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Ni-based catalysts for plasma-assisted CO₂ methanation

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Abstract:

This short review focuses on presenting recent findings on Ni-based catalysts for plasma-induced catalytic CO₂ methanation process. After a brief introduction presenting the advantages of plasma CO₂ methanation compared to the thermocatalytic approach, a discussion is given on different types of plasma used with nickel-based catalysts for CO₂ hydrogenation. The use of different supports and promoters in Ni-based catalysts for plasma DBD (Dielectric-barrier Discharge) catalysis CO₂ methanation is discussed. The present study focuses on presenting past, present and future prospects on nickel catalysed plasma-assisted CO₂ methanation reaction.

Key words: Plasma, Dielectric Barrier, Nickel, Supports, Promoters

1. Plasma-catalysis for CO₂ methanation: Advantages of the process

Nowadays, the catalytic CO₂ methanation is a process achieving high conversions of CO₂ in CH₄ yield. CO₂ methanation is thermodynamically favoured at the lower temperature range. However, kinetic limitations, together with catalysts stability, still limit the feasibility and scalability of conventional catalytic processes for this reaction at a large industrial level. Due to its nonequilibrium nature, nonthermal plasma (NTP) is able to reduce reaction barriers and make viable the CO₂ hydrogenation even at low temperatures in activating gas molecules, causing their excitation,

ionization and dissociation at room temperature [1,2,3,4,5]. For CO₂ methanation, in the absence or in presence of catalysts, the most common plasma types reported in the literature are dielectric barrier discharges (DBD), microwave discharges (MW) and other types as well (e.g. radiofrequency, corona, glow discharge (GD)) [3,4,6]. The first study dealing with a plasma catalytic Ni system for CO₂ methanation was reported by Jwa et al. [7] in 2011. The authors used alumina supported Ni catalysts and they showed, for the first time, an impressive synergy between a DBD plasma and a catalyst leading to a conversion efficiency of 90% at 240°C in adiabatic conditions, under a voltage of 10.3kV (1kHz). Then, research studies continued to focus on DBD plasma but also more recently on MW and GD plasma and finally on nano-pulsed DBD in 2021.

2. Types of plasma used for assisted catalysis of CO₂ methanation.

As reported in the literature, the efficiency of plasma for CO₂ hydrogenation was found to be highly dependent on the plasma itself [6]. Indeed, the higher CO₂ conversions were reported when using microwave or glow discharge plasmas versus DBD configurations. However, the high CO₂ conversions not always provide high quantity of produced CH₄, which was almost always reported as minor product compared to the CO. In order to increase the CH₄ selectivity, a synergy between plasma and catalysis is mandatory, the catalyst being there in order to lead to a higher selective reaction. Depending on the catalysts used, the plasma discharges types reported in literature involved mainly 4 plasma types: Corona discharge [8], Radio Frequency discharges (RF) [9], Microwave (MW) discharges [10,11], Glow discharge (GD) [12-16], and DBD [6,17-37]. However, on plasma Ni-based CO₂ methanation, nano-pulsed plasma was presented in 2021 based on typical DBD configuration [38]. The plasma type has a significant influence on the CO₂ conversion and also on the CH₄ selectivity. Based on a literature review on plasma Ni-catalytic studies described since 2011, the distribution of the plasma type used for CO₂ methanation has been summarized in Figure 1. One can note that the DBD plasma type is the most commonly used for such application.

Figure 1:

Microwave discharge assisted CO₂ methanation on Ni-based catalysts

Ni/TiO₂ catalysts in a microwave discharge were studied by Chen et al. [11]. They showed a synergetic effect of plasma catalytic process as the presence of catalyst led to an increase of both CO₂ conversion and energy efficiency. However, the selectivity of obtained products was not discussed and is probably very low due to thermodynamic limitations since the MW is not a cold plasma, with operating temperatures higher than 500°C. Similar results were obtained over Ni/Al₂O₃ catalysts [10], in which it was shown that the reduction of CO₂ under MW is governed by a combined effect between the plasma induced electronic excitation and catalysis at the reduced nickel particles surface.

Glow discharge assisted CO₂ methanation on Ni based catalysts

The main results reported in the literature are presented in Figure 2. It is worth noting that in glow discharge plasma CO₂ dissociation proceeds mainly via electron impact dissociation or vibrational excitation [6,39,40].

Figure 2:

As reported in Figure 2, glow discharge plasmas, operating from 2 to 6 kV, show high conversion of CO₂ (around 60%) at relatively low temperatures ($T < 200^{\circ}\text{C}$). Among the studied catalysts, two types lead to moderate CO₂ conversion: zeolite and alumina-based ones. Thus, the CO₂ methanation in a low-pressure glow discharge was investigated over nickel supported on USY and ZSM-11 zeolite-based catalysts [15,16]. The high activity in CO₂ conversion presented by the glow discharge in these plasma zeolite systems can be linked with the high complex permittivity of zeolites. Also, the main observed product was CO. CH₄ released only after plasma extinction and was linked with Ni reduction properties and the subsequent Ni⁰ content, showing a competition between CO and H₂ in the Ni⁰ species playing a significant role for CH₄ selectivity. Another important parameter evidenced by the authors was the position of a catalyst in the plasma reactor (in plasma vs. post-plasma) as the lifetime of the active species played an important role in the CO₂ methanation activity. Other Ni-based materials, such as Ni/Al₂O₃ or Ni/CeO₂-ZrO₂ were also used [12, 14.](Figure 2). The enhanced activity has been observed over Ni/Al₂O₃ at 200 °C (40% CO₂ conversion and 8% CH₄ selectivity).

Although, MW and GD plasmas allow to convert CO₂, the selectivity towards methane production remains very low. As evidenced before, in order to reach high CO₂ conversion and selectivity in methane, the best configurations are DBD plasmas. This type of plasma will be discussed in the following sections with the special focus laid on the Ni-based materials, i.e. the choice of support and promoters used.

3. The influence of support and the promotion by another metal for a high efficiency and lower energy consumption.

DBD-assisted Ni catalytic process is the most used plasma-assisted CO₂ methanation reported in the literature (Figure 3). Among the 21 studies, various supports, such as alumina [7,22-24,31], ceria [28], zirconia [36], ceria-zirconia [17-21,25,33,34,36], titania [37], zeolites [23,26,32], metal-organic framework [22] or mixed-oxides derived from hydrotalcites [27,29] were used. Most of the studies are then in the same range in terms of power and voltage. Thus, for all these studies the applied voltage was varying from 7 to 20 kV, with a power varying from 3 to 15 W (Figure 3).

For the first time, in 2011, alumina and alumina-titania supported Ni catalysts were studied in plasma-CO₂ methanation [7]. It was reported that the performance of Ni/Al₂O₃ was better than Ni/Al₂O₃-TiO₂ and a clear link between activity and specific surface area was proposed. More recently, a study by Zeng et al. dealt with the CO₂ hydrogenation on Ni/Al₂O₃ for the cogeneration of CO and CH₄ using a DBD and adding argon to the system [31]. The authors demonstrated a plasma-catalytic synergistic effect at low temperatures, showing that the presence of the Ni catalyst genuinely boosts the plasma-catalytic CO₂ hydrogenation at low temperature (150°C).

Nizio et al. investigated Ni/Ce_xZr_yO₂ catalysts with the different Ce/Zr ratio. The highest conversion of CO₂ (85%) under adiabatic conditions on 15%Ni/Ce_{0.52}Zr_{0.48}O₂ was reported [17]. The same catalyst was investigated by adjusting operation parameters of DBD plasma [19,20,30,33,34], such as applied voltage, Gas Hourly Space Velocity (by adjusting catalyst volume and flow rate), discharge length and catalyst grain-size. It was shown that an In-Plasma Configuration (catalyst covered by the plasma discharge) led to high performances with an energy consumption twice lower when compared to a Post Plasma Configuration [19,20]. These latter results were linked to the role of short-life

reactive species and a higher temperature in the in-plasma system compared to the post-plasma system in applying a similar inlet power. Moreover, an optimal grain size of 0.5 mm (Ni/Ce_{0.52}Zr_{0.48}O₂ catalyst) for the DBD configuration was proposed [33,34]. All these results pointed out that the plasma parameters may have a significant effect on overall performance and the increase of the synergetic effects between plasma and catalyst.

Due to their typical structures, zeolites were also proposed as supports for DBD plasma methanation applications. Ni-based zeolite catalysts were extensively studied in DBD plasma systems [23,26,32]. In the presence of Ni/Beta catalysts an increase in selectivity of methane [32] was reported. Moreover, the authors showed that the dispersion of Ni increased after the plasma-catalytic tests, corresponding to nickel particles redispersion during the reaction. Moreover, the authors proposed that the plasma allowed, even in the presence of the catalysts, to increase the dissociation of adsorbed molecules. Indeed, the adsorbed molecule has much weaker bond than in gaseous state. Meanwhile the reactive species produced by plasma can help to dissociate the adsorbed molecule, resulting in plasma helps in dissociation of adsorbed CO molecule. Dissociation of CO bond is the rate determining step (RDS), leading then to high CH₄ production. Other Ni-zeolite catalysts (USY with various Si/Al ratios) were investigated by Bacariza et al. [23], who pointed out that water adsorption on the active sites, which is present as one of the products of the reaction would be one of the main limiting factors for thermal CO₂ methanation, in blocking the active sites as figured out by Sabatier's principle [41]. However, by using plasma this problem can be solved to the limited extent. According to the authors the hydrophobic characteristics of the used catalyst are of key importance for the development of highly active CO₂ methanation processes. The role of water was similarly revealed on Ni/SBA-15/CeZrO₂ catalysts [18].

Recently, other types of catalysts, such as Ni–Ce three-dimensional catalysts [28], Ni/Silicalite-1 [35] were studied for NTP coupled catalytic methanation. The studies demonstrated the crucial role of catalyst design in NTP activated catalysis, in which the Ni species should be accessible for being active in DBD Plasma catalytic methanation. Moreover, on Ni–Ce three-dimensional catalysts [28], it was found that plasma created more abundant basic sites for CO₂ adsorption which is primordial for its transformation into CH₄. Also, Chen et al. showed an improvement of Ni based Metal Organic

Framework (15Ni/UiO-66) in the plasma catalytic methanation at moderate temperature [22]. Furthermore, double-layered hydroxide derived Ni catalysts were found to be promising catalysts for NTP catalytic methanation reaction when promoted with cerium [29] or iron [27]. Finally, nickel foams Ni-Fe_{0.25}-Al/NF were tested with a nano-pulsed DBD system [38]. It was shown that catalysts with appropriate Fe/Ni ratio (0.25–0.5) presented highly-dispersed and small-sized nanoparticle, and strengthened Ni-Fe interactions, which could lead the high plasma-catalytic activity. This clearly showed the impact of Fe on the Ni based catalyst for DBD Plasma catalytic methanation. It is worth noting that apart from the promotion with Fe, only few studies dealt with the promotion of Ni-based catalysts with another metal. Only cerium [18,21,23,29] and lanthanum [26,36] appeared to promote Ni-based catalyst for DBD plasma methanation process. Accordingly, Chen et al. [26] demonstrated that compared to the non-promoted catalyst, the addition of La resulted in an improvement of the turnover frequency and selectivity towards CH₄. Moreover, the La-developed catalyst also exhibited excellent stability during 15 h TOS under NTP conditions.

6. Future prospects and outlook

Since the beginning of 2010's, a renewed interest in the development of Ni-based catalytic plasma-induced systems for CO₂ methanation has been reported. In recent years, some studies have been able to understand in more detail what would be the desired chemical and physical properties of the Ni-based materials used, as well as the characteristics of the plasma to drive the appropriate species through surface of the catalysts. Plasmas, such as DBD, GD are now used as a pre-treatment of desired materials that can be used in the plasma catalytic CO₂ methanation, or in thermal CO₂ methanation [7,13,20,42,43]. Thus, the possibilities in the coupled plasma catalytic systems used to develop CO₂ methanation as an efficient process becomes feasible if the energy consumption is controlled and the energy comes from renewable sources. Furthermore, the development of such systems requires both an understanding of plasma catalytic surface reactions and the design of catalytic systems that can be scaled out and reduce energy consumption [3,6].

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References:

[1]. B. Ashford, Y. Wang, L. Wang, and X. Tu, **Plasma-Catalytic Conversion of Carbon Dioxide**, in Plasma Catalysis Fundamentals and Applications, Springer Series on Atomic, Optical, and Plasma Physics 106 (2019) pp. 271-307, X. Tu et al. (eds.), Springer Nature Switzerland AG. https://doi.org/10.1007/978-3-030-05189-1_9

[2]. A. Bogaerts, X. Tu, J. C. Whitehead, G. Centi, L. Lefferts, O. Guaitella, F. Azzolina-Jury, H.-H. Kim, A. B. Murphy, W. F. Schneider, T. Nozaki, J. C. Hicks, A. Rousseau, F. Thevenet, A. Khacef and M. Carreon, **The 2020 plasma catalysis roadmap**, J. Phys. D: Appl. Phys. 53 (2020) pp.443001-443052 <https://doi.org/10.1088/1361-6463/ab9048>

[3]. *R. Snoeckx, A. Bogaerts, **Plasma technology – a novel solution for CO₂ conversion?** Chemical Society Reviews. 46 (2017) pp. 5805–5863. <https://doi.org/10.1039/C6CS00066E>.

The authors discussed about new approaches in order to find the most efficient CO₂ conversion technology and among them plasma approach is one of the pioneers however the real question is “when” and “which one” of these new technologies will play the leading role.

[4]. A. Bogaerts, R. Snoeckx, **Plasma-Based CO₂ Conversion**, in: M. Aresta, I. Karimi, S. Kawi (Eds.), An Economy Based on Carbon Dioxide and Water, Springer International Publishing, Cham, (2019) pp. 287–325. https://doi.org/10.1007/978-3-030-15868-2_8.

[5]. B. Ashford, X. Tu, **Non-thermal plasma technology for the conversion of CO₂**, Current Opinion in Green and Sustainable Chemistry. 3 (2017) pp.45–49. <https://doi.org/10.1016/j.cogsc.2016.12.001>.

[6]. R. Dębek, F. Azzolina-Jury, A. Travert, F. Maugé, **A review on plasma-catalytic methanation of carbon dioxide – looking for an efficient catalyst**, Renewable and Sustainable Energy Reviews, 116 (2019) pp.109427-109451, , <https://doi.org/10.1016/j.rser.2019.109427>

[7]. *,*E. Jwa, Y.S. Mok, S.B. Lee, **Nonthermal plasma-assisted catalytic methanation of CO and CO₂ over nickel-loaded alumina**, WIT Transactions on Ecology and the Environment, 143 (2011) : pp. 361–368. <https://doi.org/10.2495/ESUS110311>.

As the first published literature on plasma catalysis, this work claims that the nonthermal plasma combined with catalyst like Ni/Al₂O₃ and Ni-TiO₂/Al₂O₃ can accelerate the rate-determining step by breaking carbon-oxygen bonds of carbon oxides adsorbed on the catalyst active sites.

[8]. W. F. L. M. Hoeben, E. J. M. van Heesch, F. J. C. M. Beckers, W. Boekhoven, A. J. M. Pemen, **Plasma-Driven Water Assisted CO₂ Methanation**, IEEE Transactions on Plasma Science. 43 (2015) pp.1954–1958. <https://doi.org/10.1109/TPS.2015.2429316>.

[9]. *R. Yang, D. Zhang, K. Zhu, H. Zhou, X. Ye, A.W. Kleyn, Y. Hu, **In Situ Study of the Conversion Reaction of CO₂ and CO₂-H₂ Mixtures in Radio Frequency Discharge Plasma**, Acta Physico-Chimica Sinica. 35 (2019) pp.292-298. <https://doi.org/10.3866/PKU.WHXB201803121>.

The authors pointed out that with increasing the RF power, the CO₂ conversion increased, while the energy efficiency decreased and also the addition of hydrogen could significantly reduce the time required to reach the equilibrium state of carbon dioxide decomposition reaction. With increasing H₂ content, initially CO₂ conversion decreased and then increased.

[10]. *B. Alrafei, J. Delgado-Liriano, A. Ledoux, I. Polaert, **Synergetic effect of microwave plasma and catalysts in CO₂ methanation**, in: Proceedings 17th International Conference on Microwave and High Frequency Heating, Universitat Politècnica de València, AMPERE 19, (2019) pp.51-58 ISBN: 978-84-9048-719-8 <https://doi.org/10.4995/AMPERE2019.2019.9806>

The study showed that in using 20%Ni/Al₂O₃ coupled with Micro-Wave Plasma, the CO₂ conversion increased from 75% to more than 90%. As well, after catalyst addition methanol production increased from 900 ppm to 1900 ppm, and methane production from 6 ppm to 25 ppm.

[11]. G. Chen, N. Britun, T. Godfroid, V. Georgieva, R. Snyders, M.-P. Delplancke-Ogletree, **An overview of CO₂ conversion in a microwave discharge: the role of plasma-catalysis**, *J. Phys. D: Appl. Phys.* 50 (2017) pp.084001-084012. <https://doi.org/10.1088/1361-6463/aa5616>.

[12]. *,*F. Azzolina-Jury, **Novel boehmite transformation into γ -alumina and preparation of efficient nickel base alumina porous extrudates for plasma-assisted CO₂ methanation**, *J. of Ind. and Eng. Chem.* 71 (2019) pp.410–424. <https://doi.org/10.1016/j.jiec.2018.11.053>.

Novel glow discharge plasma-assisted boehmite transformation into alumina was successfully achieved at lower temperature (80 °C less) and shorter period (1 h less) than the classical transformation. The nitric acid concentration shows a key role in the catalytic properties of alumina catalyst leading to the active phase dispersion and reducibility improvement. As a result, methane yield was also improved with support acidity.

[13]. R. Dębek, D. Wierzbicki, M. Motak, M.E. Galvez, P. Da Costa, F. Azzolina-Jury, **Operando FT-IR study on basicity improvement of Ni(Mg,Al)O hydrotalcite-derived catalysts promoted by glow plasma discharge**, *Plasma Sci. Technol.* 21 (2019) pp.045503-045516. <https://doi.org/10.1088/2058-6272/aaf759>

[14]. R. Dębek, F. Azzolina-Jury, A. Travert, F. Maugé, F. Thibault-Starzyk, **Low-pressure glow discharge plasma-assisted catalytic CO₂ hydrogenation-The effect of metal oxide support on the performance of the Ni-based catalyst**, *Catalysis Today* 337 (2019) pp.182-194. <https://doi.org/10.1016/j.cattod.2019.03.039>.

[15]. F. Azzolina-Jury, F. Thibault-Starzyk, **Mechanism of Low Pressure Plasma-Assisted CO₂ Hydrogenation Over Ni-USY by Microsecond Time-resolved FTIR Spectroscopy**, *Topics in Catalysis.* 60 (2017) pp.1709–1721. <https://doi.org/10.1007/s11244-017-0849-2>.

[16]. F. Azzolina-Jury, D. Bento, C. Henriques, F. Thibault-Starzyk, **Chemical engineering aspects of plasma-assisted CO₂ hydrogenation over nickel zeolites under partial vacuum**, *Journal of CO₂ Utilization.* 22 (2017) pp.97–109. <https://doi.org/10.1016/j.jcou.2017.09.017>

[17]. *,*M. Nizio, A. Albarazi, S. Cavadias, J. Amouroux, M.E. Galvez, P. Da Costa, **Hybrid plasma-catalytic methanation of CO₂ at low temperature over ceria zirconia supported Ni**

catalysts, Int. J. of Hydrogen Energy. 41 (2016) pp.11584–11592.

<https://doi.org/10.1016/j.ijhydene.2016.02.020>.

The authors claimed that adding 15%Ni/CeZrO₂ to DBD plasma reactor resulted in CO₂ conversion around 80% and CH₄ selectivity of 100% around 300°C while with plasma alone they were 5% and 0%, respectively.

[18] J. Amouroux, S. Cavadias, **Electrocatalytic reduction of carbon dioxide under plasma DBD process**, J. Phys. D: Appl. Phys. 50 (2017) pp465501-465512. <https://doi.org/10.1088/1361-6463/aa8b56>.

[19] R. Benrabbah, C. Cavaniol, H. Liu, S. Ognier, S. Cavadias, M.E. Gálvez, P. Da Costa, **Plasma DBD activated ceria-zirconia-promoted Ni-catalysts for plasma catalytic CO₂ hydrogenation at low temperature**, Catal. Comm. 89 (2017) pp.73–76. <https://doi.org/10.1016/j.catcom.2016.10.028>.

[20] M. Mikhail, B. Wang, R. Jalain, S. Cavadias, M. Tatoulian, S. Ognier, M.E. Gálvez, P. Da Costa, **Plasma-catalytic hybrid process for CO₂ methanation: optimization of operation parameters**, React. Kinet. Mech. Cat. 126 (2019) pp.629–643. <https://doi.org/10.1007/s11144-018-1508-8>.

[21] *M. Biset-Peiró, J. Guilera, T. Zhang, J. Arbiol, T. Andreu, **On the role of Ceria in Ni-Al₂O₃ catalyst for CO₂ plasma methanation**, Applied Catalysis A: General. 575 (2019) pp.223–229. <https://doi.org/10.1016/j.apcata.2019.02.028>.

The effect of Ce loading (0-50% wt) on Ni-CeO₂/Al₂O₃ catalysts for CO₂ plasma methanation was evaluated for the first time. The optimum loading of Ce for highest conversion was found to be 10% wt.

[22] *H. Chen, Y. Mu, Y. Shao, S. Chansai, H. Xiang, Y. Jiao, C. Hardacre, X. Fan, **Nonthermal plasma (NTP) activated metal–organic frameworks (MOFs) catalyst for catalytic CO₂ hydrogenation**, AIChE Journal. Reaction Engineering Kinetics and Catalysis, 66.e16853 (2019). pp.1-16, <https://doi.org/10.1002/aic.16853>.

Based on characterization of surface species with *in-situ* DRIFTS on different catalysts the 15Ni/UiO-66 catalyst is much more active under the NTP conditions than the conventional ones like Ni/ α -Al₂O₃ and Ni/ZrO₂ and the conversion is 85% and selectivity about 100%.

[23] *,*M.C. Bacariza, M. Biset-Peiró, I. Graça, J. Guilera, J. Morante, J.M. Lopes, T. Andreu, C. Henriques, **DBD plasma-assisted CO₂ methanation using zeolite-based catalysts: Structure composition-reactivity approach and effect of Ce as promoter**, Journal of CO₂ Utilization. 26 (2018) pp.202–211. <https://doi.org/10.1016/j.jcou.2018.05.013>.

It was found that a higher Si/Al ratio in the zeolite structure leads to better performances under plasma conditions. Furthermore, the addition of Ce as promoter increased basic sites for CO₂ activation leading to much better results than the obtained for a commercial Ni/ γ -Al₂O₃. Also, Ni-Ce/Zeolite in this work reported a CH₄ yield of 75% with a power supply of 25W.

[24] F. Ahmad, E.C. Lovell, H. Masood, P.J. Cullen, K.K. Ostrikov, J.A. Scott, R. Amal, **Low-Temperature CO₂ Methanation: Synergistic Effects in Plasma-Ni Hybrid Catalytic System**, ACS Sustainable Chem. Eng. 8 (2020) pp.1888–1898. <https://doi.org/10.1021/acssuschemeng.9b06180>.

[25] M. Mikhail, P. Da Costa, J. Amouroux, S. Cavadias, M. Tatoulian, S. Ognier, M.E. Gálvez, **Electrocatalytic behaviour of CeZrOx-supported Ni catalysts in plasma assisted CO₂ methanation**, Catal. Sci. Technol. 10 (2020) pp.4532–4543. <https://doi.org/10.1039/D0CY00312C>.

[26] H. Chen, Y. Mu, Y. Shao, S. Chansai, S. Xu, C.E. Stere, H. Xiang, R. Zhang, Y. Jiao, C. Hardacre, X. Fan, **Coupling non-thermal plasma with Ni catalysts supported on BETA zeolite for catalytic CO₂ methanation**, Catal. Sci. Technol. 9 (2019) pp.4135–4145. <https://doi.org/10.1039/C9CY00590K>.

[27] D. Wierzbicki, M.V. Moreno, S. Ognier, M. Motak, T. Grzybek, P. Da Costa, M.E. Gálvez, **Ni-Fe layered double hydroxide derived catalysts for non-plasma and DBD plasma-assisted CO₂ methanation**, Int. J. of Hyd. Energy. 45 (2020) pp.10423-10432. <https://doi.org/10.1016/j.ijhydene.2019.06.095>.

- [28] Y. Ge, T. He, D. Han, G. Li, R. Zhao, J. Wu, **Plasma-assisted CO₂ methanation: effects on the low-temperature activity of an Ni–Ce catalyst and reaction performance**, Royal Society Open Science. 6(10) (2019) pp.190750-190759. <https://doi.org/10.1098/rsos.190750>.
- [29] M. Nizio, R. Benrabbah, M. Krzak, R. Debek, M. Motak, S. Cavadias, M.E. Gálvez, P. Da Costa, **Low temperature hybrid plasma-catalytic methanation over Ni-Ce-Zr hydrotalcite-derived catalysts**, Catalysis Communications. 83 (2016) pp.14–17. <https://doi.org/10.1016/j.catcom.2016.04.023>.
- [30] R. Benrabbah, M. Nizio, S. Cavadias, M. Tatoulian, M.E. Galvez, P.D. Costa, **Plasma-catalytic hybrid process for CO₂ methanation**, Conference Paper. 43rd EPS Conference on Plasma Physics, Europhysics Conference Abstracts Vol. 40A (2016) pp.29-32, Editor: R. Bingham et al. Publ:European Physical Society (EPS), POD Publ: Curran Associates, Inc. ISBN 9781510829473
- [31] Y. Zeng, X. Tu, **Plasma-catalytic hydrogenation of CO₂ for the cogeneration of CO and CH₄ in a dielectric barrier discharge reactor: effect of argon addition**, J. Phys. D: Appl. Phys. 50 (2017) pp.184004- 184014. <https://doi.org/10.1088/1361-6463/aa64bb>.
- [32] E. Jwa, S.B. Lee, H.W. Lee, Y.S. Mok, **Plasma-assisted catalytic methanation of CO and CO₂ over Ni–zeolite catalysts**, Fuel Processing Technology. 108 (2013) pp.89–93. <https://doi.org/10.1016/j.fuproc.2012.03.008>.
- [33] B. Wang, M. Mikhail, M.E. Galvez, S. Cavadias, M. Tatoulian, P. Da Costa, S. Ognier, **Coupling experiment and simulation analysis to investigate physical parameters of CO₂ methanation in a plasma-catalytic hybrid process**, 17 (9) (2020) pp.1900261- 1900269. <https://doi.org/10.1002/ppap.201900261>
- [34] *B. Wang, M. Mikhail, S. Cavadias, M. Tatoulian, P. Da Costa, S. Ognier, **Improvement of the activity of CO₂ methanation in a hybrid plasma-catalytic process in varying catalyst particle size or under pressure**, Journal of CO₂ utilization, 46 (2021) pp.101471-101479, <https://doi.org/10.1016/j.jcou.2021.101471>

Here, the authors clearly show the importance of the grain size on the plasma catalytic performance, with an optimal performance for 0,5 mm grain size of the catalyst.

[35] *,*H. Chen, F. Goodarzi, Y. Mu, S. Chansai, J. J. Mielby, B. Mao, T. Sooknoi, C. Hardacre, S. Kegnaes, X. Fan, **Effect of metal dispersion and support structure of Ni/silicalite-1 catalysts on non-thermal plasma (NTP) activated CO₂ hydrogenation**, Applied Catalysis B: Environmental, vol. 272 (2020) pp.119013-119024 <https://doi.org/10.1016/j.apcatb.2020.119013>

The authors showed that an encapsulated catalyst with hierarchical meso-micro-porous structure (i.e. Ni/D-S1) which has relatively small particles (i.e. average Ni particle sizes of 2.8 ± 0.7 nm) and dispersed Ni nanoparticles (i.e. Ni dispersion of 2.5 %) presents comparatively the best catalytic performance (i.e. CO₂ conversion of 75 %) at 7.5 kV.

[36] M. Mikhail, P. Da Costa, S. Cavadias, M. Tatoulian, S. Ognier, and M. E. Galvez, **Nickel Supported Modified Zirconia Catalysts for CO₂ Methanation in DBD Plasma Catalytic Hybrid Process**, Materials Science Forum, 1016 (2021) Trans Tech Publ, pp. 894-899. <https://doi.org/10.4028/www.scientific.net/MSF.1016.894>

[37] R. Zhou, N. Rui, Z. Fan, and C.-j. Liu, **Effect of the structure of Ni/TiO₂ catalyst on CO₂ methanation**, International Journal of Hydrogen Energy, 41 (47) (2016) pp. 22017-22025, <https://doi.org/10.1016/j.ijhydene.2016.08.093>

[38] *,*Y. Gao, L. Dou, S. Zhang, L. Zong, J. Pan, X. Hu, H. Sun., K. Ostrikov, T. Shao, **Coupling bimetallic Ni-Fe catalysts and nanosecond pulsed plasma for synergistic low-temperature CO₂ methanation**, Chemical Engineering Journal, (2020), 127693, <https://doi.org/10.1016/j.cej.2020.127693>

The electron- induced vibrational excitations CO(ν) and small-sized Ni-Fe active phases (<10 nm) are the essential factors for overcoming the catalytic energy barriers at nanosecond pulsed plasma. Ni-Fe_{0.25}-Al/NF catalyst showed 67.5% CO₂ conversion and 99% CH₄ selectivity at 231°C.

- [39] A. Bogaerts, W. Wang, A. Berthelot, V. Guerra, **Modeling plasma-based CO₂ conversion: crucial role of the dissociation cross section**, Plasma Sources Sci. Technol. 25 (2016) pp.055016-055025, <https://doi.org/10.1088/0963-0252/25/5/055016>
- [40] A.S. Morillo-Candas, T. Silva, B.L. M. Klarenaar, M. Grofulović, V. Guerra and O. Guaitella **Electron impact dissociation of CO₂**, Plasma Sources Sci. Technol. 29 (2020) pp.01LT01, <https://doi.org/10.1088/1361-6595/ab6075>
- [41] A.J. Medford, A. Vojvodic, J.S.Hummelshøj, J. Voss, F. Abild-Pedersen, F. Studt, T. Bligaard, A. Nilsson, J.K. Nørskov **From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis**. Journal of Catalysis 328 (2015) pp.36–42. doi:10.1016/j.jcat.2014.12.033
- [42] L. Bian, L. Zhang, R. Xia, and Z. Li, **Enhanced low-temperature CO₂ methanation activity on plasma-prepared Ni-based catalyst** Journal of Natural Gas Science and Engineering, 27, (2015) pp. 1189-1194, <https://doi.org/10.1016/j.jngse.2015.09.066>
- [43] L. Bian, L. Zhang, Z. Zhu, and Z. Li, **Methanation of carbon oxides on Ni/Ce/SBA-15 pretreated with dielectric barrier discharge plasma**, Molecular Catalysis, 446 (2018) pp. 131-139, <https://doi.org/10.1016/j.mcat.2017.12.027>