Ni-La Perovskite Catalysts for CO_2 Methanation: Uncovering the Structure-Function Correlation

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Significance and Relevance

This work explores Ni-La perovskite catalysts for CO_2 methanation, emphasizing the critical role of catalyst structure and pre-reduction temperature in enhancing conversion efficiency. By comparing one-pot-synthesized lanthanum nickelate with Ni-impregnated lanthanum oxide, it reveals how advanced synthesis techniques, like microwave-assisted methods, improve Ni dispersion and oxygen vacancy formation—key factors for catalytic performance. Findings show that structural modifications and pre-reduction temperature in Ni-La perovskites directly influence CO_2 adsorption and methane production rates, offering insights for designing efficient, sustainable catalysts. This research supports advanced CO_2 utilization technologies crucial for global carbon neutrality efforts.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport/CO_2 utilization and recycling
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In response to global carbon neutrality goals, particularly the European Union's target of achieving carbon neutrality by 2050[1], CO_2 methanation offers a promising pathway to synthesize synthetic natural gas (SNG) within the power-to-gas (PtG) framework. The Sabatier reaction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$)[2] provides a thermodynamically favourable method to convert CO_2, a greenhouse gas, into valuable methane. However, the reaction is kinetically limited, requiring efficient catalysts to enhance conversion rates[3]. Nickel (Ni)-supported systems are widely studied as active and selective catalysts, owing to Ni's cost-effectiveness and availability[4]. Catalysts based on Ni and non-stoichiometric materials are particularly promising, as oxygen vacancies within these materials play a critical role in CO_2 adsorption, enhancing metal dispersion, and improving resistance to coking[5]. Perovskite structures, in particular, offer excellent oxygen mobility and are resistant to reductive conditions, making them ideal for CO_2 methanation[6]. Previous studies, including work by Grabchenko et al.[7], have demonstrated the superior performance of Ni-La perovskites, with the $Ni/La_2O_2CO_3$ interface playing a significant role in performance, influenced by synthesis methods.

This study evaluates two catalyst structures: lanthanum nickelate prepared via one-pot synthesis and Ni-impregnated lanthanum oxide. Both were synthesized using microwave radiation-assisted (MW) method to improve Ni dispersion and phase uniformity[8]. The results establish key correlations between catalyst structure and CO_2 methanation performance, with a focus on surface species and their impact on reaction rates. Additionally, the study highlights the importance of oxygen vacancies and catalyst reduction in enhancing performance.

Materials and Methods

The one-pot synthesis of lanthanum nickelates was achieved in a single step using microwave radiation-assisted precipitation (MW-OP), employing the corresponding nitrates as precursors. For comparison, lanthanum oxide was prepared using the same procedure and subsequently impregnated with 12 wt.% Ni via the wetness method (MW-Imp). Physicochemical properties were analyzed using XRD, N_2-physisorption, H_2–TPR, and XPS techniques. CO_2 methanation reaction was conducted on partially and fully pre-reduced samples (at 500 and 750 °C for 1 hour under H_2/Ar flow) in a fixed-bed tubular reactor, with a CO_2 and H_2 gas mixture (1:4 ratio) diluted in N_2. In situ DRIFTS-MS studies were performed reducing the samples at 500 °C or 750 °C in a 10% H_2/Ar stream for 1 hour to evaluate the active phases formed from the reduction treatment. The reaction was monitored by feeding an H_2/CO_2 mixture (4:1 ratio) diluted in argon into the IR cell at 250 °C, allowing for steady-state analysis with spectra recorded every 120 seconds. Effluent gases were analyzed via mass spectrometry.

Results and Discussion

The comparison of XRD patterns of MW-OP and MW-Imp confirmed perovskite-like structures in fresh catalysts, with distinct phases emerging after pre-reduction at 500°C and 750°C (**Figure 1A**), highlighting the influence of synthesis and reduction conditions on catalyst properties. These structural variations impact CO_2 conversion rates, with catalysts containing a higher fraction of perovskite structures demonstrating improved catalytic efficiency. Notably, pre-reducing the catalysts at 500°C preserves Ni-perovskite interfaces, which enhances CO_2 adsorption and conversion, attributed to the unique Ni-La interphase created within perovskite structures (**Figure 1B**). In situ DRIFTS further showed that different active phases formed at each reduction temperature, aligning with the observed improvements in methanation efficiency.

These insights into structure-to-function relationships underscore the critical role of phase composition, Ni dispersion, and oxygen vacancies in optimizing CO_2 conversion.

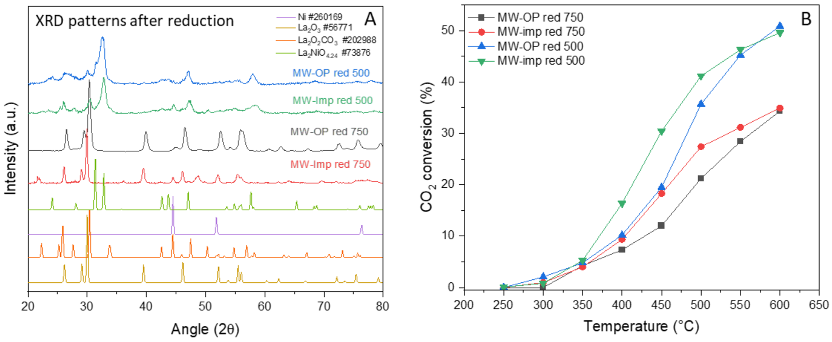

Figure 1 XRD patterns of catalysts after reduction at 500 and 750°C (A), CO2 conversion of the catalysts pre-reduced at 500 and 750°C (B).

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