Dry Reforming of Biogas over $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ Perovskite for Syngas Production

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Significance and Relevance

The presented research addresses the primary challenges associated with the dry reforming of biogas for syngas production, a pivotal process for sustainable industrial applications. The effect of reaction temperature and simulated biogas composition is studied using a previously optimized $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite as catalyst and oxygen carrier. Advanced characterization techniques revealed exsolution of Ni nanoparticles and higher amounts of oxygen vacancies than the Ni-free perovskite, which account for its high activity and H_2/CO ratios of 1 under certain conditions. Impurities of water and O_2, however, led to significant changes in H_2/CO ratio. Finally, its application in chemical looping DRM denoted a remarkable stability after 50 cycles.

Introduction and Motivations

Dry reforming (DR) is recognized as one of the most cost-effective technologies for simultaneously capturing CO_2 and converting CH_4 into valuable syngas ($CO+H_2$). A promising strategy for conducting DR is chemical looping mediated by solid oxygen carriers, which involves alternating reduction and oxidation steps. During the reduction step, the oxide releases oxygen, and it is subsequently regenerated in the oxidation step[1]. Perovskite-type catalysts are particularly well-suited for DR due to their high thermal stability and exceptional oxygen mobility[2].

This study introduces an innovative approach to DR by implementing the chemical looping process using an enhanced perovskite composition ($La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$)[3], assessing its stability and catalytic activity over 50 cycles of alternating reduction and reoxidation with CO_2. In addition, tests were carried out to simulate the composition of biogas by adding oxygen, water or both molecules to the feed. Furthermore, it provides a novel methodology for optimizing processes involving complex compositions, such as biogas, through applying linear programming (LP) as an analytical tool to identify competing reactions.

Materials and Methods

The $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite was prepared using a modified Pechini method. The catalytic tests were carried out in a vertical fixed-bed reactor coupled to a Mass Spectrometer. Isothermal reactions were run at three temperatures (800, 850 and 900 °C) and co-feeding different CH_4/CO_2 ratios with a constant WHSV of 6000 L/(kg.h). The effect of impurities was evaluated performing reactions at 900°C using different proportions of water and oxygen. Redox cycles were performed at 900 °C: a DR stage (25 min co-feeding CH_4/CO_2=1.5/1) was alternated with an oxidation step (feeding CO_2 for 5 min), in total 50 cycles were accomplished. The structure of the perovskites before and after reaction was determined by XRD and the chemical mapping of the catalysts was carried out employing SEM technique. XPS spectra were acquired to check the different oxygen states in the perovskite before and after reaction. Elemental analysis was carried out to determine the amount of carbon deposited on the perovskite after reaction. The extent of the simultaneous reactions occurring during the catalytic tests was evaluated using linear programming (LP) optimization.

Results and Discussion

The impact of reaction temperature was first assessed during the reduction step using the $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite at 800, 850, and 900 °C for 3 h with a CH_4/CO_2 ratio of 1.5:1, similar to biogas composition. Higher temperatures significantly enhanced CH_4 and CO_2 conversions and brought the H_2/CO ratio closer to 1, highlighting the dominance of the DR reaction. Remarkably, no catalyst deactivation was observed throughout the process. SEM analysis of the post-reaction sample revealed the formation of small (40–50 nm) spherical Ni-rich particles exsoluted on the perovskite surface. It is also remarkable that a greater quantity of oxygen vacancies, associated with higher O donation and CO_2 activation capacity, were observed in the O1s XPS spectra of this particular perovskite.

Given the superior performance at 900 °C, this temperature was chosen to study feed composition. Lowering the CH_4 proportion boosted the conversion of both CH_4 and CO_2, with the H_2/CO ratio stabilizing around 1, reaffirming the DR reaction's prevalence. In contrast, introducing only CH_4 shifted the process toward methane decomposition, significantly compromising the perovskite's stability. Linear programming (LP) optimization was used to identify the dominant reactions at different stages of isothermal tests conducted at 900 °C for the $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite. This approach provided insights into how the composition of the perovskite influences the extent of the reactions that take place. Moreover, tests were conducted by adding oxygen and water, similar amounts to those in a biogas, to the feed. Results showed minimal impact on CH_4 and CO_2 conversions, but with a slight increase in hydrogen production during steam reforming and lower H_2/CO in the case of O_2 addition.

Finally, after 50 redox cycles, the perovskite's effectiveness in chemical looping DRM (CL-DRM) was validated alternating DRM and CO_2 regeneration. CH_4 and CO_2 conversions slightly decreased to 84.3% and 93.6% (Figure 1), respectively, which is an outstanding result. Notably, the H_2/CO ratio, stayed consistently within the 1.0–1.1 range throughout the experiment, confirming the sustained dominance of the dry reforming of methane (DRM) reaction over the 50 cycles. This approach demonstrates strong potential for maintaining the performance of an optimized Ni-perovskite in long-term DRM process.

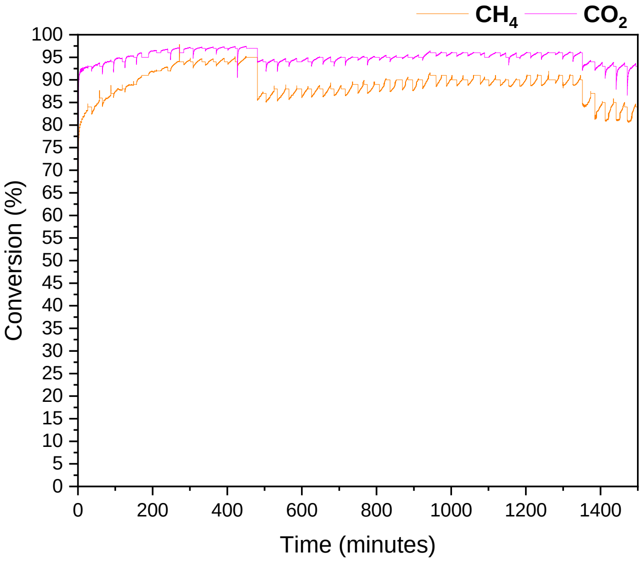

Figure 1. CH_4 and CO_2 conversions of the 50 redox cycles carried out with the $La_{0.9}Sr_{0.1}Fe_{0.95}Ni_{0.05}O_3$ perovskite.

In summary, higher temperatures in the range from 800 to 900 ºC affords greater conversions and H_2/CO ratios closer to 1, enhancing the efficiency of the DR reaction. Co-feeding CO_2 with CH_4 is pivotal to sustain DR dominance and protect the perovskite's structure. The introduction of oxygen and water impurities has negligible impact on the conversions in DR process, but modifies the H_2/CO ratio. Additionally, the cycling process demonstrates the perovskite's prolonged stability and activity after 50 cycles, confirming its significant potential for chemical looping dry reforming (CL-DR).

References

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