Microwave-assisted dry reforming of methane for CO_2 valorization in structured monoliths coated with $LaNiO_3$ perovskites

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Highlights

- $LaNiO_3$ yield excellent CO_2 and CH_4 conversions in the DRM reaction with reduced catalyst loadings.
- Perovskites serve as excellent templates towards evolved Ni/La_2O_3 catalysts.
- Homogeneous deposition protocol on structured monoliths is developed to prevent hot spots under MW-heating conditions.

1. Introduction

Dry reforming of methane (DRM) is an attractive route for the simultaneous utilization of CO_2 and CH_4 to produce syngas, yet its strong endothermicity and the susceptibility of conventional catalysts to sintering and carbon deposition continue to hinder practical deployment under conventional thermal operation. Microwave-assisted DRM has recently emerged as a promising electrified alternative because it enables rapid and selective heating of MW-responsive catalyst beds, lowers external heat demand, and can generate localized high-temperature regions that enhance reactant activation and mitigate coke formation relative to conventionally heated systems. Recent studies indicate that reactor development in this area includes catalytic MW reactors while future scale-up is expected to benefit from designs beyond traditional fixed beds, including fluidized, monolithic, and distributed reactor concepts that improve heating uniformity and address MW penetration-depth limitations. For instance, a 2024 study on $NiFe/MgAl_2O_4$ catalysts under microwave irradiation reported CH_4 and CO_2 conversions of 85% and 62%, respectively, at 700 °C, highlighting the potential of MW-heated catalytic beds for syngas production [1]. Likewise, recent studies have also reported the increased reducibility of perovskites in the presence of microwaves to boost the selectivity of different reactions [2-3]. Herein, we present a monolith structured reactor coated with a colloidal suspension of $LaNiO_3$ perovskite nanoparticles that operates extremely well under both conventional and MW-driven conditions in the DRM to yield high CO_2 and CH_4 conversions towards syngas.

2. Methods

Rod-shaped $LaNiO_3$ particles were obtained under refluxing conditions and these rods were solubilized to form a stable suspension to sequentially coat cordierite monoliths (Fig.1). SEM evaluation confirmed the optimal perovskite loadings to prevent an uneven dispersion of the catalyst and the potential generation of hot spots under MW heating conditions. The conventional heating experiments were carried out in a tubular furnace. MW heating tests were carried out in a monomode cylindrical MW resonator (ITACA Institute, Spain), designed for homogeneous MW field distribution in the reactor. The external surface temperature in the quartz tube was measured with a pyrometer and a high-temperature infrared camera, compatible with quartz measurements, (450–1800°C; Optris PI 1M), measured the temperature in the monolith wall. Microwave temperature was regulated by PID (proportional–integral–derivative) control using the pyrometer. DRM reaction tests were carried out between 650-750 ºC. Once the targeted temperature was reached, a reaction mixture of CO_2 and CH_4

with N_2 as an internal standard was introduced, in a ratio of 40:40:20. This reaction was monitored over time using a GC to track products (i.e. H_2 and CO), CO_2 and CH_4 conversions, and the by-products generated.

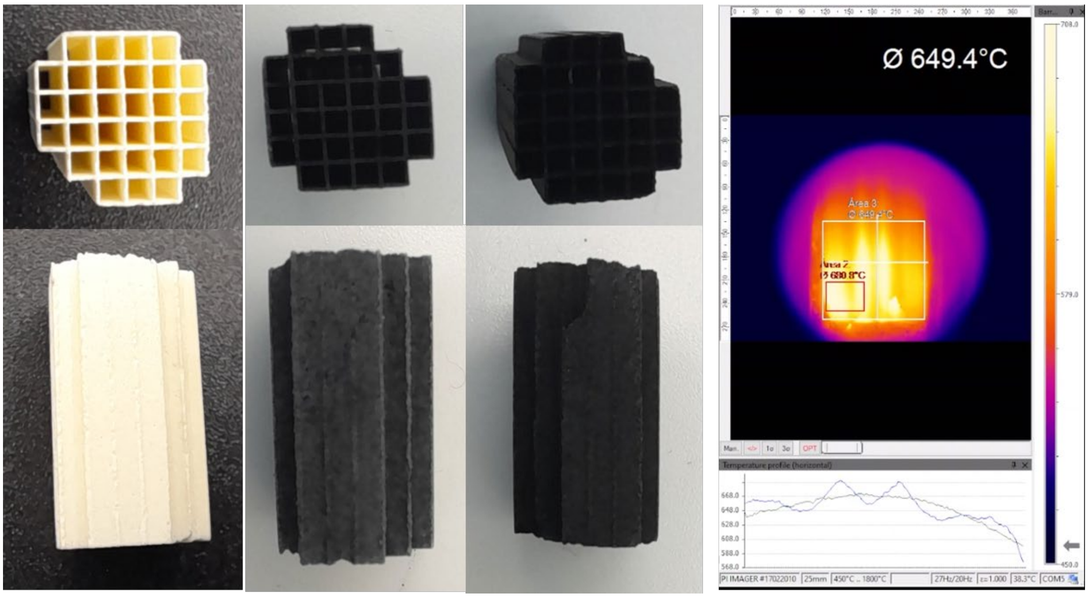

Figure 1. (Left) Digital photographs of monoliths before and after different loadings cycles with $LaNiO_3$ particles; (Right) Temperature profiles of the coated monolith under MW heating conditions at 650 ºC.

3. Results and discussion

$LaNiO_3$ perovskites evolve due to the ex-solution of Ni from the perovskite lattice and favors an excellent dispersion of the active metal site (Ni) within a basic matrix (La_2O_3). MW-driven DRM tests led to CO_2 and CH_4 conversions close to 85% and 70% at 650 ºC, respectively. These values were two times and three times lower under conventional heating conditions, thereby highlighting the intensification of the MWs. Likewise, the H_2/CO ratios (main by-products in the form of syngas) remained almost constant (0.75-0.80) throughout all the reaction temperatures evaluated under MW-heating conditions.

4. Conclusions

MW-heating of structured monoliths containing reduced loadings of $LaNiO_3$ perovskites represents a promising alternative to promote the electrification and intensification of the DRM process and yield extremely competitive conversions of two greenhouse effect gases into valuable by products.

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Keywords

Microwave-chemistry; Structured reactors; Monoliths; Perovskites; Dry reforming; CO_2 valorization; Intensification