

Nanostructured catalyst for plasma assisted CO₂ methanation

Beatrice Musig^{1,2}, Maria Victoria Navarro^{1,*}, Maria Elena Galvez²

Keywords: plasma catalysis, CO₂ methanation, cerium oxide

ABSTRACT

The major challenge that humankind is facing nowadays is to limit global warming below 1.5 °C and restrain the consequent climate change, which will lead to irreversible endangering of all ecosystems and hazards for humanity as well [1]. The priority is to reduce greenhouse gas emissions, mainly carbon dioxide (CO₂), by switching to renewable and green energy sources and electrification, as well as capturing of the excess CO₂ in the atmosphere [2]. CO₂ valorisation is one of the main players for the de-fossilization of energy production and industrial manufacturing, it comprises of different strategies of CO₂ capture and utilization (CCU). The development of CCU requires fundamental research and engineering to efficiently break the CO₂ molecule and have it react to form added-value chemicals. One of the possible reactions is the reduction of CO₂ to methane, a.k.a. Sabatier's reaction. This reaction between CO₂ and H₂ has been widely studied in conventional catalysis: it is known to be exothermic but kinetically hindered, therefore happening with the aid of a catalyst typically between 200°C and 450°C, at pressures between atmospheric and 100 bar [3]. In addition to efforts made in the thermal catalysis field, plasma catalysis stands as a promising method for advancements in CO₂ valorisation. The use of non-thermal plasmas is promising for energy efficient CO₂ conversion exploiting the dissociation happening in plasma via electron impact and vibrational excitation. Additionally, the synergy between the plasma and the catalytic material can further enhance the reaction performance.

Ni-based catalysts are widely used in thermal CO₂ methanation, combining good properties of selectivity and performance with reduced cost of the metal. It has been recently demonstrated that the use of a non-thermal plasma in combination with Ni-containing catalysts results in an enhanced reaction yield even at atmospheric pressure and mild reaction temperatures (around 200°C) [4]. Optimise plasma-catalyst synergy still represents one of the biggest challenges. Tailoring the physicochemical and electrical properties of catalytic materials can lead to improved conversion with lower energy consumption.

In this study, different nanostructured CeO₂ supports were prepared for the Ni catalysts to be used for CO₂ methanation in a dielectric barrier discharge (DBD) reactor. The main goal was to vary the morphology of CeO₂ support through the modification of the synthesis pathway, assessing its influence on the properties of the catalysts and their performance. Different shapes at nanoscale such as polyhedral nanoparticles, nanorods or nanocubes were tuned through the choice of the hydrothermal synthesis conditions, namely NaOH concentration, time and temperature, following a design of experiments (DOE) procedure. Subsequently, the supports were wet impregnated with 15 %wt. Ni, calcined in air at 550°C and reduced in 5% H₂ at 600°C for 2 hours. The catalysts were characterized by means of XRD, XPS, H₂ TPR, CO₂ TPD, TGA, and N₂ physisorption. The catalysts were tested in thermal CO₂ methanation to have a comparison between conventional and plasma-assisted performance, mechanism, and effect on the materials.

¹ Instituto de Carboquímica (CSIC), Zaragoza, Spain

² Institut Jean le Rond d'Alembert, CNRS UMR 7190, Sorbonne Université, Paris, France

*corresponding author: navarro@icb.csic.es



Characterization of the spent catalysts was performed as well, in order to assess the impact of plasma on their structure and physicochemical properties.

The packed DBD plasma reactor was electrically characterised by means of Q-V Lissajous figure analysis, from which we calculate the power, the charge transferred and the reactor capacitance, and plasma current amplitude study.

We report that the synthesis conditions of the CeO₂ supports strongly influence their physicochemical properties as well as their plasma-assisted catalytic performance. Most catalysts of the DOE achieve good conversion with selectivity for methane above 90%. The Table 1 reports a summary of the results concerning 3 of the 9 catalysts that were synthesised following the DOE. The most relevant physicochemical properties as well as the CO₂ conversion for the thermal and plasma-assisted reaction are shown in the table. The main findings concern the different physicochemical properties that should be considered for an efficient catalyst in plasma, which do not necessarily agree with the conventional catalysis case. An intermediate surface area, well dispersed Ni in contact with the support, and presence of medium basic sites improve the plasma-assisted catalytic methanation. Furthermore, electrical properties, e.g. dielectric and charge transfer behaviour, should be evaluated and linked with the yield in plasma catalysis. The lowest reactor capacitance is linked with decreased power consumption. The CeO₂ support morphology that achieves such characteristics are very thin nanorods (or “needles”) synthesised at 8M, 125°C for 14.5 h.

Table 1. Physicochemical properties and catalytic results obtained with plasma-assisted and thermal methanation with Ni/CeO₂.
a. N₂ physisorption; b. XRD; c. SEM; d. H₂ TPR; e. CO₂ TPD

	DOE5	DOE0	DOE6
Synthesis parameters			
[NaOH], M	1	8	15
T oven, °C	70	125	180
time, h	5	14.5	24
Physicochemical properties			
BET Surface area, m ² /g	70	44	8
CeO ₂ crystallite size, nm	11	12	1/36
Ni crystallite size, nm	28	21	28
CeO ₂ shape	●		■
H ₂ TPR consumed H ₂ , umol/g	3282	2460	2946
CO ₂ TPD, sites of medium basicity, %	67	53	14
Plasma CO₂ methanation			
CO ₂ conversion, %	70	82	13
T reactor, °C	144	147	130
Power, W	20.1	20.9	22.6
Capacitance, F	1.92·10 ⁻¹¹	1.66·10 ⁻¹¹	1.84·10 ⁻¹¹
Thermal CO₂ methanation 300 °C			
CO ₂ conversion, %	78	54	9

[1] R.P. Allan, E. Hawkins, N. Bellouin, B. Collins, IPCC, 2021: Summary for Policymakers, Cambridge University Press, 2021, In Press.

[2] D.P. Van Vuuren, E. Stehfest, D.E.H.J. Gernaat, M. Van Den Berg, D.L. Bijl, H.S. De Boer, V. Daioglou, J.C. Doelman, O.Y. Edelenbosch, M. Harmsen, Nature Climate Change, 8 (2018) 391–397

[3] M. Younas, L. Loong Kong, K.J.K. Bashir, H. Nadeem, A. Shehzad, S. Sethupathi, Energy and Fuels, 30 (2016) 8815–8831

[4] R. Dębek, F. Azzolina-Jury, A. Travert, F. Maugé, Renewable Sustainable Energy Reviews, 116 (2019) 109427

