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P.II.2 — Development of Ce promoted Ni/Al₂O₃ catalysts for non-thermal plasma reforming reactor

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Non-thermal plasma (NTP) technologies have emerged as promising alternatives for the conversion of waste-derived feedstocks into syngas under mild operating conditions. In plasma-catalytic processes, catalyst properties play a crucial role in determining product distribution, energy efficiency, and long-term stability. Within the framework of the BIVALIA project, non-thermal plasma technology is focused on the treatment of process streams generated during biomass valorisation. Among the different catalytic formulations, Ni-based catalysts are particularly attractive due to their high activity for hydrocarbon reforming and syngas production, as well as their relatively low cost compared with noble-metal catalysts. In this work, a series of Ni/Al₂O₃ catalysts modified with cerium were developed for application in a rotating gliding arc plasma reactor.

A first series of Ni/CeO₂-Al₂O₃ catalysts was prepared using γ-Al₂O₃ support modified with different ceria loadings (10 and 15 wt.% CeO₂) and a constant nickel loading of 15 wt.%. The influence of ceria content and catalyst reduction temperature (650 and 800 °C) on the physicochemical properties of the catalysts was investigated. Comprehensive characterization included X-ray fluorescence, N₂ physisorption, X-ray diffraction, temperature-programmed reduction and hydrogen chemisorption. The catalysts exhibited highly dispersed NiO and CeO₂ phases supported on mesoporous alumina, while ceria incorporation preserved the porous structure and promoted favourable metal-support interactions. Reduction studies showed the formation of metallic Ni without detectable NiAl₂O₄ spinel species, whereas increasing the reduction temperature slightly increased Ni particle size because of thermal sintering while decreasing metal dispersion. Catalytic performance in ethanol ATR was employed as the primary selection criterion because this reaction reproduces the key requirements expected during plasma-assisted reforming, including C–C bond cleavage, hydrogen generation, catalyst stability and resistance to carbon formation. The results demonstrated (Table 1) that the catalyst formulation containing 10 wt.% CeO₂ provided the most favourable balance between structural properties and catalytic behaviour, making it the most suitable candidate for further integration into the non-thermal plasma reactor. This screening methodology establishes a route for catalyst selection prior to plasma operation and provides the basis for the subsequent evaluation of plasma-catalytic systems dedicated to the upgrading of BIVALIA-derived process streams.

Table 1 Ethanol conversion and carbon product distribution for the autothermal ethanol reforming on Ni/CeO₂-Al₂O₃ catalysts (T=650 °C, EtOH/H₂O/O₂= 1/1.8/0.6 (mol), Qt= 56.7 NmL/min, mcat=0.1 g)

	Ni/A-10Ce (R650)	Ni/A-15Ce (R650)	Ni/A-10Ce (R800)	Ni/A-15Ce (R800)
Ethanol conversion (%)	100	100	100	100
H ₂ extraction (%)	66.3	66.4	62.0	65.0
C product distribution (mol %)				
CO ₂	45.0	45.7	49.2	47.6
CO	52.6	52.0	46.3	48.6
CH ₄	2.3	2.4	4.5	3.8

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