

Afterthoughts of the workshop Challenges in Plasma and Catalysis, 17th & 18th October 2019, Le Havre, France Plasma-Assisted Catalysis of CO₂ Methanation

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Abstract. The main objective of the project CO₂ VIRIDIS was to study interactions between catalysis and different types of plasmas. The methanation of CO₂ with hydrogen on different catalysts was used as a model reaction. To investigate how plasma-assisted catalysis could help the activation of CO₂ in an energy efficient way, CO₂ Viridis has started two years ago as a collaboration among four laboratories in Normandie, France:

- CORIA (Complexe de Recherche Interprofessionnel en Aérothermochimie) Rouen, involved with the optical emission spectroscopy for the measurement of species formed in different plasmas (DC, microwave, low pressure, atmospheric pressure), which helped to build theoretical models based on collisions, vibrational excitations and energy levels of the formed species, particularly using CO₂ plasmas;
- LCS (Laboratoire Catalyse et Spectrochimie) Caen, in charge with the development of highly efficient catalysts for CO₂ methanation and with the testing of the obtained catalysts in DBD plasma;
- LOMC (Laboratoire Ondes et Milieux Complexes) Le Havre, looked at mechanisms and kinetics of CO₂ dissociation;
- LSPC (Laboratoire de Sécurité des Procédés Chimiques) Rouen, developed a microwave plasma pilot and tested CO₂ conversion using microwave plasmas.

The workshop benefited from talks given by international guests working on similar subjects and who have been invited to share their experience and to contribute with ideas towards the understanding of the complex system involving plasma-assisted catalysis; a list of participants and their shared expertise is given at the end of the article.

The workshop's main goal was to disseminate the results of the carried-out research during the project - system modelling, catalyst development/selection, plasma type - and to assess the results in view of process scale up.

1 Introduction

Over the last 10 years or so, several technologies have been developed to utilize renewable sources to produce value added chemicals, and CO₂ has been discussed widely as a potential renewable source¹⁻⁴. The utilization of CO₂ not only contributes to the decrease of greenhouse gas emissions, but also produces useful chemicals such as C1 building blocks, syngas, and higher hydrocarbons. However, its activation generally requires high temperatures (>540 °C to obtain more than 50 % CO₂ conversion in CO₂ reforming with methane) because of its large ionization potential and a small electron affinity, which leads inevitably to a massive energy consumption. This disadvantage limits practical applications even if renewable sources are used,

therefore, energy efficient improvements are necessary for CO₂ utilization technology.

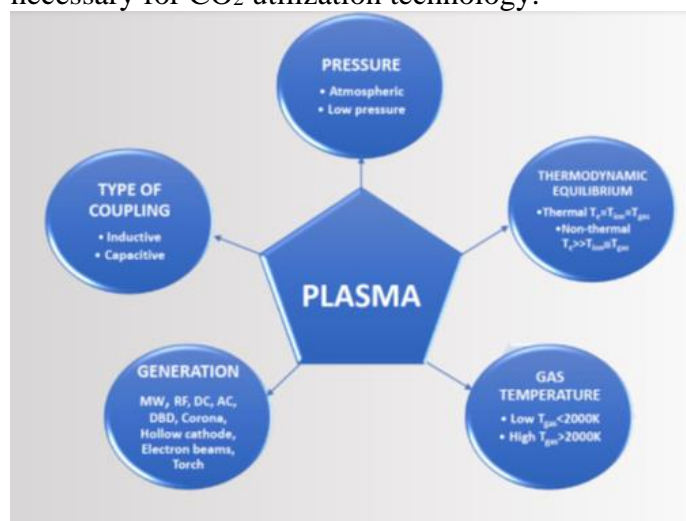


Figure 1: Plasma classification

At present there are a few strategies for the conversion of CO₂ that could be an effective alternative to a thermochemical reactor system. These alternative strategies include the use of an electric field, microwave dielectric heating, plasma-catalysis hybrid system, and a light assisted catalytic system. These methods, however, also require excessive energy input to overcome the activation energy of the target reaction and although some papers reported a reduced operating temperature with high efficiency conversion, up to present these processes can only be operated on a small scale that is suitable only for localized CO₂ conversion and is not acceptable for industrial production¹⁻³.

Understanding the interaction between plasma and catalyst is not an obvious subject: essentially, plasma is an ionized gas containing an equal number of positive ions as of electrons and negative ions. Plasma is electrically neutral, and its degree of ionization can range from very low, i.e., partially ionized, to 100%, or fully ionized. Technically, plasma can be created by a variety of discharge techniques (electrode or electrode-less), which initiate a breakdown of the gas and create a range of reactive species such as electrons, ions, dissociated and excited species leading to chemical transformations. Plasmas can be characterized by the pressure regime in which they operate, either low pressure (< 1 atm) or high pressure (>1 atm). Low-pressure conditions favour surface collisions making catalytic effects easier to notice and they also minimise the deactivation of the excited states produced in the plasma through gas-phase. Another distinction concerns the degree of thermal equilibrium in the plasma. It may be thermal with all the degrees of freedom including the electrons, ions and neutral species having the same temperature as the bulk gas (typically > 1000 K). In contrast, non-thermal plasma has a high degree of disequilibrium between the light electrons and the heavier particles (ions, radical and molecules). Little kinetic energy is transferred between the light electrons and the heavy atomic and molecular species that remain close to their ambient temperature. Thus, a non-thermal discharge can create excited and reactive species that can normally only be produced in an equilibrium system such as an arc or flame at very high temperatures. Hence, plasma typically produces ionised, excited and reactive gaseous species in

relatively low concentrations compared with the bulk neutral atomic and molecular species providing the means by which the key components in the gas stream are destroyed or converted into other potentially useful chemicals. In plasma-catalysis, these ionised, excited and reactive gaseous species can also interact with a catalyst at near ambient temperatures for which conventional thermal catalysis would be inactive.

2 Main topics of the workshop

2.1 Plasma modelling

Several research teams have presented their work on CO₂ plasma modelling. Most of the developed models have been based on the various energy levels of the possible excitation states of CO₂. Some models have integrated the dissociation of CO₂ in CO and O, which helped to predict the distribution of the excited species within the plasma as a function of energy levels, electric field intensity etc. In connection with the vibrational states, the cross sections calculations are very important, and they were found to depend on the excitation type, i.e. rotational, vibrational or electronic. As an example, Bultel and co-authors have simulated the concentration profiles of the species obtained in a post discharge shock wave plasma.

Fundamental studies of electron collisions with larger molecules like BF₂⁺ and NO₂ have been presented. As per CO₂ plasma modelling, the results of these studies emphasize the importance of accurate cross section calculations.

From all presentations, it was concluded that plasma modelling must be done via a double approach, which combines the scientific procedure with an engineering point of view. First, the fundamental properties of thermal plasmas that are required in the models are to be considered, followed by the basic equations and structures of the models. The third part must be devoted to test cases, with the objective of studying some basic phenomena to show their influence on plasma behaviour in simple configurations, and the validation of the models pointing out the roles of radiation, thermal conductivity and electrical conductivity.

In the specific case of microwave-excited plasma, one must consider that these plasmas are more complex. The charged particles are both

affected by external electromagnetic fields and contribute to them. The resulting system is nonlinear and therefore difficult to analyse. Electromagnetic waves carry energy from the plasma surface into the bulk plasma, where the major part of energy carried by the electromagnetic wave can be absorbed. Electromagnetic wave propagation in plasma is similar to the electromagnetic wave propagation in a dielectric medium, similar rules apply, and concepts developed for dielectric medium can be transferred to plasma.

2.2 Modelling of catalytic systems under plasmas

Engelmann & co-workers modelled the mechanism of non-oxidative coupling of methane to ethylene and acetylene in a plasma environment. The mechanism of the methane reforming was proposed using a *microkinetic model* for the formulation of a rate law of methane decomposition to CH_3^+ , H^+ etc. and a *catalytical model* where a pure metal catalyst was used to complete the reforming reaction. The calculation of interaction forces/binding energies between formed species and different metal catalysts showed that noble metals, e.g. Ru, Pd, Pt, Rh, promote strong interactions while less noble metals, e.g. Cu, Ag, promote weaker interactions leading to the desorption of products. Furthermore, possible reaction paths were proposed on coupling reaction of methane through plasma and studied theoretically using the transition state theory; methane excitation depends on the vibrational mode and the temperature. The use of plasma allows to obtain high density excited-state populations in binding mode however, with low efficiency. The choice of temperature and catalyst can be used to ‘tune’ the plasma-assisted methane reforming reaction paths towards acetylene production or towards other products.

2.3 Experimental testing

Plasma-catalysis can be considered as a variant of heterogeneous catalysis where the gaseous phase of the reagents and products differs from the solid phase of the catalyst. Solid catalysts come in a variety of forms that all have the property of absorbing species onto their surface and thereby allowing possible migration into their bulk. Commonly, an active

material such as a transition metal is placed onto a support material such as metal oxide or silica. The role of the support is to provide a high surface area, with defined porosity and to give thermal and mechanical stability. The species that are adsorbed onto the catalyst can remain in their gaseous form upon adsorption and be weakly bound (physisorption) or they may become dissociated into fragments and be strongly bound to the surface (chemisorption) and then react with either other species on the surface or by contact with an incoming gas-phase species. In contrast to thermal catalysis where the reactive species are formed dissociatively only on the surface of the heated catalyst, in plasma-catalysis reactive species can also be formed in the gas-phase either by dissociation within the plasma or by subsequent gas-phase reactions of plasma-excited species.

The chemical system most studied in this project was CO_2 methanation using Ni catalysts in various plasmas. The gas pressure and the type of discharge are reported to have great importance on the reaction path.

It was reported that DBD plasmas offer interesting results at low gas pressure, and not only for CO_2 methanation on Ni catalysts. The effect of various supports like alumina, silica, zeolites and the effect of a cocatalyst (Ce, Co) addition have been presented. Equally, the use of a plasma may allow the activation and the possible usage of less active catalyst like Fe or Co, which are more economically attractive to a scale-up scenario. Research was also conducted towards plasma catalytic surface treatments that may help in catalyst synthesis, in preventing coke deposition or in the regeneration of coked catalysts.

In the specific case of microwave excited plasmas, the presented results showed that more investigations are required as to find out the optimised conditions for favouring methane production; these investigations include *i*) the location of the catalyst, within or after the discharge; *ii*) gas pressure; *iii*) microwave frequency.

2.4 Challenges of scaling-up catalytic-plasma processes

Plasma-assisted catalysis of CO_2 methanation is an emerging concept towards sustainable economies

however, when evaluating the development of a new process, the production/processing capacity represents the main design guideline, thus dictating the equipment requirements. From an industrial perspective, one of the most important input parameters is that the scaling up of such system must consider the need to operate at considerably high throughput and therefore demanding high energy input.

In addition to this, challenges related to characterization of the structural and dynamic aspects of the plasma-catalyst aspects across a wide range of scales must be resolved before assessing the scaling-up. These challenges mainly concern:

Development of chemical kinetic models that can be implemented into multidimensional multiphysics models for process design, optimization, and control. Plasma-catalysis is a complex process which is non-trivial to model; in situ measurements are required to provide the fundamental information about the behaviour of the different species created in the gas-phase and on the catalytic surface that is necessary to test and develop the modelling. The modelling must also be able to incorporate the wide range of inhomogeneity in properties such as electric field, concentration, temperature etc. that are caused by the non-equilibrium nature of the plasma and the morphology of the catalyst. However, it is only by obtaining a fundamental understanding of these effects that we will be able to determine and specify the most effective composition and structure of catalysts for best performance under plasma activation and determine the optimal design, configuration and operating conditions for the plasma. The interaction between modellers and experimentalists is a vital part of understanding plasma catalysis and thereby determining and developing the full potential of the technique.

Choice of the plasma system. If plasma catalysis shall be a valuable option for CO₂ reforming, the process should be performed at atmospheric pressure due to higher space time yields and lower operating costs by avoiding the generation and sustainment of low pressures. However, at atmospheric pressure the

gas has a high particle density, which makes non ionizing collisions of the electrons with the heavy particles inevitable resulting in thermal arc discharges. In comparison to the established atmospheric pressure non-thermal plasma sources such as DBD and corona discharge, microwave discharges can generate homogenous plasmas. Microwave discharges favour lower gas temperature at low pressure and quite high gas temperature at atmospheric pressure. The temperature increase can be limited via two main approaches:

- By pulsing the microwave field;
- By choosing a different microwave frequency.

Within the ISM band, microwave frequencies at 433.92 MHz, 915 MHz, 2.45 GHz and 5.8 GHz can all have potential applications in plasma assisted catalysis. At present, microwave plasmas for industrial applications are commonly excited at 2.45 GHz; some applications at 915 MHz are also reported. When choosing the frequency of the microwave field, the following factors must be correctly assessed:

- Increase in frequency decreases the transferred energy from electrons to other species leading to lower reaction temperature;
- Increase in frequency decreases the volume & cross-section of the plasma.

Another factor that must be taken into account when scaling up microwave plasma reactors is that, in contrast to dielectric heating, the scale up by use of more efficient high-power magnetrons at lower frequencies¹ is not sufficient in the case of the plasma reactor scale-up. If the power density in the reactor is important for the chemical reaction, the total power scale-up is non-trivial and can be estimated via equation 1.

Example: The equivalent power density of a 6 kW, 2.45 GHz process can be obtained at 915 MHz using ~ 115 kW – equation 1.

$$6 \text{ kW} \times \left(\frac{2450}{915}\right)^3 = 115 \text{ kW} \quad (1)$$

¹ The availability of industrial microwave generators is directly linked to the maximum nominal power of CW magnetrons, i.e. 6 kW at 2.45 GHz (overall mains electrical efficiency ~60%) and 100 kW at 915 MHz (overall mains electrical efficiency ~80%). Due to poor

performance and high cost, magnetrons at 433.96 MHz and 5.8 GHz are not discussed. Similarly, CW magnetrons at 2.45 GHz with nominal power > 6 kW are not considered suitable for industrial applications.

The main industrial applications of microwave excited plasmas include photoresist stripping in semiconductor manufacturing, deposition of barrier layers in PET bottles, high rate deposition process of quartz on polycarbonate windows, plasma photo curing of paint applied in the automotive industry, UV disinfection for water treatment, waste gas treatment for decomposition of fluorine-based components such as CF_4 , C_2F_6 , CHF_3 , and SF_6 or ammonia, and plasma reforming to increase efficiency in wood gas engines^{4,6}. Specific advantages of the technology include the enablement of a high energy density source and a highly reactive medium, operational flexibility, fast response time to inlet variations and reduced footprint. These aspects make microwave-assisted plasma a promising alternative technology to conventional thermal chemical processes provided that certain technical and operational challenges related to scalability are overcome. An important drawback of microwaves, very often not mentioned, is the high cost of equipment and the relatively low (~1 year) lifetime of the magnetrons. However, in terms of microwave technology successful implementation in industry, a more complex analysis of benefits is required: technical and economic advantages as well as those process specific must be analysed together.

Finally, understanding how microwaves can enhance plasma-assisted catalysis requires a good knowledge of not only the fundamentals of microwaves and their interaction with matter, but also of the hardware, the practical advantages and limitations of the available tools. Understanding the pros and cons of microwave energy is very important in deciding when and where microwaves can replace other plasma sources.

3 Conclusions

To understand how plasma and catalyst might interact, we need to better understand the nature of plasma and catalyst separately and to find how to bridge the fundamental knowledge of the two scientific fields.

The project CO_2 Viridis enabled to obtain satisfactory results for the modelling of single or dual gas plasmas (e.g. CO_2 , $\text{CO}_2 + \text{H}_2$) if limited to the generated species & kinetics. To further progress, the consortium will focus on:

- Modelling & experimental validation of a solid catalyst presence within the plasma by considering more complex plasmas consisting of reagents & the reaction's products including methane, water etc., but equally considering the time evolution of different species within the plasma;
- Identification of the interaction mechanism between active species absorbed on the catalyst and the activated species formed within the plasma (electrons or activated molecules) understanding that the choice of catalyst (metal & support) is of primary importance, the energetic levels of interactions depending on both the active metals and the support. Macroscopically, one area of interest where we can see the effect of scale concerns the pores that lead from the surface into bulk of the catalyst. Pores in catalytic materials can selectively adsorb species depending on their size, which may affect the overall reactivity and selectivity of the plasma process. Penetration of plasma into the pores may specifically excite the adsorbed atoms or molecules creating localized reactive species. In the particular case of the microwave excited plasmas but not only, the electrical properties of the catalytic material can also play an important role in how the plasma interacts with the catalyst. The use of dielectric materials can have a profound effect on the electrical properties of the discharge by changing the capacitance of the plasma reactor.

A reference experiment will be designed and applied for the experimental validation of these interactions.

4 Acknowledgments

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For further reading

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List of participants, invited speakers and their field of contribution

Plasma modelling: Daniela Pietanza & Vincenzo Laporta, P.LAS.M.I. Lab, Bari, Italy; Vasco Guerra, Technical University of Lisbon, Portugal; Arnaud Bultel, Université de Rouen Normandie, France; Janos Zsolt Mezei, Institute of Nuclear Physics of the Hungarian Academy of Sciences, Debrecen, Hungary; Viatcheslav Kokoouline, University of Central Florida, Orlando, US; Mehdi Ayouz, Centrale Supélec, Saclay, France.

Modelling of catalytic systems under plasmas: Yannick Engelmann, University of Antwerpen, Belgium

Experimental testing: Bachar Alrafei, Institut National de Sciences Appliquées, Rouen, Isabelle Polaert, Institut National de Sciences Appliquées, Rouen, France ; Alain Ledoux, Institut National de Sciences Appliquées, Rouen, France; Carlos Manuel Faria De Barros Henriques, Technical University of Lisbon, Portugal; Radoslaw Debek, Sorbonne Universités, UPMC, Université Paris 6, France; Federico Azzolina-Jury, Ecole Nationale Supérieure d'Ingénieurs de Caen, France; Teresa Grzybek, AGH University of Science and Technology, Kraków, Poland ; Savita Kaliya, Université de Lille, France; Catherine Batiot Dupeyrat, Université de Poitiers, France.

Challenges of scaling-up catalytic-plasma processes: Jean-Pierre Dath, Total, France; Marilena Radoiu, Microwave Technologies, France



Figure 2: Group photo of all participant of the workshop

About the Author:

Marilena Radoiu (Chartered Chemist, Member of the Royal Society for Chemistry) received her M.Sc. in Organic Technological Chemistry from the Polytechnic University of Bucharest in 1993 and her Ph.D. in Radiochemistry and Nuclear Chemistry from the same University in 1998. In 2018 she received an Executive Master's degree in Business Administration

(MBA) from the Ecole de Management Lyon (EM Lyon) France. She is author or co-author of more than 50 publications in peer reviewed journals. She received the Rustum Roy Award (2016), AMPERE Medal (2019) and the award Femme de R&D of the Trophées des Femmes de l'Industrie (2019). With an international experience of more than 15 years in the development of microwave-assisted technologies with applications to chemical synthesis, biomass extraction, plasma etc., since January 2018 she has been acting as the Managing Director of Microwave Innovation for Radient Technologies Inc. Canada where she focuses on the development of new extraction solutions and the manufacturing of high-value natural ingredients and products from biomass. In February 2018 she has founded Microwave Technologies Consulting (MTC) specializing in research & process development using microwaves (915 MHz, 2.45 GHz and 5.8 GHz) for applications in the field of biotech, food technology, nanotechnology, medical technology, and the chemical and pharmaceutical industries. The focus of MTC activity is to deliver customer-specific industrial solutions, technical, environmental and economic process benefits.

Dr. Radoiu is also a member of several professional associations, including the Association for Microwave Power, Education and Research in Europe (AMPERE).

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Isabelle Polaert received her M.Sc. in Chemical Engineering from the National School of Chemical Engineering (ENSIC, France) and National Polytechnic Institute of Lorraine in 1993. During her PhD, she was involved in studying three phase catalytic reactors for highly exothermic reactions such as hydrogenations. She received her PhD in 1997 from National Polytechnic Institute of Toulouse.

After four months at National Chemical laboratory, Pune, India, she got the position of Assistant Professor at the Laboratory of Chemical Engineering, LGC Toulouse. Particularly involved in environmental processes, she developed a coupled adsorption-reaction process for the depollution of phenolic effluents and co-authored a patent.

In 2003, Isabelle Polaert moved at INSA Rouen and integrated the LSPC (Laboratory of safety and chemical processes) where she developed her research activity on microwave processes and process intensification. Specialized in dielectric properties measurements, microwave processes modelling and experimental pilot scale development, she works on various applications such as green chemistry in continuous flow, new materials treatment under microwaves or biomass valorisation. Dr Polaert is also member of AMPERE Association.

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