Characterization of a Plasma Dielectric Barrier Discharge Reactor Packed with Ni/CeO$_2$ Nanostructured Catalysts for CO$_2$ Methanation

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Among the different processes for the chemical utilization of CO_2, its methanation, i.e. through the Sabatier's reaction, stands as a promising technology allowing both the synthesis of a carbon-neutral fuel and the storage of off-peak renewable electricity (power-to-gas concept). The Sabatier's reaction is exothermic but strongly hindered by kinetics. It has been recently demonstrated that the use of a non-thermal plasma in combination with a Ni-containing catalyst results in an enhanced methane yield even at atmospheric pressure and mild reaction temperatures (around 200°C)[1]. Plasma-catalyst coupling still represents one of the biggest challenges. Two different efforts for catalyst optimization should be developed side by side to improve performance and energy efficiency: first, tailoring the physicochemical properties, such as surface area, basicity, and oxygen storage capacity; secondly, considering the electrical behaviour of the material packed in the dielectric barrier discharge (DBD) reactor when in contact with plasma.

In the present study, different nanostructured CeO_2 supports were prepared for the Ni catalysts to be used for CO_2 methanation in a DBD reactor, with focus on the contribution of CeO_2 morphology on the CO_2 conversion performance and electrical characterization by Q-V Lissajous figure analysis[2] and plasma current amplitude study[3].

The supports were synthesised by NaOH hydrothermal method and characterized via XRD, SEM, TEM, N_2 physisorption and XPS to confirm the achieved different morphologies (such as polyhedral nanocrystals, nanorods or nanocubes) and variation physicochemical properties with tuning of synthesis parameters. Subsequently, the supports were impregnated with Ni, calcinated at 550 °C and reduced at 600 °C.

The synthesis conditions of the CeO_2 supports influenced in-plasma behaviour of the catalysts. The catalytic performance for plasma-assisted CO_2 methanation is tested at frequency of 12.3 kHz with increasing peak-to-peak voltage from 21 to 25 kV. The CO_2 conversion, CH_4 selectivity and power consumption vary with the different catalysts. In Table 1 it is shown that the power requirement to achieve a conversion of 79 % is different in the case of the needles and particles catalysts, indicating that Ni/CeO$_2$ supported on nano-needles is a more efficient material for plasma-assisted methanation. In addition, the catalyst presenting large cubes and rods structures does not achieve such high conversion >70 % even with larger applied power (32.8 W). Furthermore, the measured effective capacitance, the charge transferred and the plasma current envelope are considered for the electric characterization of the packed bed DBD reactor and linked with the catalytic performance in plasma.

Table 1. Comparison of plasma-assisted CO_2 methanation with Ni/CeO$_2$ catalysts possessing different morphologies

Synthesis parameters			CO_2 methanation		Power	SEM observed shape of CeO_2 support
[NaOH] (M)	T (ºC)	Time (h)	CO_2 conversion	CH_4 selectivity		
8	125	14.5	79 %	100 %	18.2 W	Needles
1	70	5	79 %	100 %	25.4 W	Particles
15	180	25	45 %	-	32.8 W	Micrometric cubes + rods

The synthesised ceria nanomaterials prove to have good potential as supports for catalysts in plasma-assisted process. Further electrochemical and dielectric behaviour characterization is due in order to gain further insights on the plasma-catalyst synergy.

References

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