–2199.
- [7] P. Kasinathan, S. Park, W. Choi, Y. Hwang, J. Chang, Y. Park, *Plasma Chem Plasma Proc.*, 34 (2014) 1317–1330.
- [8] A. Górská, K. Krawczyk, S. Jodzis, K. Schmidt-Szałowski, *Fuel*, 90 (2011) 1946–1952.
- [9] J. Kim J, M.S. Abbott, D.B. Go, J.C. Hicks, *ACS Energy Lett.*, 1 (2016) 94–99.
- [10] S. Kim, B. Kwon, J. Kim, *Catal Commun.*, 8 (2007) 2204–2208.
- [11] T. Nozakia, K. Okazaki, *Catalysis Today.*, 211 (2013) 29– 38.
- [12] X.S. Li, A.M. Zhu, K.J. Wang, Y. Xu, Z.M. Song, *Catalysis Today*, 98 (2004) 617–624.
- [13] S. Jo, D. H. Lee, W. S. Kang, Y.H. Song, *Physics of plasmas*, 20 (2013) 083509.
- [14] J. Sentek, K. Krawczyk, M. Młotek, M. Kalczewska, T. Kroker, T. Kolb, A. Schenk, K.H. Gericke, K. Schmidt-Szałowski, *Appl Catal B: Env.*, 94 (2010) 19–26.
- [15] S. Jo, T. Kim, D. H. Lee, W. S. Kang, Y.H. Song, *Plasma Chem Plasma Process*, 34 (2014) 175–186.
- [16] S. Kim, J. Choi, J. Kim, H. Lee, H.K. Song, *J Ind Eng Chem.*, 11 (2005) 533–539.
- [17] D. Mei, X. Zhu, Y.L. He, J. D. Yan, X. Tu, *Plasma Sources Sci. Technol.* 24 (2015) 015011 (10pp).
- [18] N.N. Gadzhieva, *High Energy Chem.*, 37 (2003) 38–43.
- [19] T. Nozaki, N. Muto, S. Kado, K. Okazaki, *Catalysis Today.*, 89 (2004) 57–65.

- [20] I. Belov, S. Paulussen, A. Bogaerts, *Plasma Sources Sci. Technol.* 25 (2016) 015023 (13pp).
- [21] T. H. Chandrashekaraiyah, R. Bogdanowicz, E. Rühl, V. Danilov, J. Meichsner, S. Thierbach, R. Hippler, *Materials*, 9 (2016) 594.
- [22] O. Khalifeh, H. Taghvaei, A. Mosallanejad, M.R. Rahimpour, A. Shariati, *Chem Eng J.*, 294 (2016) 132-145.
- [23] Ch. De Bie, B. Verheyde, T. Martens, J. van Dijk, S. Paulussen, A. Bogaerts, *Plasma Process Polym.*, 8 (2011) 1033-1058.
- [24] X. Tu, H. J. Gallon, M. V. Twigg, P. A. Gorry, J. Ch. Whitehead, *J. Phys. D: Appl. Phys.*, 44 (2011) 274007 (10pp).
- [25] M. Scapinello, E. Delikonstantis, G. D. Stefanidis, *Chemical Engineering & Processing: Process Intensification.*, 117 (2017) 120–140.
- [26] J. Lu, Z. Li, *J. Nat. Gas Chem.*, 19 (2010) 375–379.
- [27] S. Kado, K. Urasaki, Y. Sekine, K. Fujimoto, T. Nozaki, K. Okazaki, *Fuel.*, 82 (2003) 2291-2297.
- [28] A. Sárkány, A.H.Weiss, L.Gucz, *Journal of Catalysis*, 98 (1986) 550-553.
- [29] K. van Laer, A. Bogaerts, *Plasma Process Polym.*, 14 (2017) 1600129.
- [30]. G. Correale, R. Winkel, M. Kotsonis, *Journal of Applied Physics*, 118 (2015) 083301.
- [31] A. Fridman, *Plasma Chemistry*, 1st ed., Cambridge, (2008).
- [32] X. Tu, H.J. Gallon, J.C. Whitehead, *Catalysis Today.*, 211 (2013) 120-125.
- [33] W. Cho, Y. Baek, Y. Chaikim, M. Anpo, *Res. Chem. Intermed.*, 28 (2002) 343–357.
- [34] T. Butterworth, R. W. K. Allen, *Plasma Sources Sci. Technol.*, 26 (2017) 065008 (16pp).
- [35] A. Tomaszewska, Z.M. Stępień, *Journal of Physics*, 79 (2007) 012028.

Chapter 5

The effect of dielectric property of the packing materials on the performance of the packed-bed DBD plasma reactor for non-oxidative coupling of methane

In this chapter, the effect of the dielectric property of different packing materials is investigated for coupling of methane in a dielectric barrier discharge (DBD) plasma reactor. BaTiO₃ with a high dielectric constant is packed inside the discharge gap for comparison with γ -alumina, α -alumina, silica-SBA-15, ZrO₂ and MgO/Al₂O₃, which all possess notably lower dielectric constants than BaTiO₃. The results indicate that for a constant power input (7-8W), packing BaTiO₃ results in a lower conversion of methane (6-17%) during the reaction time than that achieved for other tested materials (18-50%). Comparably, BaTiO₃ shows a tendency to produce more C₂H₄, where the selectivity of C₂H₄ reaches 32%, almost two times higher than what would result for the reactor packed with low dielectric materials. However, considering a remarkable drop for the conversion of methane, the yield of C₂ products is still low for the BaTiO₃ packed plasma reactor, with respect to the C₂ yield obtained for other tested materials and even compared to the blank reactor. It is found that for a BaTiO₃ packed bed DBD reactor the conversion of methane has only a small dependence on the applied discharge power, where applying a discharge power higher than 5.5W slightly promotes the conversion of methane. On the contrary, a γ -alumina packed reactor shows a considerable enhancement in the conversion of methane and the yield of C₂ products by increasing the discharge power up to 11.0 W. It is concluded that, in order to enhance the conversion of methane, the yield of C₂ products as well as the energy efficiency, a packing of a low dielectric material, like γ -alumina or α -alumina, is preferred over a packing of a high dielectric constant material, such as BaTiO₃. The reason is attributed to a combined effect of dielectric constant and porosity of the packing, where for a high dielectric material, which possesses small pore sizes in the range of nm, the polarization inside the pores does not lead to the formation of a strong electric field inside the pores. This consequently weakens the overall generated electric field between the high voltage electrode and the ground electrode, thus resulting in a low conversion of methane and the yield of C₂ products.

5.1. Introduction

The properties of packing materials can remarkably influence the performance of DBD plasma reactors, resulting in changes for the conversion and the selectivity of the desired products. The introduction of a packing inside the discharge gap has a mutual impact on the properties of both the plasma and the packed material [1]. The packing can change the characteristics of the plasma by its presence, modifying the strength of the electric field, resulting in a different distribution of energy among plasma species (e.g., radicals, electrons, ions), which evidently affects the distribution of final products. On the other hand, the plasma can influence the properties of the catalyst surface, by changing the catalytic activity of the surface as well as modifying the morphology of the surface, which can result in altering the adsorption, reactivity and desorption properties of the surface. Several studies have investigated these mutual effects of the plasma and catalyst and their synergy for different applications such as methane conversion and the removal of volatile organic compounds (i.e., VOCs like toluene) [2-9]. According to these studies, different parameters such as dielectric constant, surface area, porosity, packing density and the shape of the packing are considered as the parameters that effectively influence the conversion and the yield of products.

The influence of the packing on the plasma originates from its impact on the mechanism of the formation of plasma discharges as well as on the properties of the discharges. Among all important properties of the packing material such as dielectric constant, surface area, particle size, morphology, the dielectric property of the packing is one of the determining factors in creating the synergy between the plasma and the catalyst, highly influencing the productivity of the process [10].

The effect of the dielectric constant has been reported for different applications in several studies. Van Laer et al. [11] investigated the effect of ZrO_2 on the conversion of CO_2 and the efficiency of the process and found that the presence of dielectric beads of ZrO_2 can enhance

the electric field and efficiently increase the energy transferred to electrons, particularly at contact points of the beads. This improvement in the strength of the electric field and the properties of the plasma could boost the conversion as well as the energy efficiency two times higher than the values obtained for the DBD reactor without packing.

Rico et al. [12] investigated the effect of packing γ -alumina and BaTiO_3 for dry reforming of methane as well as for the decomposition of methanol to hydrogen. According to their study, γ -alumina showed a better performance in improving the conversion and the yield of H_2 compared to the reactor packed with BaTiO_3 . The authors explained that a better performance of γ -alumina can be ascribed not only to its dielectric property in comparison with BaTiO_3 but also to an additional effect attributing to the catalytic activity of γ -alumina, which can create a cumulative synergy in improving the conversion of methane. Chiremba et al. [13] studied the conversion of methane using BaTiO_3 in different process conditions. It was found that the yield of H_2 is dependent on the presence of BaTiO_3 as well as on the applied specific energy density. It was reported that the distribution of C_2 products can be greatly influenced by the value of the specific energy density, where a low specific energy density (≤ 100 kJ/L) was favourable for achieving a higher selectivity of C_2H_4 rather than C_2H_6 . Furthermore, their results indicated that the conversion of methane is almost independent of the applied discharge power for a BaTiO_3 packed reactor, however, they did not report these results in comparison with the performance of the non-packed DBD plasma reactor.

Considering the importance of the effect of dielectric constant as well as its possible combined effect with the catalytic property of dielectric materials, in this chapter, the performance of the implemented DBD plasma reactor is investigated at the presence of several packing materials including γ -alumina, silica-SBA-15, ZrO_2 , $\text{MgO}/\text{Al}_2\text{O}_3$ and α -alumina in comparison with BaTiO_3 . Results will be presented in terms of the conversion of methane and the distribution of products (including deposits) for all tested materials. Furthermore, the effect

of the discharge power is evaluated for a BaTiO₃ packed-bed reactor in comparison with a γ -alumina packed-bed reactor and a blank reactor. Ultimately, the energy efficiency is analysed in terms of the conversion of methane, the amount of the energy input as well as the heat value of the products.

5.2. Experimental

5.2.1. Materials and characterizations

The following materials were utilized as the packing materials: BaTiO₃ (Alfa Aesar, 18 m²/gr), γ -alumina (Alfa Aesar, 234 m²/gr), α -alumina (Alfa Aesar, 0.82 m²/gr), silica-SBA-15 (Sigma Aldrich, 673 m²/gr), ZrO₂ (RC 100, Gimex, 97 m²/gr), MgO/Al₂O₃ (Sasol Company, 440 m²/gr). The surface area of the samples was measured with nitrogen physisorption at 77 K with Surface area and Porosity Analyzer, TriStar, Micrometrics, as mentioned inside the brackets for each material above.

5.2.2. Experimental setup

The experimental setup and the procedure of the experiments including the packing and the plasma generation and diagnostics have been explained in detail in Chapter 2. For each experiment 450-600 mg (depending on the material) was sieved within the particle size range of 100-300 μ m and packed inside the discharge gap of the DBD plasma reactor, where the 10cm length of the plasma discharge zone was fully packed for all tested materials. All experiments in this chapter have been performed at atmospheric pressure. The experiments were initiated at room temperature. The temperature of the outer surface of the ground electrode was monitored with a thermocouple. The temperature increases with time for about 1hr, until it reached 52 °C, at which it stayed constant for the rest of the reaction time for the blank reactor, as depicted in Fig.3 of Chapter 2 as well. A similar trend was observed for the packed reactors, as all experiments were performed by applying an average discharge power within the range of 7-8 W.

5.3. Results and discussion

5.3.1. The dielectric constant of the packed materials

The values for the dielectric constant of the tested materials are represented in Table 1, which are taken from the existing literature. Among all tested materials, BaTiO₃ possesses the highest dielectric constant (>1000) [10]. In general, the dielectric constant of ferroelectric materials, i.e., BaTiO₃, can largely vary depending on the applied frequency and temperature. Dong et al. [14] measured the dielectric constant of BaTiO₃ powder, supplied from Alfa Acer, similar to the powder tested in the present study. It was found that the value for the dielectric constant of BaTiO₃ is above 1000 for a wide range of applied frequencies and temperatures.

Table 1. The dielectric constant of tested packing materials

Material	BaTiO ₃	γ -alumina & α -alumina	ZrO ₂	Silica-SBA-15	MgO/Al ₂ O ₃
Dielectric constant	>1000	9-10	22-27	2-5	9-10

Other materials including γ -alumina, α -alumina, silica-SBA-15, ZrO₂, MgO/Al₂O₃ possesses a significantly lower dielectric constant, as reported in several studies [10,11,16,24]. ZrO₂ has the highest dielectric constant among known catalyst supports including γ -alumina, α -alumina, MgO/Al₂O₃, Silica-SBA-15. The lowest dielectric constant belongs to silica-SBA-15 [15].

In the next sections, the effect of packing materials with different dielectric constants on the electrical parameters of the plasma as well as their influence on the conversion and the selectivity of the products are presented for non-oxidative coupling of methane.

5.3.2. The effect of packing on plasma electrical parameters

The presence of packing with different dielectric constants can influence the plasma electrical parameters such as applied voltage, discharge power and the characteristics of discharges, which can be observed in Lissajous figures.

Fig.1. The effect of packing on applied voltage and discharge power for the blank reactor and the packed reactor with packing materials with different dielectric constants: (a) applied voltage (kV); (b) discharge power (W); Total flow rate = 50 ml/min, CH₄ concentration = 5 %, f = 23 kHz.

The applied voltage and discharge power are shown in Fig.1 for the blank reactor and the reactor packed with different packing materials. When the plasma gap is packed with different materials, a higher voltage of 8.8-10.0 kV is required to keep the energy input in the range of 7-8 W, compared to the voltage applied for the blank reactor (7.6 kV).

Due to the presence of solid particles, the gap between the high voltage electrode and the ground electrode decreases. Therefore, the space for the formation of discharges becomes less in comparison with the blank reactor. As a result, the breakdown voltage of a packed-bed DBD plasma reactor is expected to be lower than the breakdown voltage of a DBD plasma reactor without packing. This has been experimentally demonstrated in previous studies [16,18,19], and the results of the present study, represented in Table 2, also exhibit a lower breakdown voltage for all packed experiments. This effect does not depend much on the dielectric constant of the packing, except for the significantly lower breakdown voltage in the case of BaTiO₃ (ca. 30% lower than that of the other materials). Therefore, it can be stated that the reduction of the breakdown voltage for packed bed DBD reactor occurs mainly owing to the reduction of discharge gaps [10].

Table 2. The breakdown voltage for the blank and the packed reactor obtained from Lissajous Figures

Experiment with and without packing	Blank	BaTiO ₃	γ -alumina	α -alumina	ZrO ₂	Silica-SBA-15	MgO/Al ₂ O ₃
Breakdown voltage	1.86 kV	1.10 kV	1.72 kV	1.40 kV	1.64 kV	1.64 kV	1.69 kV

The plasma volume can be entirely covered with discharges as long as the charges generated on the high voltage electrode can be fully transferred to the ground electrode, which is a typical case for a non-packed DBD reactor. This becomes a different case when the plasma discharge gap is occupied by solid particles, as each particle of the packing functions as a capacitor which can bridge the transfer of charges across the plasma volume as well as, while,

at the same time, it can trap the charges. This phenomenon is called “partial discharging” for packed-bed DBD plasma reactors, as explained in previous studies for the PBRs [12,16,17,20]. Consequently, this affects the strength of the electric field, causing a different level of conversion and furthermore, a different distribution of products.

The presence of dielectric materials increases the overall capacitance of the plasma electric circuit due to their high dielectric constant compared to an empty reactor. The capacitance (C) is inversely proportional to the applied voltage (V) and correlated by $C = Q/V$, where Q is the amount of the charge, which is transferred across the discharge gap. In order to inhibit the partial discharging, the applied voltage should be sufficiently higher than the breakdown voltage to generate a full discharging across the packed bed. According to Fig.1, this is the case for the experimental results of the present study, as in all cases the applied voltage is considerably higher than the breakdown voltage of the reactor.

The formation of discharges is greatly influenced due to the presence of the particles. In addition, the porosity of the packing as well as the size and the shape of the packing can greatly influence the formation of discharges. These differences in the plasma characteristics can be further seen in Lissajous Figures, which plot instantaneous charge Q transferring through the plasma electrical circuit as a function of the applied voltage V.

Fig.2. The Lissajous figures for different packing materials packed inside the DBD plasma reactor, measured in total flow rate = 50 ml/min, CH_4 concentration = 5 %, $V = 7\text{--}10$ kV, $f = 23$ kHz, $P = 7\text{--}8$ W.

Fig. 2 depicts Lissajous figures for the blank reactor as well as for the packed reactor, tested with different materials. It can be seen that the presence of the packing influences the shape of the Lissajous figure, changing from a parallelogram form, which is a typical form for non-packed DBD plasma reactors, to an oval form (almond shape), when the discharge gap is packed with catalyst. This can be attributed to the occurrence of a combination of filamentary discharges accompanying with surface discharges, which are formed across the packed bed rather than only filamentary discharges which is typically formed when no packing is utilized [21,22]. The filamentary pattern of discharges usually takes place when high voltages are applied to the gap between the high voltage electrode and the ground electrode. Packing this gap with solid particles limits the spaces for the formation and for the propagation of

discharges, generating more localized discharges in the forms of local streamers and surface discharges [23]. Furthermore, in PBRs, the electric field is more profoundly enhanced at contact points of the particle, which can be significantly higher than the void spaces, however, this depends on the properties of the packing [16].

To estimate the capacitance of the blank reactor one has to take into account the capacitance of the quartz tube wall, C_{wall} , and that of the gas gap, C_{gas} . For the applied cylindrical reactor configuration, both these values can be calculated with:

$$C_x = \frac{2\pi L \epsilon_r \epsilon_0}{\ln\left(\frac{b}{a}\right)} \quad (1)$$

where b is the outer radius and a the inner radius of the circularly or ring shaped capacitor (in this case, the dielectric quartz tube wall), L the length of the plasma zone (100 mm) and ϵ_r the dielectric constant of the medium. With $b = 3.0$ mm (i.e., the outer radius of the quartz tube), $a = 2.0$ mm (i.e., the inner radius of the quartz tube) and 3.9 for the dielectric constant of quartz, it is found that $C_{wall} = 53.5$ pF. Similarly, with $\epsilon_{gas} = 1$, $a = 0.8$ mm (i.e., the outer radius of the high voltage electrode) and $b = 2$ mm (i.e., the inner radius of the dielectric quartz tube), it is found that $C_{gas} = 6.1$ pF. The total capacitance of the blank reactor, C_{blank} , is a series capacitance, given by:

$$C_{blank} = \frac{C_{gas} C_{wall}}{C_{gas} + C_{wall}} \quad (2)$$

which gives the value of $C_{blank} = 5.4$ pF. The Lissajous figure for the blank reactor has a typical shape, as given in Figure 3.

Fig.3. Ideal QV plot for a non-packed DBD reactor (adapted from [10]).

The lines AB and CD represent the phase of the voltage cycle where the discharge is off. The slope at any point of the line AB indicates the reactor capacitance in that instant. In this phase, there is only a displacement current and the slopes (i.e., indicated as C_{cell}) correspond to C_{blank} . The lines BC and DA represent the “discharge on” situation when gas breakdown and plasma ignition are occurring in the gap. Effectively the capacitance C_{gap} has then be short-circuited because of the conductivity of the plasma to transfer the charges across the gap, and thus the remaining capacitance in the circuit is equal to C_{wall} , but it can be also smaller than C_{wall} , because of partial discharging, which still leaves some capacitance in the gas gap of the reactor [10].

From the experimental Lissajous curve for the blank reactor (Fig. 2), the following slopes are extracted: for AB and CD 5.8 and 6.3 pF, respectively, and for BC and AD 22.4 and 22.5 pF, respectively. The values for the "plasma off" state correspond reasonably well with the calculated values. Those for the "plasma on" state are more than a factor of 2 lower than calculated, which implies that the plasma still has a considerable capacitance when it is on, which can be explained by considering the partial discharging in DBD plasma reactors [25], where it is expected that a part of the area of the electrodes is not discharging.

For a packed bed DBD plasma reactor (PBR), in addition to the capacitance of the gas gap and the dielectric quartz tube, the capacitance of the packing also contributes to the overall capacitance of the reactor. As earlier mentioned, the slope of the Q-V plot indicates the instantaneous capacitance of the reactor in that moment. Therefore, the contribution of the capacitance of the packing in the overall capacitance of the reactor changes the slope of the Q-V plot, shifting it to a different shape than that of typically obtained for a non-packed DBD reactor. Buttterworth et al. [10] has demonstrated that the main reason for obtaining this almond shape in the case of a packed bed reactor is attributed to the ignition of the plasma discharges at contact points of the particles and their expansions across the packed bed, simultaneously by increasing the applied voltage during the AC discharge cycle. Consequently the oval shape (i.e., the almond shape) is obtained due to the presence of the packing in PBRs. However, the electric field created by the actual plasma discharges in PBRs, which passes the electrical energy to the reactant, therewith promoting ionization as well as dissociation reactions, does not necessarily become more intense for a high dielectric packing. This was found to greatly depend on other physical properties of the packing such as surface area and porosity.

Zhang et al. [26] studied the influence of dielectric constant on the formation of plasma discharges inside catalyst pores, and found that small pores enhance the electric field only for materials with dielectric constant below 200. It can be seen in Table 2 that BaTiO₃ possesses the lowest breakdown voltage among the tested materials. However, in order to keep the same level of discharge power within the range of 7-8 W, an average applied voltage of 10.0 kV is still required. This therefore indicates the possible impact of other physical properties such as surface area and porosity in combination with the effect of dielectric constant, which influences the performance of the packed bed DBD plasma reactor. This will be further discussed in the next section.

5.3.3. The effect of the dielectric constant of the packing on the conversion of methane

The conversion of methane as a function of time is shown in Fig.4. As can be seen, packings of γ -alumina, α -alumina and ZrO_2 improve the conversion of methane. The BaTiO_3 packed-bed reactor demonstrates a remarkably lower conversion of about 6% at the end of the reaction time, in contrast to other tested materials like γ -alumina, α -alumina and ZrO_2 , which exhibit a conversion of 30-33%. This indicates that using BaTiO_3 with a high dielectric constant as packing leads to a lower conversion of methane.

Fig.4. The conversion of methane as a function of time for different packing materials. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, V = 7-10 kV, f = 23 kHz, P = 7-8 W.

Silica-SBA-15 and $\text{MgO/Al}_2\text{O}_3$ packed reactors show a relatively lower conversion of methane compared to other packing materials (i.e., γ -alumina, α -alumina and ZrO_2). This may be ascribed to the high surface area of silica-SBA-15 ($673 \text{ m}^2/\text{gr}$) and $\text{MgO/Al}_2\text{O}_3$ ($440 \text{ m}^2/\text{gr}$) as well as their high porosity rather than the differences in dielectric constant of the materials. A high surface area and porosity of a packed material can influence the formation of discharges, where discharges are partially formed due to charge traps in highly porous materials, which prevents the plasma discharges from propagating throughout the complete packed bed. This can be the case for the highly porous silica-SBA-15 packing, where the interrupted plasma propagation causes a lower conversion of methane. In addition, it should be noted that the

conversion of methane is accompanied with the formation of deposits, which can be significantly greater for a highly porous material, additionally influencing the formation of discharges and therefore the intensity of the electric field, leading to a low conversion of methane. This was recently reported by Kim et al. [27], where the formation of deposits became significant for a packed DBD reactor used ordered meso-porous silica (KIT-6) as the packing, notably lowering the conversion of methane during the reaction time.

As earlier discussed in the previous section, Zhang et al. [21] studied the rate of electron impact ionization for a DBD plasma reactor in combination with catalyst particles in a modelling study. They considered a wide range of dielectric constants for the catalyst, starting from 4 up to 1000 and investigated the strength of the electric field formed inside the catalyst pores with different sizes. It was found that the formation of microdischarges can be greatly affected by the dielectric constant of the packing, where the effect of dielectric constant depends on the porosity of the catalyst as well. It was discussed that, for a pore size of 100 μm , the rate of ionization is enhanced only for materials with dielectric constants below 300. It was further concluded that porous structures, i.e., Al_2O_3 and SiO_2 are more likely to allow the formation of discharges even inside the pores with small sizes, due to their low dielectric constant in comparison with materials, i.e., BaTiO_3 . It should be noted that the pore sizes studied by Zhang et al. [21] are in the range of 10 to 100 μm , whereas typical pores in catalytic packings can be much smaller.

BaTiO_3 tested in the present study has a pore size distribution within the range of 10-200 nm, as shown in Fig.5. The pore volume of the tested γ -alumina is shown in Fig.6. It can be seen that compared to BaTiO_3 , γ -alumina possesses smaller pore diameters with a narrow size distribution around 20 nm.

Fig.5.The pore volume of tested BaTiO₃ as a function of pore diameter

Fig.6.The pore volume of tested γ -alumina as a function of pore diameter

The results indicate that high dielectric materials like BaTiO₃ with small pore sizes did not enhance the electric field, due to the combined effect of dielectric constant and the porosity. This can be explained by considering the close proximity of the walls of the pores, where the mutual polarization of the walls counteract the effect of each other, resulting in a weak electric field. Thus, a high dielectric material like BaTiO₃ with small pore sizes can be considered as a medium that can mainly store the energy rather than transfer it to methane molecules. In

contrast, ZrO_2 , γ -alumina, α -alumina with remarkably lower dielectric constants improve the strength of the electric field and consequently enhance the conversion of methane, regardless of the porosity.

5.3.4. The effect of the dielectric constant of the packing on the selectivity of the products

The selectivity of C_2 products is shown in Fig.7. BaTiO_3 exhibits a higher selectivity towards unsaturated molecules like C_2H_2 and C_2H_4 compared to other packing materials. For all packing materials such as ZrO_2 , γ -alumina, α -alumina, $\text{MgO}/\text{Al}_2\text{O}_3$, silica-SBA-15, the distribution of C_2 products shifts towards a higher production of unsaturated molecules like C_2H_2 and C_2H_4 compared to the blank reactor. This is due to the presence of the solid particles, which can magnify the strength of the electric field, providing a higher amount of energy transferred to CH_4 molecules. Thus, this can enhance the H abstraction from CH_x primary radicals (i.e., generated via the dissociation of CH_4 molecules), resulting in a higher production of CH_2 and CH radicals rather than CH_3 radicals, leading to a higher production of C_2H_4 and C_2H_2 , which are produced via recombination of CH_2 and CH radicals.

Fig.7. The selectivity of C₂ products as a function of time for different packing materials: (a) acetylene selectivity; (b) ethylene selectivity; (c) ethane selectivity; Total flow rate = 50 ml/min, CH₄ concentration = 5 %, V = 7-10 kV, f = 23 kHz, P = 7-8 W.

Fig.7 shows that for the BaTiO₃ packed plasma reactor, the selectivity towards unsaturated compounds C₂H₂ and C₂H₄ reaches respectively to 18% and 32%, which is significantly higher than the values of 7% and 6% obtained for the selectivity of C₂H₂ and C₂H₄ for the blank reactor. On the other hand, as discussed in the previous section, the conversion of methane declines when BaTiO₃ is used as the packing. Therefore, for a better comparison of results, the yield of C₂ products is depicted in Fig.8. A lower yield of C₂ products is obtained for BaTiO₃ packed plasma reactor. Similarly, as shown in Fig.8, the yield of C₂H₄ is lower for the packed reactor with BaTiO₃ compared to other tested materials.

Fig.8. The yield of C₂ products as a function of time for different packing materials. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, V = 7-10 kV, f = 23 kHz, P = 7-8 W.

Fig.9. The yield of C₂ products as a function of time for different packing materials. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, V = 7-10 kV, f = 23 kHz, P = 7-8 W.

Fig.9 clearly shows that for all packed materials, C₂H₄ yield boosts to a higher value compared to the blank reactor, except BaTiO₃ which shows almost the same yield as the blank reactor. The value of C₂H₄ yield reaches a range of 3.3-3.8% for ZrO₂, γ -alumina, α -alumina and silica-SBA-15, nearly two times more than the value of 1.8% obtained for the blank reactor. This further implies that the distribution of CH_x radicals can be greatly influenced by the presence of the packing, shifting to a greater production of CH₂ radicals, which therefore increases the production of C₂H₄.

Fig.10. The selectivity of C_3 and other hydrocarbons (C_{4+}) products as a function of time for different packing materials: (a) C_3H_6 selectivity; (b) C_3H_8 selectivity; (c) other hydrocarbons selectivity; Total flow rate = 50 ml/min, CH_4 concentration = 5 %, $V = 7-10$ kV, $f = 23$ kHz, $P = 7-8$ W.

The selectivity of C_3 and other hydrocarbons is depicted in Fig.10. For all packing materials, the selectivity of C_3H_6 increases to a higher value compared to the blank reactor. In contrast, the formation of C_3H_8 is reduced by using packing. The enhancement of the electric field and therefore the extra energy generated by the presence of the packing, increases the energy of the electrons to a higher level and consequently influences the distribution of CH_x

radicals, which are formed via collisions with high energy electrons, as well as the distribution of C_2H_y radicals, which are formed via recombination of CH_x radicals. This shifts the distribution of CH_x radicals to a higher amount of CH_2 and CH rather than CH_3 . Similarly, this can happen to C_2H_y radicals, changing the selectivity of these radicals to a higher production of C_2H_3 and C_2H rather than C_2H_5 . As a result, the rate of the formation of unsaturated C_2 products (i.e., obtained from dimerization of CH_2 and CH) as well as the rate of the formation of C_3H_6 product (i.e., obtained from recombination of CH_2 and C_2H_3 and H) become greater, resulting in a higher selectivity of C_2H_2 , C_2H_4 and C_3H_6 .

Fig. 11. The selectivity of deposits as a function of time for different packing materials. Total flow rate = 50 ml/min, CH_4 concentration = 5 %, $V = 7-10$ kV, $f = 23$ kHz, $P = 7-8$ W.

Fig. 10 (c) shows that the formation of C_{4+} is slightly influenced by the packing, where it remains in a constant level of $8.5 \pm 1\%$ for all materials as well as the blank reactor. This indicates that most C_{4+} compounds are formed in the gas-phase (i.e., the gap between the particles). From this it can be implied that even in the case of the interactions of C_{4+} with solid particles, the formation of C_{4+} is not remarkably influenced.

The selectivity of deposits is depicted in Fig.11. It can be seen that a lower amount of deposits are formed when BaTiO_3 is used compared to other tested materials. This can be attributed to a lower conversion of methane, which therefore leads to a lower formation of deposits as well. Although, on one hand, a lower formation of deposits is favourable for the sustainability of the process, on the other hand, C_2 yield can consequently drop, due to a low conversion of methane, as shown in Fig.8. According to the results of the present study, a low dielectric material, i.e., alumina is preferred to be integrated with DBD plasma reactor rather than a high dielectric material, i.e., BaTiO_3 in order to achieve a higher conversion of methane as well as a higher yield of C_2 products.

5.3.5. The behaviour of high and low dielectric materials packed inside the DBD plasma reactor in different discharge powers

The effect of input power on the performance of BaTiO₃ packed into the discharge gap of the DBD plasma reactor was investigated. Fig.12 represents the changes over the conversion of methane and the selectivity of the products as a function of discharge power.

Fig.12. The effect of discharge power on the conversion of methane and the selectivity of products for the reactor packed with BaTiO₃. Total flow rate = 50 ml/min, CH₄ concentration = 5 %, f = 23 kHz.

The conversion of methane tends to increase from 7.8% to 16.5% by increasing the discharge power from 3.0 W to 5.5 W. Applying a higher amount of discharge power does not promote the conversion of methane significantly. This can be seen in Fig.12, as increasing the discharge power from 5.5 W to 10.2 W only changes the conversion of methane from 16.5% to 17.2%. As also discussed in the previous section, although BaTiO₃ possesses a high dielectric constant (> 1000) which can locally magnify the strength of the electric field, the

material does not promote CH_4 conversion effectively and the rate of dissociation of CH_4 is only slightly influenced by increasing the discharge power. This is attributed to the porosity of the tested BaTiO_3 . In this case, applying a greater amount of discharge power can only increase the charge density inside the pores, but does not lead to a strong polarization due to small size of the pores.

The selectivity of deposits increases from 36.1% to 44.5% by increasing the discharge power from 3.0 W to 10.2 W, as shown in Fig.12. In contrast, the selectivity of C_2 products decreases from 48.5% to 38.4%. This indicates that the extra energy provided to the plasma zone mainly contributes to the decomposition of methane, which generates a higher amount of C radicals rather than CH_x radicals (i.e., CH_3 , CH_2 , CH). In this way, a lower formation of CH_x radicals therefore leads to a lower formation of C_2 products, which are produced via dimerization reactions of CH_x radicals.

In order to evaluate the effect of high and medium dielectric constant materials in different discharge powers, the conversion of methane versus discharge power for the reactor packed with BaTiO_3 , γ -alumina as well as the blank reactor is shown in Fig.13. It can be seen that increasing the discharge power has a positive effect in improving the conversion of methane in the case of using γ -alumina as packing. In contrast, as discussed above, the presence of BaTiO_3 leads to a weaker electric field and then a lower conversion of methane. Similarly, H_2 yield follows the same trend as the conversion of methane, as shown in Fig.14.

The yield of C_2 products versus discharge power is depicted in Fig.15. The yield of C_2 products is lower than those obtained for the blank reactor as well as for the reactor packed with γ -alumina. This is due to a lower conversion of methane, as obtained for the BaTiO_3 packed reactor.

Fig.13.The conversion of methane as a function of discharge power for the reactor packed with BaTiO₃ and γ-alumina and the blank reactor. Total flow rate = 50 ml/min, CH₄ concentration =5 %, f=23 kHz.

Fig.14.The yield of H₂ as a function of discharge power for the reactor packed with BaTiO₃ and γ-alumina and the blank reactor. Total flow rate = 50 ml/min, CH₄ concentration =5 %, f=23 kHz.

Earlier in this chapter, it was discussed that packing solid materials inside the plasma changes the distribution of C₂ products towards a higher production of unsaturated hydrocarbons like C₂H₂ and C₂H₄. Fig.16 shows the yield of C₂H₄ as a function of discharge power. The yield of C₂H₄ remains almost unchanged by increasing the discharge power. From this, it can be stated that increasing the discharge power mainly increases the formation of deposits and C₂H₆. In contrast, the presence of BaTiO₃ and γ-alumina leads to a remarkable

increase for the yield of C_2H_4 . Thus, it can be concluded that materials with low dielectric constants, i.e., γ -alumina, can be used as packing inside the DBD plasma in order to achieve a higher yield of C_2H_4 .

Fig.15.The yield of C_2 products as a function of discharge power for the reactor packed with $BaTiO_3$ and γ -alumina and the blank reactor. Total flow rate = 50 ml/min, CH_4 concentration = 5 %, $f=23$ kHz.

Fig.16.The yield of C_2H_4 as a function of discharge power for the reactor packed with $BaTiO_3$ and γ -alumina and the blank reactor. Total flow rate = 50 ml/min, CH_4 concentration =5 %, $f=23$ kHz.

5.3.6. The analysis of the energy efficiency

In order to analyse the energy efficiency, two definitions are considered. In the first analysis, the energy efficiency is defined based on the amount of converted methane divided by the discharge power, applied for the plasma reaction as shown in the equation below:

$$\text{Energy Efficiency } \left(\frac{\text{mmol}}{\text{kJ}} \right) = \frac{\text{CH}_4 \text{ converted } \left(\frac{\text{mmol}}{\text{s}} \right)}{\text{Discharge Power } \left(\frac{\text{kJ}}{\text{s}} \right)}$$

These values are represented in Table 3.

Table 3. The energy efficiency for the blank reactor and the reactor packed with different dielectric materials

Experiment with and without packing	Blank	BaTiO ₃	γ-alumina	α-alumina	ZrO ₂	Silica-SBA-15	MgO/Al ₂ O ₃
Energy Efficiency (mmol/kJ)	0.1122	0.0265	0.1315	0.1468	0.1316	0.0938	0.1189

The second definition is based on the high heat value of the products, the amount of converted methane as well as the discharge power as represented in the equation below:

$$\text{Energy Efficiency \%} = \frac{\sum_{i=\text{product}}^n \text{HHV}(i) \times \text{molar flow rate}(i)}{\text{HHV of CH}_4 \times \text{molar flow rate of reacted CH}_4 + \text{Discharge Power}} \times 100$$

- i = product

-HHV(i) = High Heat Value of i (J/mol)

-Molar flow rate of i (mol/s)

-Discharge power (Watt)

The results of the second definition are represented in Fig.16. Similar conclusions can be drawn from both definitions of the energy efficiency. It can be seen that BaTiO₃ converts a lower amount of methane compared to other packing materials as well as compared to the blank reactor. This implies that a high dielectric material like BaTiO₃ transfers a small part of the input energy for the activation of methane. In this case, compared to other tested materials, a

part of the energy input is dissipated into BaTiO₃ packed-bed, instead of being transferred to methane molecules. For the reactor packed with alumina and zirconia, the energy efficiency improves to a higher value than that obtained for the blank reactor, according to Table 3.

Fig.16.The energy efficiency for the blank reactor and the packed reactor with different packing materials. Total flow rate = 50 ml/min, CH₄ concentration =5 %, V= 7-10 kV, f=23 kHz, P=7-8 W.

Among all tested materials with low dielectric constant, silica-SBA-15 packed-bed plasma reactor possesses the lowest amount of energy efficiency with the value of 0.0938 mmol/kJ. As earlier discussed in this chapter, this can be explained by the phenomenon “partial discharging”, which is intensified in the case of a packing with a high surface area and porosity like silica-SBA-15, where charges can be trapped inside the pores and therefore discharges are not able to bridge the gap between the high voltage electrode and the ground electrode. As a result, the strength of the electric field becomes relatively weaker. This has been evidenced in previous studies, where DBD plasma was combined with different packing materials utilized for different applications [16,20,21]. In order to achieve a complete discharging in the plasma

zone, charges generated on the high voltage electrode should be entirely transferred to the ground electrode. In the case of using packing, the particles behave as a capacitor, which is capable of both transferring as well as trapping charges, depending on its dielectric properties and its porosity. In other words, owing to the presence of solid particles inside the discharge gap, the formation of plasma discharges can be interrupted, which can lead to a non-uniform plasma. This therefore causes a weaker electric field and consequently a lower conversion of the methane.

The energy efficiency for MgO/Al₂O₃ is nearly similar to that obtained for silica-SBA-15. These two materials possess the highest surface areas with values of 673 m²/gr for silica-SBA-15 and 440 m²/gr for MgO/Al₂O₃, which is an indication of a high porosity of these materials compared with γ -alumina, α -alumina and ZrO₂. The difference between the energy efficiency of γ -alumina, α -alumina and ZrO₂ packed reactors is small in comparison with their differences in the value of the dielectric constant, which is 9-11 for alumina (α and γ) and 22-27 for zirconia.

The dielectric constant of α -alumina and γ -alumina is nearly the same. The conversion of methane as well as the energy efficiency for both α -alumina and γ -alumina packed reactor are also similar, despite their differences in surface area and porosity. Thus, it can be stated that in the case of alumina, the dielectric constant has a dominant effect compared to its surface area and its porosity. On the other hand, this shows that the catalytic activity of γ -alumina has a slight effect in improving the conversion, as α -alumina which is known to have no catalytic activity still can boost the conversion of methane, due to its dielectric property.

5.4. Conclusions

In this chapter, the conversion of methane in a packed bed DBD plasma reactor was carried out, aiming at studying the effect of dielectric constant of the packing on the conversion and the yield of products for non-oxidative conversion of methane. Results indicated that high dielectric constant BaTiO_3 results in achieving a lower conversion of methane compared to the blank reactor and other tested materials with low dielectric constants such as γ -alumina, α -alumina and ZrO_2 . This was elucidated based on the small size of BaTiO_3 pores, i.e., within the range of nm, which leads to a weak polarization inside the pores, thus forming a weak electric field. It was also found that increasing the discharge power more than 5.5 W can only slightly promote the conversion of methane for a BaTiO_3 packed plasma reactor, due to the counteraction of polarization inside the small pores of BaTiO_3 . In contrast, for a γ -alumina packed plasma reactor, increasing the discharge power strongly promoted the conversion of methane as well as the yield of C_2 products. Ultimately, it was discussed that the energy efficiency can be improved by packing low dielectric materials, where the highest energy efficiency was achieved for α -alumina and γ -alumina within the range of 0.13-0.15 mmol of converted methane /kJ.

References

- [1] E. C. Neyts, A. Bogaerts, J. Phys. D: Appl. Phys., 47 (2014) 224010 (18pp).
- [2] J.C. Whitehead, Pure Appl. Chem., 82 (2010) 1329-1336.
- [3] T. Nozaki, N. Muto, S. Kado, K. Okazaki, Catal. Today., 89 (2004) 57-65.
- [4] A.E. Wallis, J.C. Whitehead, K. Zhang, Catal. Lett., 113 (2007) 29-33.
- [5] S. Jo, D. H. Lee, W. S. Kang, Y. H. Song, Physics of plasmas, 20 (2013) 123507.
- [6] X.B. Liao, Y. F. Guo, J. H. He, W.J. Ou, Q.D. Ye, Plasma Chem. Plasma Proc., 30 (2010) 841-853.
- [7] S. Jo, T. Kim, D. H. Lee, W. S. Kang, Y.H. Song, Plasma Chem Plasma Process., 34 (2014) 175-186.
- [8] P. Kasinathan, S. Park, W. Choi, Y. Hwang, J. Chang, Y. Park, Plasma Chem Plasma Proc., 34 (2014) 1317-1330.
- [9] M. Kraus, W. Egli, K. Haffner, B. Eliasson, U. Kogelschatz, A. Wokaun, Phys. Chem. Chem. Phys., 4 (2002) 668-675.
- [10] T. Butterworth, R. W. K. Allen, Plasma Sources Sci. Technol., 26 (2017) 065008 (16pp).
- [11] K. V. Laer, A. Bogaerts, Energy Technol., 3 (2015) 1038-1044.
- [12] V. J. Rico, J. L. Hueso, J. Cotrino, A. R. Gonzalez-Elipé, J. Phys. Chem. A., 114 (2010) 4009-4016.
- [13] E. Chiremba, K. Zhang, C. Kazak, G. Akay, AIChE Journal., 63 (2017) 4418-4429.
- [14] L. Dong, D. S. Stone, R. S. Lakes, Journal of Applied Physics, 109 (2011) 063531.
- [15] K. Sethuraman, T. Lakshmikandhan, M. Alagar, Polymer Composites, 37 (2016) 3433-3441.
- [16] D. Mei, X. Zhu, Y. L. He, J. D. Yan, X. Tu, Plasma Sources Sci. Technol., 24 (2015) 015011 (10pp).

- [17] X. Tu, H. J. Gallon, M. V. Twigg, P. A. Gorry, J. C. Whitehead, *J. Phys. D: Appl. Phys.*, 44 (2011) 274007 (10pp).
- [18] H. J. Gallon, X. Tu, J. C. Whitehead, *Plasma Process. Polym.*, 9 (2012) 90-97.
- [19] X. Tu, B. Verheyde, S. Corthals, S. Paulussen, B. F. Sels, *Physics of Plasma*, 18 (2011) 080702.
- [20] B. Dou, F. Bin, C. Wang, Q. Jia, J. Li, *J. Electrostat.*, 71 (2013) 939-44.
- [21] X. Tu, H. J. Gallon, M. V. Twigg, P. A. Gorry, J. C. Whitehead, *J. Phys. D: Appl. Phys.*, 44 (2011) 274007 (10pp).
- [22] T. Butterworth, R. Elder, R. Allen, *Chemical Engineering Journal.*, 293 (2016) 55-67.
- [23] K. V. Laer, A. Bogaerts, *Plasma Sources Sci. Technol.* 28 (2017) 085007.
- [24] Q. Yu, M. Kong, T. Liu, J. Fei, X. Zheng, *Plasma Chem Plasma Process*, 32 (2012) 153-163.
- [25] F. J. J. Peeters, M. C. M. van de Sanden, *Plasma Sources Sci. Technol.*, 24 (2015) 015016 (9pp).
- [26] Y.R. Zhang, E. C. Neyts, A. Bogaerts, *J. Phys. Chem. C.*, 120 (2016) 25923-25934.
- [27] J. Kim, J. Jeoung, J. Jeon, J. Kim, Y. S. Mok, K.S. Ha, *Chemical Engineering Journal.*, (2018).

Chapter 6

The high resolution scanning electron microscopy (HRSEM) and energy dispersive X-ray spectroscopy (EDX) characterization of the deposits formed during the DBD plasma reaction for non-oxidative coupling of methane

In this chapter, the deposits formed on the inner surface of the dielectric quartz tube as well as on the catalyst samples after exposure to $\text{CH}_4 + \text{Ar}$ plasma are characterized by high resolution scanning electron microscopy (HRSEM) and energy dispersive X-ray elemental analysis (EDX). It is found that the deposits formed on the inner surface of the dielectric quartz tube constitute of a polymer-like layer throughout the length of the quartz tube, possessing an amorphous structure. EDX elemental analysis of this layer shows the same atomic percentage of carbon in its chemical composition, without notable changes from the beginning till the end of the plasma zone. For catalyst samples used as packing inside the DBD discharges, the morphological changes as well as the formation of carbon-containing deposits are observed by SEM as well as detected by EDX, respectively. In the case of γ -alumina, carbon-rich agglomerates are formed after exposure to plasma, showing high content of carbon as detected by EDX as well. In contrast, the formation of agglomerates is not observed for Pd-containing catalysts. This is in agreement with the experimental results obtained for the conversion of CH_4 in a Pd/ γ -alumina packed bed DBD reactor, whereas a notably lower amount of deposits is formed, due to the presence of Pd. It is further found that the structure of all other plasma-processed materials including $\text{MgO}/\text{Al}_2\text{O}_3$, silica-SBA-15, ZrO_2 , BaTiO_3 and α -alumina undergoes morphological changes during the exposure to plasma. These changes arise not only due to the formation of solid products during $\text{CH}_4 + \text{Ar}$ plasma reactions, which leads to the formation of agglomerates, but also due to the treatment of the surface by DBD plasma discharges, which are observed in the forms of the generation of new pores (voids) in the structure as well as the moderation of the surface roughness towards a smoother surface.

6.1. Introduction

Scanning electron microscopy (SEM) is a characterization method to study the morphology of a surface using a focused beam of high-energy electrons. The interactions of electrons with the atoms on the surface of the sample results in the generation of signals by the electrons emitted from the sample. The signals are then scanned to form an image, which contains information about the surface topography and its composition. The main signals are usually produced by the secondary electrons and the backscattered electrons, however, the interaction of electrons with the sample's surface can generate other signals, for instance X-rays, which are able to provide additional information about the composition of the sample. The method is called energy dispersive X-ray spectroscopy (EDX) in which X-ray photons emitted from the sample can identify the elements of the sample as well as the mass fraction of each element in atomic (at%) or weight percentages (wt%). The fundamental principle of EDX analysis originates from that each element of the sample has a unique atomic structure, allowing a unique set of peaks in its electromagnetic emission spectrum [1]. This method relies on the interaction of the electron beam, which contains a beam of X-rays, with the electrons in the sample. Once the electron beam hits the sample, it transfers part of its energy to the atoms of the sample. This energy is then used by the electrons of the atoms to become excited to an energy shell with a higher energy or to be ejected from the atom. This therefore creates holes with positive charges due to the transition of the electrons in the sample. The higher energy shell then fills the hole, and the difference in energy between the higher energy shell and the lower energy shell can be emitted in the form of an X-ray. It is known that the energy of X-rays is a characteristic of the difference in energy between two shells. Depending on the atomic number of the element, the X-rays are considered as the fingerprint of each element and can be used to identify the type of elements that exist in a sample [1]. Therefore, spectra of the elements can be obtained, allowing their identification via a comparison with reference spectra.

SEM/EDX studies have been extensively used to analyse the surface morphology of catalyst samples. The surface morphology of a catalyst can play a key role in determining the activity, the selectivity as well as the stability of the catalyst. The surface morphology can be manipulated by the methods utilized to prepare the catalyst as well as the additional treatment of the catalyst, i.e., calcination or reduction. In recent years, the low temperature non-thermal plasma systems have been exploited for preparation and treatment (e.g., reduction) of supported metal catalysts, advantageously preferred to the conventional thermal approaches, which need quite high operating temperature for the preparation as well as the treatment of catalysts [2-4].

Plasma treatment of the catalyst can result in effective changes in the morphology as well as the catalytic properties of the surface. However, this depends on the amount of applied power, the exposure time as well as the type of the gases, which are used to create the plasma discharges. Tu et al. [5] reported the treatment of NiO/Al₂O₃ using H₂/Ar DBD plasma at atmospheric pressure and a rather low temperature (< 300 °C). It was found that plasma is capable to reduce NiO to Ni, increasing the surface conductivity as well as modifying the discharge characteristics of the plasma. Liu et al. [6] studied the influence of non-thermal plasma on the catalytic properties of various metal supported catalysts such as Pt, Pd, Ni on alumina and HZSM-5 as the supports. These authors revealed that the plasma treatment remarkably enhanced the dispersion of the metal on the surface of the support, which promoted the activity of the catalyst at low temperatures by generating and redistributing the acidic and basic sites as well as improved the stability of the catalyst. It was further found that the plasma-treated catalysts show a higher resistance to carbon deposition compared to those prepared by conventional thermal synthesis methods, where, in addition to the modification of the surface acidity, this was furthermore attributed to an improved interaction between the metal and the support after treating with the plasma as well as to a higher dispersion of metal active sites. The enhancement of the dispersion was also reported in a study by Karuppiyah et al. [7], which

investigated the plasma reduction of Ni/Al₂O₃ and CeO₂-Ni/Al₂O₃. Their results indicated that a better dispersion for nanoparticles of the metal was obtained due to the treatment of the surface with DBD plasma discharges.

The integration of plasma and catalyst aims at the improvements for the productivity of the process towards desired products. Despite the synergy of plasma and catalyst, still the formation of undesired products can take place, which can therefore influence the overall performance of the plasma-catalyst system. As a typical instance, the plasma-driven conversion of hydrocarbons (e.g., CH₄) usually produces carbon-containing deposits, which is considered as a drawback in such processes, due to its influences on the stability of the plasma as well as on the catalytic activity of the catalyst.

Khoja et al. [8] studied dry reforming of methane in a DBD plasma reactor packed with γ -alumina. SEM images showed the formation of carbonaceous species on alumina. In addition, EDX elemental analyzer detected the presence of carbon in the composition of alumina, comparably higher than the fresh γ -alumina powder. Chiremba et al. [9] performed SEM characterization of BaTiO₃ after 80 hr exposure to CH₄ plasma. BaTiO₃ spheres were used as packing for the conversion of methane in a packed-bed DBD reactor. It was revealed that the grain structure of BaTiO₃ was influenced by exposure to DBD discharges, where the grains tend to agglomerate to form larger ones, forming a layered structure. The presence of carbon-containing deposits was confirmed by EDX spectra, as a higher amount of carbon was detected in the chemical composition of BaTiO₃ after exposure to CH₄ plasma.

The conversion of CH₄ with DBD plasma reactors is inevitably accompanied with the formation of deposits. The integration of catalyst surfaces with the DBD plasma discharges is one of the approaches that can reduce the formation of deposits, however, still the carbonaceous species are formed on the catalyst surface. Furthermore, the formation of deposits can influence the stability for the operation of packed-bed DBD reactors. Thus, it is important to characterize

the formed deposits, which can then supplement the findings obtained from experimental results, as represented in Chapter 4 and Chapter 5, as well as it can be helpful to have more insight about the nature of the deposits and its morphology.

In the present chapter, the deposits formed during the plasma reaction for both the blank reactor as well as for the reactor packed with different catalysts are characterized using high resolution scanning electron microscopy (HR-SEM) to study the structural changes of the catalyst samples after being exposed to CH₄+Ar DBD plasma discharges. In addition, energy dispersive X-ray analysis (EDX) is utilized to analyze the elemental composition of the deposits formed on the inner surface of the dielectric quartz tube as well as on the catalyst samples.

6.2. Experimental

Scanning electron microscopy (SEM) with high resolution was performed using a Zeiss MERLIN HR-SEM instrument. This instrument was also equipped with energy dispersive X-ray spectroscopy from OXFORD Instruments for obtaining the elemental composition of the samples. The tube covered with deposits, which was obtained from the experiment performed with the blank DBD reactor, as also depicted in Chapter 2, was cut in different pieces in order to see the variation of the deposits structure from the beginning of the plasma zone until the end of the plasma zone. The pieces of the coated quartz tube were directly mounted inside the chamber of the SEM instrument. For the catalyst samples, the typical SEM sample holder was used. A small amount of the catalyst powder was attached to the sample holder using carbon adhesive tape and then the holders were mounted inside the chamber.

It should be mentioned that for both the deposits formed on the quartz tube as well as the catalyst, 3-4 nm chromium-sputtered coating was employed, however, the results obtained with the coated samples were not notably different than the uncoated samples, whereas the same conclusions were drawn from SEM/EDX results of the uncoated and the coated samples.

Therefore, all SEM/EDX experiments, which are reported in this chapter, were performed by directly using the samples without further preparation.

For SEM images, a low acceleration voltage around 1kV was applied, in order to avoid the charging effects that may occur due to the low conductivity of the deposits formed on the quartz tube. This was preferred to metal-coating of the samples, as sputter coating has the drawback of altering the atomic composition of the surface, which can then lead to false elemental information, particularly when an EDX analyser is utilized for elemental analysis of the sample. The surface charging became extreme when an acceleration voltage higher than 3kV was applied, where it was not possible to see a clear image of the sample and, where instead a large white (bright) area on the image was observed. For energy dispersive X-rays (EDX) analysis, a higher voltage of 10kV was applied in order to have the emission of X-rays from the sample. In the next section, the images and the elemental analysis of the samples will be presented.

6.3. Results and discussion

6.3.1. SEM/EDX characterization of deposits formed on the dielectric quartz tube

A layer of yellowish deposits was formed during the plasma reaction for a blank experiment, as explained in Chapter 2, on the inner surface of the dielectric quartz tube, as depicted in Fig.1.

Fig.1. The yellowish deposits formed on the dielectric quartz tube during the DBD plasma reaction with the mixture of CH_4 and argon.

The deposits are formed on the inner surface of the reactor for a length of 10 cm, which includes the area of the plasma zone. To analyse the deposits in different lengths along the plasma zone, the quartz tube was cut in 5 different pieces, as shown in Fig.2. It can be seen that the yellowish deposits have formed with a similar appearance along the quartz tube.

Fig.2. Picture of the inner surface of the quartz tube covered with deposits formed during coupling of CH_4 with DBD plasma, cut in 5 pieces and ordered from the beginning of the plasma zone till the end of the plasma zone used for SEM images and EDX analysis; (a) piece 1; (b) piece 2; (c) piece 3; (d) piece 4; (e) piece 5.

SEM images of the deposits on these pieces are represented in Fig.3. The results indicate that the deposits possess an amorphous structure with irregular pores and cracks on the surface. This structure remains the same throughout the length of the quartz tube, where there is no difference for the structure of the deposits at the beginning of the plasma zone (piece 1) with the other pieces. For all pieces, it can be seen that the surface structure possesses a combination of both smooth areas as well as rough areas. In addition, surface cracks can be observed in smooth areas of the layer. This can be explained considering that a large part of energy of DBD plasma streamers are dissipated in the form of surface discharges on the dielectric electrode, as reported by Nozaki et al. [15]. This energy of DBD streamers can anneal the formed deposits, which therefore creates cracks and voids in the structure of the deposits.

Furthermore, according to Fig.2, some rather black spots can be seen on the tube, in particular on the pieces (b) and (c). One sample of these particles was separately analysed by SEM, which indicated similar amorphous structure as observed for other areas of the quartz tube. This may be attributed to randomly local heating of the dielectric quartz tube, where it can be in contact with some energetic plasma streamers with a significantly higher energy and consequently the formed layer of deposits can be further annealed, and for instance, be dehydrogenated from CH_x to carbon, and thus leaving these black spots in some local areas of

the dielectric surface. However, the area of these black spots is quite small and minor compared to the total surface area of the dielectric surface.

Fig.3.SEM images of deposits formed on the inner surface of quartz tube;
(a) piece 1; (b) piece 2; (c) piece 3; (d) piece 4; (e) piece 5.

The composition of this layer of deposits was analysed using a CHN elemental analyser, which is capable to determine the amount of hydrogen and carbon in the composition of the

deposits. It was revealed that the H/C atomic ratio for the deposits is equal to 1.7 ± 0.1 . From this, it was concluded that the deposits possess a polymer-like structure, considering a higher atomic content of H ($\sim 60\text{at}\%$) [10]. This further indicated that the layer of deposits is not a highly conductive material, due to a low atomic content of carbon. The result of the CHN elemental analysis was also matched with the H/C molar ratio calculated from the reaction mass balance of C and H, for those quantities of hydrogen and carbon consumed for the formation of deposits, as earlier discussed in Chapter 2.

The composition of the deposits can be also determined by EDX analysis, as depicted in Fig.4. However, it should be noted that it is not possible to detect hydrogen with EDX analysis and therefore the chemical composition is reported excluding the content of H. The elemental analysis shows a high content of carbon in the structure of deposits, with an average of 88.6 wt% (91.2 at%) and the rest is oxygen, which either originates from the quartz tube structure (SiO_2) or, from the moisture, that usually exists in argon flow and which is difficult to avoid, even in a vacuum system. The impurity of oxygen has been reported in previous studies during the growth of plasma polymerized films using the mixture of CH_4 and Ar [11,12]. It should be noted that there is a trace of Si, which can be ascribed to the structure of the quartz tube (SiO_2), however, its amount is not significant.

Fig.4.EDX spectra of deposits formed on the inner surface of quartz tube;
(a) piece 1; (b) piece 2; (c) piece 3; (d) piece 4; (e) piece 5.

6.3.2. SEM/EDX characterization of γ -alumina and Pd/ γ -alumina after exposure to DBD plasma

The catalyst samples, which were used as packing inside the discharge gap of the implemented DBD plasma reactor, are characterized by high resolution scanning electron microscopy. Results indicate that the structure of the catalyst samples can be influenced when they are exposed to $\text{CH}_4 + \text{Ar}$ DBD plasma. The changes on the structure of the catalyst originate from the formation of solid products on the catalyst, obtained from CH_4 decomposition as well as from plasma treatment of the catalyst due to exposure of the packing to plasma-induced species (ions, electrons, radicals) upon the generation of the discharges.

Fig.5. SEM images of γ -alumina (a,b) before exposure to DBD plasma; (c,d) after exposure to DBD plasma

Fig.5 shows the images of γ -alumina before and after exposure to plasma. It can be seen that the surface of γ -alumina is covered with amorphous carbon-containing agglomerates, and has a different structure than the fresh γ -alumina sample, indicating morphological changes during the plasma reactions. This is also in agreement with the experimental results discussed in Chapter 4, where the γ -alumina packed bed DBD reactor yielded a higher amount of deposits formation in comparison with the non-packed DBD reactor as well as the reactor packed with Pd/ γ -alumina catalyst. The presence of carbonaceous species on the γ -alumina structure is further confirmed by EDX spectra, as depicted in Fig.6.

Fig.6. EDX spectra of γ -alumina (a) before exposure to DBD plasma; (b) after exposure to DBD plasma

It should be noted that the formation of carbon-containing deposits was randomly dispersed on γ -alumina structure, as can be seen in Fig.7, which shows a SEM/EDX mapping analysis of γ -alumina after exposure to plasma. This further indicated that deposits did not cover the structure uniformly.

Fig.7. EDX mapping of γ -alumina after exposure to $\text{CH}_4 + \text{Ar}$ DBD plasma. (a) Layered image; (b) Al map; (c) O map; (d) C map.

In contrast, the formation of agglomerates was not observed in SEM images for Pd-loaded catalysts after exposure to plasma, as shown for 1wt% Pd-loaded catalyst in Fig.8. This can further confirm that the Pd-containing surface becomes resistant to the deposition of solid products, due to the presence of Pd active sites on γ -alumina. On the other hand, the surface morphology of Pd/ γ -alumina has been modified after exposure to plasma, where the surface has become smoother, as can be seen in Fig.8 (c) and (d), compared to a rough surface observed for the fresh sample before exposure to plasma, according to Fig.8 (a) and (b).

Fig.8. SEM images of Pd/ γ -alumina (a,b) before exposure to DBD plasma; (c,d) after exposure to DBD plasma

The result of EDX mapping for Pd (1wt%)-loaded catalyst, as shown in Fig.9, also exhibits the presence of carbon-containing areas, however, the amount of carbon was notably lower and more scattered, which therefore could not lead to the formation of agglomerates. As a result, the chemical composition of the Pd catalyst is less affected by solid products, due to the presence of Pd particles on γ -alumina, which promotes the hydrogenation of the deposits-precursors, before being deposited on the catalyst, as elucidated in Chapter 4 as well.

It should be noted that for some areas of the fresh samples (i.e., before the exposure to plasma), a small amount of carbon was detected in EDX spectra. This can be ascribed to reagents that were used in the preparation of the catalyst, e.g., carbonate (CO_3)⁻², which can remain as impurities in the sample because it has not been completely removed after the sequence of the treatments (e.g., drying, calcination). On the other hand, it may also originate from the carbon adhesive tape, used for sampling, which is in direct contact with particles. Regardless of the source of the small amount of carbon detected in the fresh samples, the atomic percentage of carbon in the fresh samples was always significantly lower than that detected in the plasma-processed samples.

Fig.9. EDX mapping of Pd/γ-alumina after exposure to CH₄ +Ar DBD plasma. (a) Layered image; (b) Pd map; (c) Al map; (d) O map; (e) C map.

6.3.3. SEM/EDX characterization of dielectric materials after exposure to DBD plasma

Different dielectric materials were tested as packing in the implemented DBD plasma reactor, as illustrated in Chapter 5. In this section, the results of high resolution SEM for these packing materials after exposure to plasma are presented.

The SEM images of BaTiO_3 show a porous structure, according to Fig.10 (a), which increases the possibility for charges (i.e., those charges transferred between the high voltage electrode and the ground electrode) to be trapped inside the pores. In combination with the high dielectric constant of BaTiO_3 , this porous structure consequently strengthens the occurrence of “partial discharging”, thus causing a weak electric field and therefore a lower conversion of methane was achieved. This was earlier explained in Chapter 5 to be due to the weak polarization inside the pores with small sizes, which occurs for ferroelectric materials like BaTiO_3 .

Fig.10. SEM images of BaTiO_3 (a) before exposure to DBD plasma; (b) after exposure to DBD plasma

As can be seen in Fig.10 (b), the exposure of BaTiO_3 to DBD discharges results in the treatment of the surface in such a way that some new voids (pores) are created in the structure of BaTiO_3 . The formation of pores (voids) inside the structure of plasma-treated materials (e.g., silica) has been previously observed and was attributed to the treatment of the surface by Ar plasma [13,14].

Fig.11. EDX mapping of BaTiO_3 after exposure to $\text{CH}_4 + \text{Ar}$ DBD plasma. (a) Layered image; (b) Ba map; (c) Ti map; (d) O map; (e) C map.

It should be noted that the formation of agglomerates, as observed for γ -alumina, is not observed for BaTiO_3 . The reason could be related to the weak electric field formed at contact

points of particles, which then leads to a low conversion of methane and as a consequence to a lower formation of deposits for the BaTiO₃ packed-bed DBD reactor. In this case, a lower amount of solid products become deposited on the surface, which then lowers the probability of the formation of agglomerates during the plasma reaction.

In order to see the presence of carbon in the elemental composition of BaTiO₃, SEM/EDX mapping was performed, as shown in Fig.11. It can be seen that carbon-rich deposits do not form a dense layer on the catalyst surface, and their presence is scattered, whereas some areas are not covered with deposits. This further indicated a low amount of deposits on the surface of BaTiO₃.

SEM images of MgO/Al₂O₃ exhibit that its morphology was highly affected after exposure to CH₄ + Ar plasma, where the formation of agglomerates can be clearly seen in Fig.12 (c) and (d).

Fig.12. SEM images of MgO/Al₂O₃ (a,b) before exposure to DBD plasma; (c,d) after exposure to DBD plasma

Fig.13. EDX mapping of $\text{MgO}/\text{Al}_2\text{O}_3$ after exposure to $\text{CH}_4 + \text{Ar}$ DBD plasma.(a) Layered image; (b) Al map; (c) O map; (d) Mg map; (e) C map.

This is attributed to a high selectivity of solid products which are deposited on the surface of $\text{MgO}/\text{Al}_2\text{O}_3$, and then become agglomerated during the CH_4 plasma reaction. Similar to other materials tested as packing, the structure of $\text{MgO}/\text{Al}_2\text{O}_3$ is influenced by the presence of carbon-rich deposits randomly, whereas the formation of agglomerates occurs regionally. This can be further seen by SEM/EDX mapping, as shown in Fig. 13.

Fig.14 depicts the morphology of silica-SBA-15 for the fresh sample and the one used as packing inside the discharge gap of the DBD plasma reactor. The tested silica-SBA-15 constitutes from a meso-porous rope-like structure, according to Fig.14 (b).

Fig.14. SEM images of silica-SBA-15 (a,b) before exposure to DBD plasma; (c,d) after exposure to DBD plasma

The formation of agglomerates can be seen on the ropes, but not as much as the changes observed for $\text{MgO}/\text{Al}_2\text{O}_3$, as shown in Fig.10. This is in agreement with the results of the selectivity, discussed in Chapter 5, where at the same level of energy input the selectivity of deposits was lower for the reactor packed with silica-SBA-15 than that obtained for the reactor

packed with MgO/Al₂O₃. The scattered presence of carbon in the structure of silica-SBA-15 was also observed by SEM/EDX mapping, as shown in Fig.15.

It should be noted that, in addition to the deposition of solid products, silica-SBA-15 further undergoes structural changes, when it is treated with DBD plasma discharges. These changes can be seen in the structure of silica-SBA-15 in the form of the generation of new voids (pores) after exposure to plasma, as shown in Fig.14 (c).

Fig.15. EDX mapping of silica-SBA-15 after exposure to CH₄ +Ar DBD plasma.(a) Layered image; (b) Si map; (c) O map; (d) C map.

Similarly, the formation of agglomerates was observed for α -alumina after exposure to CH_4 plasma, as shown in Fig.16 (b).

Fig.16. SEM images of α -alumina (a) before exposure to DBD plasma; (b) after exposure to DBD plasma

It can be seen that fresh α -alumina possesses a crystalline structure, according to Fig.16 (a). This crystalline structure is partially influenced by exposure to the plasma, where the formation of agglomerates can be observed in the structure of α -alumina. Moreover, EDX results indicate that carbon-rich areas are regionally dispersed in the structure of α -alumina, as depicted in Fig.17, for two different regions of the analysed sample. It can be seen that the atomic percentage of carbon changes from 3.6 to 70.6 at%, respectively for the region A and the region B of the analysed sample.

Fig.17. EDX electron image and elemental analysis of α -alumina sample after exposure to CH_4 +Ar DBD plasma. (a,b) Region A; (c,d) Region B.

It can be clearly seen in Fig.17 (c) that Region B of the sample has been covered with carbon-containing deposits. On the contrary, the region A of the sample (Fig.17 (a)) is almost clean, similar to the structure of the fresh sample, as depicted in Fig.16 (a). For a better understanding of the distribution of carbon-containing deposits in the carbon-rich region (B), EDX mapping was also performed, as represented in Fig.18. The carbon-containing agglomerates are observable according to EDX mapping.

Fig.18. EDX mapping of α -alumina after exposure to $\text{CH}_4 + \text{Ar}$ DBD plasma. (a) Layered image; (b) Al map; (c) O map; (d) C map.

The SEM images of ZrO_2 are presented in Fig.19. The exposure of ZrO_2 to plasma decreased the surface roughness, and also generated new pores, similar to what was observed in the case of silica-SBA-15. The formation of agglomerates was not observed for ZrO_2 , however, the scattered presence of carbon was detected by EDX mapping analysis, as represented in Fig.20.

Fig.19. SEM images of ZrO_2 (a,b) before exposure to DBD plasma; (c,d) after exposure to DBD plasma

Fig.20. EDX mapping of ZrO_2 after exposure to $\text{CH}_4 + \text{Ar}$ DBD plasma.(a) Layered image; (b) Zr map; (c) O map; (d) C map.

6.4. Conclusions

In this chapter, high resolution scanning electron microscopy (HR-SEM) was utilized in order to characterize the deposits formed during the plasma reaction. A low voltage of 1kV was applied to obtain the images, because at higher voltages ($\geq 3\text{kV}$), the phenomenon of surface charging was intensively observed. This result further confirmed the low conductivity of the deposits. For the deposits formed on the dielectric quartz tube, SEM images exhibited an amorphous structure, where the morphology remained unchanged throughout the length of the plasma zone. EDX analysis indicated that the chemical composition of the deposits mainly consists of carbon ($\sim 91\text{ at\%}$), although it should be noted that this chemical composition is estimated excluding the presence of hydrogen, as the EDX detector is not able to analyse hydrogen. The presence of hydrogen was previously identified with CHN elemental analysis ($\text{H/C}=1.7\text{-}1.8$), confirming the polymeric nature of the formed deposits, due to a high content of H ($\sim 60\text{ at\%}$). SEM/EDX was also performed for catalyst samples, that were used as packing during the DBD plasma conversion of methane, as discussed in Chapters 4 and Chapter 5. The structure of γ -alumina was influenced after exposure to plasma by the formation of regionally amorphous carbon-containing agglomerates, as was further confirmed by EDX mapping. On the contrary, the structure of Pd/ γ -alumina did not exhibit the presence of carbon-rich agglomerates, in agreement with the previously found lower deposits selectivity for Pd loaded catalysts, indicating the resistance of the surface to deposits formation. SEM/EDX characterization for other tested materials further indicated that all tested materials undergo morphological changes during the plasma reaction, not only due to the formation of carbonaceous solid products but also owing to the plasma treatment of the surface, which consequently changes the surface roughness as well as generates voids in the structure of the materials.

References

- [1] J. Goldstein, Scanning Electron Microscopy and X-Ray Microanalysis, Springer, (2003).
- [2] G.H. Liu, Y.L. Liu, W. Chu, X.Y. Shi, X.Y. Dai, Y.X. Yin, Catalysis Communications, 9 (2008) 1087–1091.
- [3] X. Yan, B. Zhao, Y. Liu, Y. Li, Catalysis Today, 256 (2015) 29–40.
- [4] T. Witvrouwen, S. Paulussen, B. Sels, Plasma Process. Polym., 9 (2012) 750-760.
- [5] X. Tu, H.J. Gallon, J.C. Whitehead, Catalysis Today., 211 (2013) 120-125.
- [6] C. Liu, J. Zou, K. Yu, D. Cheng, Y. Han, J. Zhan, C. Ratanatawanate, W. L. Jang, Pure Appl. Chem., 78 (2006) 1227-1238.
- [7] J. Karupiah, Young Sun Mok, International Journal of Hydrogen Energy, 39 (2014) 16329-16338.
- [8] A. H. Khoja, M. Tahir, N. A. S. Amin, Energy Conversion and Management, 144 (2017) 262-274.
- [9] E. Chiremba, K. Zhang, C. Kazak, G. Akay, AIChE, 63 (2017) No. 10.
- [10] C. Casiraghi, F. Piazza, A.C. Ferrari, D. Grambole, J. Robertson, Diamond & Related Materials, 14 (2005) 1098-1102.
- [11] T.H. Chandrashekaraiah, R. Bogdanowicz, E. Rühl, V. Danilov 1, J. Meichsner, S. Thierbach, R. Hippler, Materials, 9 (2016) 594-606.
- [12] R.Pothiraja, N. Bibinov, P. Awakowicz, J. Phys. D: Appl. Phys., 44 (2011) 355206 (10pp).
- [13] J. Zhang, A. Palaniappan, X. Su, F. E. H. Tay, Applied Surface Science, 245 (2005) 304-309.
- [14] A. Palaniappan, J. Zhang, X. Su, F.E.H.Tay, Chemical Physics Letters, 395 (2004) 70-74.
- [15] T. Nozakia, K. Okazaki, Catalysis Today, 211 (2013) 29-38.

Chapter 7

Conclusions

7.1. Introduction

Direct conversion of methane has attracted increasing attention, considering its potential for large scale production of chemicals and fuels via processes which are more environmentally favorable due to a lower emission of CO₂, as well as are more economical owing to the integration of a multistep process to a single step process [1].

Despite preventing the generation of CO_x by-products, the conversion of methane via non-oxidative route is still challenging considering the high thermodynamic barrier for the C-H bond activation of methane molecule (434 kJ/mol) [2], which limits the equilibrium conversion of methane under non-oxidative conditions to a lower amount (below 10%) even by applying high temperatures (>700°C) [3].

Non-thermal plasma has the capability to activate C-H bond through collisions of high energy electrons with methane molecules, going beyond the thermodynamic limit of methane activation in the conventional thermal catalytic process [4]. Dielectric barrier discharge (DBD) is a type of non-thermal plasma (i.e., cold plasma), which can be used for dissociation of methane into CH_x fragments, capable of being operated in atmospheric pressure and ambient temperature, where no external heat source is needed. DBD plasmas are suitable to be integrated with catalyst surfaces considering its versatility for applying different configurations in a packed bed DBD plasma reactor (PBR) [5]. In this case, the random interactions of generated species (e.g., radicals) using only DBD plasma, which can still lead to the generation of unwanted products (e.g., deposits in methane coupling), can be thus influenced by the presence of catalyst surfaces [6], aiming at increasing the selectivity of the desired products via the synergy of the plasma and the catalyst.

In the present dissertation, the synergistic effect of the plasma and the catalyst was investigated with post-plasma catalysis and in-plasma catalysis configurations in different process conditions. It was discussed that the conversion of methane, the selectivity of C₂

products as well as the energy efficiency can be enhanced in an integrated DBD plasma-catalyst system compared with using only a DBD plasma reactor. It was further concluded that the type of the materials and the physicochemical properties (e.g., dielectric constant, conductivity, surface area, porosity) of the packing materials have a significant impact on DBD plasma characteristics (e.g., breakdown voltage, plasma discharge formation), by which consequently influences the performance of the packed bed DBD plasma reactor. The detailed conclusions will be discussed in the next sections.

7.2. The performance of the implemented DBD plasma reactor

Methane was activated by the implemented DBD plasma reactor (i.e., built during the present study) operating at ambient temperature and atmospheric pressure, forming C_2 , C_3 and hydrogen as the gas-phase products, which possessed 53% of the selectivity of the final products, as discussed in chapter 2. The solid products possessed 47% of the selectivity which was mainly deposited on the inner surface of the dielectric quartz tube. The composition of the formed deposits was identified by CHN elemental analysis, showing a 1.8 atomic H/C ratio. A higher content of hydrogen (~60 at%) indicated that the deposits has a polymeric nature, as well as has a poor conductivity. UV-Vis spectroscopy was utilized for identification of generated radicals inside and afterglow of the DBD plasma, where it was revealed that most CH_x radicals de-excited to their ground state level of energy, upon exiting the plasma zone. Therefore, the possibility of interaction of plasma species, in particular, the short-lived plasma species was quite low in the afterglow of the DBD plasma, where the presence of the packing materials (e.g., alumina, silica, zirconia) downstream did not lead to a notable impact on the distribution of the final products. The evaluation of process conditions such as residence time and methane concentration indicated that a higher residence time and a lower concentration of methane are favourable for achieving higher yield of C_2 products. It was also found that the addition of hydrogen as the feed to the inlet of the DBD reactor reduces the formation of

deposits to a lower amount, while it also changes the distribution of gas-phase products by proceeding hydrogenation of unsaturated compounds like acetylene and ethylene towards a higher production of alkanes.

7.3. The synergistic effect of Pd/ γ -alumina catalyst and the DBD plasma reactor with post-plasma catalysis configuration

Metal supported catalyst (i.e., Pd/ γ -alumina) was utilized as packing downstream of the plasma, in order to evaluate the effect of the presence of Pd metal active sites and its synergy with DBD plasma in Chapter 3. Results indicated that the C_2H_x and C_3H_y plasma reactive species, responsible for the formation of deposits downstream of the plasma, are long-lived species that were able to interact with the Pd catalyst downstream of the plasma. Simultaneously, H_2 molecules, which were earlier produced by the decomposition of methane in plasma zone, are dissociated to H radicals on Pd active sites. The successive hydrogenations of C_xH_y long-lived unsaturated species with adsorbed H therefore resulted in an extra production of alkanes, higher than what would result from complete hydrogenations of olefins and acetylene (i.e., which were earlier formed in the plasma zone). This additional formation of alkanes corresponded with the decrease obtained for the selectivity of the deposits. Thus, it was concluded that the downstream Pd catalyst enables the promotion of hydrogenation reactions, by attaching dissociated H_2 to C_2H_y and C_3H_y species on Pd active sites, faster than their oligomerization to form polymeric deposits. Consequently this leads to a higher formation of alkanes in gas-phase and a lower formation of deposits.

7.4. The synergy of DBD plasma and Pd/ γ -alumina catalyst integrated in the in-plasma catalysis configuration for non-oxidative coupling of methane

In chapter 4, Pd/ γ -alumina was used as packing inside the DBD plasma discharges in order to investigate the synergy of plasma and catalyst in the in-plasma catalysis configuration. Results

exhibited that the amount of Pd loading highly influences the distribution of C_2 products, while the presence of Pd significantly reduces the formation of deposits compared with bare γ -alumina packed bed reactor. It was revealed that the manipulation of the process conditions such as discharge power, total flow rate, methane concentration and plasma volume has a substantial impact on the overall performance of the DBD plasma reactor. It was found that Pd/ γ -alumina is resistant to the formation of deposits, due to the presence of Pd even in a low amount of Pd (0.5 wt%). The catalytic property of Pd active sites was capable of promoting hydrogenation reactions, in the way that the rate of hydrogenation reactions of CH_x and C_2H_y with H radicals on the surface became higher than the rate of their oligomerization/polymerization reactions to form deposits. In addition, the adsorption of CH_x fragments on the Pd catalyst further enhanced their recombination, generating new reaction pathways towards a higher production of C_2 compounds. This is attributed to a more efficient interaction of short-lived plasma species (CH_x) in the in-plasma catalysis system, as these species are generated very close to the catalyst surface, where they have a higher chance to be adsorbed on the surface. In this way, surface reactions can proceed faster, before they are quenched or recombined to other larger compounds like C_3H_y or C_4H_z . The presence of Pd also improved the energy efficiency of the process, 48% higher than that of obtained for the blank reactor. It was noted that the performance of the implemented DBD plasma reactor in the present study is comparable with those studies known as the promising ones in the literature. Considering the effect of the conductivity of the Pd on the surface of γ -alumina, it was further concluded that the presence of a metal (i.e., palladium) on the surface of a dielectric material like γ -alumina, has a remarkably positive effect in enhancing the synergy of plasma and catalyst compared to using a non-conductive packing (e.g., γ -alumina). This furthermore revealed that the dielectric property of the support can be influenced by the presence of a metal in such a way that it can moderate the strength of the electric field to generate more CH_3 and CH_2 rather

than CH and C radicals (i.e., highly potential to form deposits), which leads to a significantly higher yield of C₂ products, 2.6 times higher than that of obtained for the bare γ -alumina packed reactor.

7.5. The effect of dielectric property of the packing materials on the performance of the packed-bed DBD plasma reactor for non-oxidative coupling of methane

In chapter 5, the effect of dielectric constant was studied using different packing materials with different dielectric constants. For BaTiO₃ packed bed reactor, a lower conversion of methane was achieved than that of obtained for the blank reactor as well as that of obtained for the other tested materials with low dielectric constants such as γ -alumina, α -alumina and ZrO₂, MgO/Al₂O₃ and silica-SBA-15. This was attributed to a weak polarization inside the pores with small sizes (i.e., within the range of nm) for BaTiO₃. This was further explained to be a combined effect of dielectric constant and porosity in such a way that for a high dielectric packing like BaTiO₃, negative charges (i.e., electrons) accumulate mainly on the walls of the pore rather than on the bottom due to small gaps between the walls, where, as a consequence, the polarization of the right sidewall counteracts the polarization of the left sidewall for small pore sizes, resulting in an overall weak electric field. This explanation was further confirmed by increasing the discharge power to almost two times more, from 5.5 W to 11.0 W, which only slightly promoted the conversion of methane. This could further support that, despite increasing the charge density on the wall surface of the pores by increasing the discharge power, the polarization of the sidewalls becomes mainly neutralized, which therefore does not lead to a significantly stronger electric field. This was a different case when γ -alumina was evaluated in different discharge powers, as increasing the discharge power was favourable for achieving a higher conversion of methane as well as a higher yield of C₂ products. It was also found that the presence of low dielectric packing particles enhances the energy efficiency compared to the non-packed reactor, where the highest energy efficiency of 0.15 and 0.13

mmol of converted methane /kJ was achieved respectively for α -alumina and γ -alumina packed reactors.

7.6. The high resolution scanning electron microscopy (HRSEM) and energy dispersive X-ray spectroscopy (EDX) characterization of the deposits formed during the DBD plasma reaction for non-oxidative coupling of methane

In chapter 6, the HR-SEM and EDX characterization of deposits formed during $\text{CH}_4 + \text{Ar}$ plasma reactions was presented. HR-SEM was performed in a low voltage of 1kV, as in high voltages ($\geq 3\text{kV}$), the phenomenon of surface charging was intensively observed, which could further confirm the low conductivity of the deposits. For the deposits formed on the dielectric quartz tube, SEM images exhibited an amorphous structure, similar for the whole length of the inner surface of the dielectric quartz tube. EDX analysis indicated that the chemical composition of the deposits layer is mainly made of carbon ($\sim 91 \text{ at\%}$) and the rest of that (i.e., oxygen) was attributed to the impurity of the moisture originating from the argon flow. It should be noted that the chemical composition obtained by EDX excluded from the presence of hydrogen, as the EDX detector is not able to analyse the hydrogen spectrum. The presence of hydrogen was previously identified with CHN elemental analysis ($\text{H/C} = 1.7\text{-}1.8$), confirming the polymeric nature of the formed deposits, due to a high content of H ($\sim 60 \text{ at\%}$). SEM/EDX was also performed for catalyst samples used as packing. The structure of γ -alumina was influenced after exposure to plasma by the formation of regionally amorphous carbon-containing agglomerates, and furthermore was confirmed by EDX mapping. In contrast, the structure of Pd/ γ -alumina did not exhibit the formation of carbon-rich agglomerates, which was in agreement with lower selectivity of deposits as obtained for Pd loaded catalysts. All other tested materials including α -alumina, silica-SBA-15, ZrO_2 , $\text{MgO}/\text{Al}_2\text{O}_3$ and BaTiO_3 exposed to plasma were morphologically altered during the plasma reaction, not only due to the formation of carbonaceous solid products but also owing to the plasma treatment of the surface,

which resulted in changing the surface roughness as well as creating voids in the structure of the plasma-processed material.

References

- [1] C. Karakaya, R. J. Kee, *Progress in Energy and Combustion Science*, 55 (2016) 60–97.
- [2] F.P. Larkins, A.Z. Khan, *Aust J Chem.*, 42 (1989) 1655-1670.
- [3] Y. Xiao, A. Varma, *ACS Catal.*, 8 (2018) 2735–2740.
- [4] A. Górská, K. Krawczyk, S.Jodzis, K. Schmidt-Szałowski, *Fuel*, 90 (2011) 1946-1952.
- [5] I. Istadi, N.A.S. Amin, *Fuel*, 85 (2006) 577–592.
- [6] D. Park, J. Kim, T. Kim, *Catalysis Today*, 299 (2018) 86-92.

Summary

Non-oxidative coupling of methane via plasma catalysis is studied throughout this dissertation, aiming at finding the synergy of plasma and catalyst, as well as understanding the effect of plasma catalysis configurations (i.e., post-plasma catalysis and in-plasma catalysis) on the underlying mechanism of the interaction of plasma activated species with catalyst surfaces.

In chapter 2, the design of the DBD plasma catalytic reactor set-up is elaborated. The integration of different catalyst supports downstream of the DBD plasma is also evaluated in different process conditions. C₂ and C₃ hydrocarbons and hydrogen are produced as the major gas-phase products of methane activation in DBD plasma, while deposits were formed as the solid products of the process, mainly on the inner surface of the reactor wall. The analysis of the deposits layer shows the presence of 60 at% of hydrogen (H/C molar ratio=1.8), which indicates the polymeric nature of the deposits. The plasma species generated inside and in the afterglow of the DBD plasma are identified by UV-Vis spectroscopy for both inside and downstream of the plasma, where these spectra revealed that most CH_x fragments generated by CH₄ plasma are not in their reactive form in the afterglow of the plasma. Consequently the presence of a downstream packed bed did not lead to a strong interaction of plasma species with the downstream material. It is further demonstrated that the addition of H₂ to the inlet of the DBD reactor has a positive effect in reducing the deposits.

In chapter 3, Pd/γ-alumina catalyst is used as downstream packing, pursuing the interactions of long-lived activated plasma species with the catalyst, investigating the synergy of plasma and the palladium catalyst in the enhancement of C₂ yield and the reduction of deposits. It is found that at the presence of Pd/γ-alumina, the selectivity of C₂ and C₃ compounds is enhanced, corresponding with a remarkable reduction for the selectivity of deposits. It is elucidated in detail that the route of this enhancement is the interaction of plasma activated species like C₂H_y and C₃H_z that can live sufficiently long until they reach to the

catalyst downstream of the plasma. These species are unsaturated and therefore potentially reactive, meaning that they can go through successive hydrogenations by Pd active sites. This therefore leads to a higher production of saturated C_2 and C_3 compounds, while reducing the deposits formation. The discussion regarding the reaction pathways are further discussed, where the possible route for the production of C_2 and C_3 compounds as well as the formation of deposits downstream of the plasma is elaborated considering the interaction of long-lived plasma activated species with the downstream Pd catalyst.

In chapter 4, in-plasma catalysis configuration is evaluated using Pd/ γ -alumina as the packing inside the discharge gap. The effect of Pd loading, the effect of support and their separate influences on the conversion and yield of the products are furthermore discussed. Different process conditions including input power, residence time, methane concentration and plasma volume are applied to evaluate the effect of these parameters on the conversion and the distribution of the products. Results indicate that packing Pd/ γ -alumina inside the plasma discharges, even with low amounts of Pd (0.5wt% and 1wt%), remarkably reduces the formation of deposits, by consuming the C_xH_y deposit-precursors via surface reactions, which advantageously leads to a notable increase in the yield of C_2 compounds greater than those obtained for the blank reactor as well as the packed reactor with γ -alumina. It is evidenced that a low amount of Pd (1wt%) is more favourable for a higher production of unsaturated compounds like C_2H_4 . A higher loading of Pd up to 5wt% results in a higher formation of alkanes like C_2H_6 , as it provides more active sites for the hydrogenation of unsaturated compounds like C_2H_2 and C_2H_4 . Furthermore, it is discovered that the variation of process conditions largely influences the yields of C_2 hydrocarbons and deposits, by which the distribution of saturated and unsaturated C_2 compounds shows optimum points for the Pd/ γ -alumina packed bed reactor once the process conditions are manipulated. In addition to the enhancement of the C_2 yield and the notable reduction of deposits, the energy efficiency of the

process is also improved, 48% higher than that obtained for the bare γ -alumina packed bed DBD reactor.

In chapter 5, the effect of the dielectric property of different packing materials is studied for coupling of methane in the implemented DBD plasma reactor. High dielectric BaTiO₃ was packed inside the discharge gap to be compared with other packing materials with a lower dielectric constant including γ -alumina, α -alumina, silica-SBA-15, ZrO₂ and MgO/Al₂O₃. For a constant amount of energy input (7-8W), the BaTiO₃ packed bed DBD reactor results in a lower conversion of methane (6-17%) during the reaction time compared to that achieved for the other tested materials (18-50%). Comparably, the BaTiO₃ packed reactor produces more C₂H₄, where the selectivity of C₂H₄ reaches 32% almost two times higher than that obtained for the reactor packed with low dielectric materials. Considering a notable drop for the conversion of methane, C₂ yield is still lower for the BaTiO₃ packed plasma reactor, with respect to the C₂ yield obtained for other tested materials and even compared to the blank reactor. Increasing the discharge power to values higher than 5.5W for the BaTiO₃ packed plasma reactor only slightly promotes the conversion of methane. On the contrary, in the case of γ -alumina packed reactor, the conversion and consequently C₂ yield show an ascending trend by increasing the discharge power to 11.0 W. The reason is ascribed to a combined effect of dielectric constant and the size of the pores of BaTiO₃, which possesses small sizes in the range of nm and therefore for these small sizes the polarizations inside the pores are weak due to the counteraction of the polarization of the right sidewall by the polarization of the left sidewall of the pores, which causes an overall weak electric field across the BaTiO₃ packed bed. The evaluation of the energy efficiency is also performed where low dielectric materials, i.e., γ -alumina and α -alumina achieve higher values (i.e., 0.13-0.15 mmol of converted methane/kJ) compared to other tested materials.

In chapter 6, the deposits formed during $\text{CH}_4 + \text{Ar}$ plasma reactions are characterized with high resolution scanning electron microscopy (HRSEM) and energy dispersive X-ray elemental spectroscopy (EDX). For the deposits formed on the inner surface of the dielectric quartz tube, a low voltage ($\sim 1\text{kV}$) SEM-imaging was performed in order to prevent the surface charging, which furthermore indicates the low conductivity of the deposits layer. SEM images show an amorphous structure for the layer, where the structure remains unchanged throughout the length of the dielectric quartz tube. The chemical composition of the deposits layer is also analysed with EDX, indicating a high content of carbon in the layer, although it should be noted that this chemical composition is estimated excluding the presence of hydrogen, as EDX detector is not able to analyse hydrogen spectrum. For catalyst samples, the formation of carbon-containing deposits are regionally observed by SEM as well as detected by EDX, accompanied with morphological changes in the structure owing to the treatment of the surface by the DBD plasma discharges. In the case of bare γ -alumina, carbon-rich agglomerates are formed after exposure to plasma, which is different than Pd/γ -alumina, where the formation of agglomerates was not observed due to the presence of palladium on the surface, which reduces the formation of deposits, which is in agreement with the experimental results obtained for the plasma-induced conversion of methane. SEM/EDX results for other plasma-processed materials including $\text{MgO}/\text{Al}_2\text{O}_3$, silica-SBA-15, ZrO_2 , BaTiO_3 and α -alumina indicate that all these materials undergo morphological changes during the exposure to plasma. These morphological changes are observed in the forms of the generation of new pores (voids) in the structure as well as the moderation of the surface roughness towards a smoother surface.

Samenvatting

In deze dissertatie is de niet-oxidatieve koppeling van methaan via plasmakatalyse bestudeerd, met als doel te bepalen welke synergetische effecten er bestaan tussen een plasma en een katalysator, alsmede begrip te verkrijgen van het effect van verschillende plasmakatalytische configuraties (d.w.z. post-plasma katalyse en in-plasma katalyse) op het onderliggende mechanisme van de interactie van plasma-geactiveerde componenten met katalysator oppervlakken.

In hoofdstuk 2 is het ontwerp van de gebruikte DBD-plasma-katalytische reactoropstelling uitgewerkt. De integratie stroomafwaarts van het DBD-plasma van katalysatoren op verschillende ondergronden is bekeken voor verschillende procescondities. C₂ en C₃ koolwaterstoffen en waterstof worden geproduceerd als hoofdgasfaseproducten van methaanactivering in het DBD plasma, terwijl een neerslag wordt gevormd uit vaste producten uit het proces, voornamelijk op het binnenoppervlak van de reactorwand. De analyse van de gedeponeerde laag toont de aanwezigheid van 60 at% waterstof (H/C molaire verhouding=1.8), wat het polymere karakter van het neerslag aangeeft. Met UV-Vis spectroscopie zijn de plasmacomponenten in het DBD plasma en stroomafwaarts ervan geïdentificeerd, de spectra tonen aan dat de meeste CH_x fragmenten, gegenereerd door het CH₄ plasma, niet in hun reactieve vorm aanwezig zijn in de afterglow van het plasma. Dientengevolge leidt de aanwezigheid van een stroomafwaarts gepakt bed niet tot een sterke interactie van plasmacomponenten met het stroomafwaarts aanwezige materiaal. Verder wordt gedemonstreerd dat de additie van H₂ aan de inlaat van de DBD reactor een positief effect heeft op de reductie van depositielagen.

In hoofdstuk 3 is Pd/γ-alumina-katalysator gebruikt als stroomafwaartse pakking, met als doel het volgen van interacties van langlevende geactiveerde plasmacomponent met deze katalysator, om meer te weten te komen over de rol van de synergie tussen plasma en palladiumkatalysator in het verhogen van de C₂-opbrengst en de reductie van depositielagen. Er is gevonden dat in aanwezigheid van Pd/γ-alumina de selectiviteit van C₂ en C₃ componenten wordt verhoogd, samengaan met een opvallende reductie van de selectiviteit van gedeponeerde lagen. Er is in detail opgehelderd dat de oorzaak van deze verhoging ligt in de interactie van plasma-geactiveerde componenten als C₂H_y en C₃H_z die een levensduur hebben die lang genoeg is om de katalysator stroomafwaarts van het plasma te bereiken. Deze componenten zijn onverzadigd en daarom potentieel reactief, wat inhoudt dat ze opeenvolgende hydrogeneringsstappen kunnen doorlopen op actieve posities op het Pd. Dit vervolgens leidt tot een hogere productie van verzadigde C₂ en C₃ componenten, waarbij gelijktijdig de neerslagdepositie wordt verminderd. De corresponderende reactiepaden worden besproken, waarbij de mogelijk route voor zowel de productie van C₂ en C₃ verbindingen als voor de vorming van een neerslag stroomafwaarts van het plasma is uitgewerkt, in acht nemende de interactie van langlevende plasma-geactiveerde componenten met de stroomafwaarts geplaatste Pd katalysator.

In hoofdstuk 4 is de in-plasma katalytische configuratie uitgewerkt voor Pd/γ-alumina als pakking in de ontladingszone. Het effect van Pd-belading en het Pd-substraat en hun individuele invloeden op de omzetting en opbrengst van specifieke producten worden beschouwd. Verschillende procescondities, inclusief ingangsvermogen, verblijftijd, methaanconcentratie en plasmavolume zijn toegepast om de effecten van deze parameters op de conversie en de productdistributie te evalueren. De resultaten geven aan dat een pakking van Pd/γ-alumina in de plasmaontlading, zelfs met even met lage hoeveelheden van Pd (0.5wt% en 1wt%), de vorming van neerslag opmerkelijk terugdringen door de consumptie van C_xH_y neerslag-precursors via oppervlaktereacties, wat een aanzienlijke toename in de

opbrengst van C_2 -verbindingen als positief gevolg heeft, hoger dan de opbrengst behaald voor een ongepakte reactor of de met γ -alumina gepakte reactor. Er is bewezen dat een lage hoeveelheid Pd (1 wt%) gunstiger is voor een hogere productie van onverzadigde verbindingen zoals C_2H_4 . Een hogere Pd-belading, tot 5 wt%, resulteert in een toegenomen vorming van alkanen zoals C_2H_6 , omdat er meer actieve posities worden aangeboden voor de hydrogenering van onverzadigde verbindingen zoals C_2H_2 en C_2H_4 . Verder is ontdekt dat door variatie van de procescondities de opbrengst van C_2 koolwaterstoffen en neerslagen sterk kan worden beïnvloedt, waarbij de verdeling van verzadigde en onverzadigde C_2 -verbindingen optima vertoont voor de Pd/ γ -alumina gepakte-bedreactor onder specifieke procescondities. Bovenop de verhoging van de C_2 opbrengst en de aanzienlijke reductie van neerslagen wordt ook de energie-efficiëntie van het proces verbeterd, tot 48% hoger dan wat wordt verkregen voor de met γ -alumina gepakte DBD reactor.

In hoofdstuk 5 is het effect van de diëlektrische eigenschappen van verschillende pakkingsmaterialen in de gebruikte DBD plasmareactor bestudeerd voor de koppeling van methaan. Hoog-diëlektrisch $BaTiO_3$ is in de ontladingszone geplaatst en vergeleken met andere materialen met een lagere diëlektrische constante, zoals γ -alumina, α -alumina, silica-SBA-15, ZrO_2 en MgO/Al_2O_3 . Voor een constant vermogen (7-8W) resulteert de $BaTiO_3$ -pakking in de DBD reactor in een lagere conversie van methaan (6-17%) vergeleken met de andere geteste materialen (18-50%). In vergelijking produceert de $BaTiO_3$ -gepakte reactor meer C_2H_4 , terwijl de C_2H_4 -selectiviteit 32% bereikt, bijna twee keer zo hoog als wordt bereikt voor de reactor gepakt met laag-diëlektrische materialen. Neemt men hierbij de vermindering in de conversie van methaan ook in acht, dan is de C_2 -opbrengst nog steeds lager voor de $BaTiO_3$ -gepakte plasmareactor, in vergelijking met die voor de andere geteste materialen en zelfs vergeleken met de ongepakte reactor. Verhoging van het ontladingsvermogen tot waarden boven de 5.5W voor de $BaTiO_3$ gepakte plasmareactor verhoogt de methaanconversie slechts marginaal. Daarentegen vertonen in het geval van de γ -alumina gepakte reactor de conversie en dientengevolge ook de C_2 -opbrengst een stijgende trend bij verhoging van het ontladingsvermogen tot 11.0 W. De oorzaak hiervan wordt toegeschreven aan een gecombineerd effect van de diëlektrische constante van en de grootte van de poriën in $BaTiO_3$, welke laatste vrij klein zijn, in de grootteorde van nm, voor welke grootte de polarisatie in de poriën zwak is ten gevolge van de tegenwerking van de polarisatie van de rechter zijwand op die van de linker zijwand, wat opgeteld leidt tot een zwak elektrisch veld over het met $BaTiO_3$ gepakte bed. Een evaluatie van de energie-efficiëntie is ook uitgevoerd voor laag-diëlektrische materialen, waar gevonden is dat γ -alumina en α -alumina hogere waarden geven (0.13-0.15 mmol) in omgezet methaan/kJ, in vergelijking met de andere geteste materialen.

In hoofdstuk 6 zijn de gedeponeerde lagen gevormd gedurende de $CH_4 + Ar$ plasmareacties gekarakteriseerd met hoge-resolutie scanning elektronen microscopie (HRSEM) en energie-dispersieve X-ray element-spectroscopie (EDX). Voor het neerslag gevormd op het binnen oppervlak van de diëlektrische kwartsbuis is SEM-imaging bij laag voltage (~ 1 kV) uitgevoerd om te voorkomen dat het oppervlak oplaadt, wat overigens aangeeft dat de gedeponeerde lagen een lage geleidbaarheid bezitten. De SEM-beelden tonen aan dat de lagen een amorfe structuur bezitten, terwijl de structuur onveranderd blijft over de lengte van de diëlektrische kwartsbuis. De EDX-analyse van de chemische samenstelling van de gevormde laag geeft een hoog koolstofgehalte aan, al moet men in acht nemen dat de chemische samenstelling is afgeschat zonder de aanwezigheid van waterstof mee te nemen, aangezien de EDX detector dit element niet kan waarnemen. Voor de katalysatormonsters is een plaatselijke vorming van koolstofhoudende depositielagen waargenomen zowel met SEM als met EDX, gepaard gaand met morfologische veranderingen in de structuur ten gevolge van de oppervlaktebehandeling door de DBD plasmaontlading. In het geval van niet met een

katalysator bedekt γ -alumina zijn koolstofrijke agglomeraten gevormd na de blootstelling aan het plasma, anders dan bij Pd/ γ -alumina, waar de vorming van agglomeraten niet heeft plaatsgevonden ten gevolge van de reducerende actie door de aanwezigheid van palladium op het oppervlak, in overeenstemming met de experimentele bevindingen voor de plasma-geïnduceerde conversie van methaan. De SEM/EDX resultaten voor andere plasma-behandelde materialen zoals MgO/Al₂O₃, silica-SBA-15, ZrO₂, BaTiO₃ en α -alumina tonen aan dat al deze materialen morfologische veranderingen hebben ondergaan gedurende de blootstelling aan plasma. Deze veranderingen uiten zich in de generatie van nieuwe poriën (leemtes) in de structuur alsook een matiging van de oppervlakteruwheid, in de richting van gladdere oppervlaktes.