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Patrick Da Costa[a,*], Goshid Hasrack[a,b], Jérôme Bonnety[a], Carlos Henriques[b],

[a]Institut Jean Le Rond d'Alembert, Sorbonne Université, CNRS UMR 7190, 2 Place de la Gare de Ceinture, 78210 Saint-Cyr-l'Ecole, France

[b] Centro de Química Estrutural, Chemical Engineering Department, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisboa, Portugal

Corresponding authors P. DA COSTA, + 33 1 44 27 95 62, Email address: patrick.da_costa@sorbonne-universite.fr;

Abstract:

This short review focuses on presenting recent findings on Ni-based catalysts for plasma-induced catalytic CO_2 methanation process. After a brief introduction presenting the advantages of plasma CO_2 methanation compared to the thermocatalytic approach, a discussion is given on different types of plasma used with nickel-based catalysts for CO_2 hydrogenation. The use of different supports and promoters in Ni-based catalysts for plasma DBD (Dielectric-barrier Discharge) catalysis CO_2 methanation is discussed. The present study focuses on presenting past, present and future prospects on nickel catalysed plasma-assisted CO_2 methanation reaction.

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

1. Plasma-catalysis for CO_2 methanation: Advantages of the process

Nowadays, the catalytic CO_2 methanation is a process achieving high conversions of CO_2 in CH_4 yield. CO_2 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 CO_2 hydrogenation even at low temperatures in activating gas molecules, causing their excitation, ionization and dissociation at room temperature [1,2,3,4,5]. For CO_2 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 CO_2 methanation.

As reported in the literature, the efficiency of plasma for CO_2 hydrogenation was found to be highly dependent on the plasma itself [6]. Indeed, the higher CO_2 conversions were reported when using microwave or glow discharge plasmas versus DBD configurations. However, the high CO_2 conversions not always provide high quantity of produced CH_4, which was almost always reported as minor product compared to the CO. In order to increase the CH_4 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 CO_2 methanation, nano-pulsed plasma was presented in 2021 based on typical DBD configuration [38]. The plasma type has a significant influence on the CO_2 conversion and also on the CH_4 selectivity. Based on a literature review on plasma Ni-catalytic studies described since 2011, the distribution of the plasma type used for CO_2 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 CO_2 methanation on Ni-based catalysts

Ni/TiO_2 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 CO_2 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/Al_2O_3 catalysts [10], in which it was shown that the reduction of CO_2 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 CO_2 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 CO_2 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 CO_2 (around 60%) at relatively low temperatures (T < 200°C). Among the studied catalysts, two types lead to moderate CO_2 conversion: zeolite and alumina-based ones. Thus, the CO_2 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 CO_2 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. CH_4 released only after plasma extinction and was linked with Ni reduction properties and the subsequent Ni° content, showing a competition between CO and H_2 in the Ni° species playing a significant role for CH_4 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 CO_2 methanation activity. Other Ni-based materials, such as Ni/Al_2O_3 or Ni/CeO_2-ZrO_2 were also used [12, 14.](Figure 2). The enhanced activity has been observed over Ni/Al_2O_3 at 200 °C (40% CO_2 conversion and 8% CH_4 selectivity).

Although, MW and GD plasmas allow to convert CO_2, the selectivity towards methane production remains very low. As evidenced before, in order to reach high CO_2 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 CO_2 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-CO_2 methanation [7]. It was reported that the performance of Ni/Al_2O_3 was better than Ni/Al_2O_3–TiO_2 and a clear link between activity and specific surface area was proposed. More recently, a study by Zeng et al. dealt with the CO_2 hydrogenation on Ni/Al_2O_3 for the cogeneration of CO and CH_4 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 CO_2 hydrogenation at low temperature (150°C).

Nizio et al. investigated $Ni/Ce_xZr_yO_2$ catalysts with the different Ce/Zr ratio. The highest conversion of CO_2 (85%) under adiabatic conditions on $15\%Ni/Ce_{0.52}Zr_{0.48}O_2$ 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 ($Ni/Ce_{0.52}Zr_{0.48}O_2$ 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 od adsorbed CO molecule. Dissociation of CO bond is the rate determining step (RDS),

leading then to high CH_4 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 CO_2 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 CO_2 methanation processes. The role of water was similarly revealed on $Ni/SBA\text{-}15/CeZrO_2$ 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 CO_2 adsorption which is primordial for its transformation into CH_4. 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 CH_4. 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 CO_2 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 CO_2 methanation, or in thermal CO_2 methanation [7,13,20,42,43]. Thus, the possibilities in the coupled plasma catalytic systems used to develop CO_2 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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