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Ball-milling assisted synthesis of $LaNiO_3$ perovskites from different precursors for application in dry reforming of methane (DRM)

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Resumo-Abstract

Efforts to slow the rapid climate change driven by global warming have spurred research. The hydrogen economy is emerging as a greener alternative to fossil fuels, with one potential transition being the conversion of natural gas and CO_2 into syngas (a mixture of H_2 and CO) through methane reforming. These reactions use various reactants; in this study gaseous CH_4 and CO_2 were used (dry reforming). The produced syngas may be used to generate higher molar mass hydrocarbons (Silva et al., 2021). Although catalysts have shown feasibility by maintaining reaction rates and stability, further research is required for finding more stable catalysts. Nickel has been used as a cheap alternative, but present low stability. Perovskite structures, known to reduce in situ into Ni supported on lantana, are a promising strategy due to its high thermal stability (Silva et al., 2021).
The usual synthesis routes for these materials involve usage of large quantities of water and organic precursors. This work presents an alternate route where metal precursors are used in a planetary ball-miller Retsch™ PM-100 in 500 rpm for 2 h, in intervals of 5 minutes of milling and 5 of rest, diminishing as such the water consumption of the synthesis.
Five samples were synthesized using stoichiometric proportions of 1:1 La:Ni. The reactants were: 1. NiO and La_2O_3 (o-Lamech); 2. NiO and La_2O_3 with solid citric acid as a pseudo- structure director and auxiliar milling solid in equimolar to Ni proportion (κ-Lamech); 3. $NiNO_3$ and La_2O_3 (ν-Lamech); 4. $NiNO_3$, La_2O_3 and citric acid in the same mass condition as above (νκ-Lamech). The materials were calcined at 1000 ºC for 1 h and a heating rate of 10 ºC/min. The nitrates-derived materials had a step at 300 ºC for 1 h to guarantee elimination of nitrates. The sample ref. $LaNiO_3$ was synthetized as described in Silva et al. (2021). The materials were characterized through x-ray diffractometry (XRD) in a Shimadzu™ XRD-600, thermo-programed reduction by H_2 (TPR-H_2) coupled to an Omnistar™ Pfeiffer™ MS under 50 ml/min flow of H_2:He (5:95) and heating rate 10 ºC/min. Long term tests were conducted post-reduction at 800 ºC for 1 h, the reaction conditions were 100 mL/min flow of CH_4:CO_2:Ar (1:1:2) and 30 mg of perovskite precursor and 70 mg of quartz as a diluter on a fix bed PID coupled with a Shimadzu™ GC-2014.
The XRD characterized the samples as mostly consisted of a perovskite $LaNiO_3$ and spinel $NiLa_2O_4$ phases. The TPR's results shows the characteristic three-way reduction of perovskite phases, the first peak attributed to the formation of La2Ni2O5, second to the formation of Ni0 from NiO phases and the last events usually attributed to the reduction of La2Ni2O5 into Ni0 and lanthanum oxide (Silva et al., 2021). The samples synthetized from nitrates tended to present peaks in higher temperature indicating stronger metal-support interactions in the reduced product. Meanwhile, the addition of citric acid was successful in improving this same interaction. Higher reduction peaks were observed in ν and νκ-Lamech even if compared with ref. $LaNiO_3$. The long-term tests show that the materials derived from nitrates (ν and νκ-Lamech) were significantly more active than their oxides counterparts in the reaction, indicating that the synthetic route using nitrates favors higher metal-support interaction and greater activity. The inclusion of citric acid in the milling was also successful in heightening activity, but not by much compared to the effect of nitrates. Except for the o-Lamech, none of the samples showed significant deactivation during the 20h of reaction. The better sample prepared through ball-milling showed similar CO_2 conversion rates to the ref. $LaNiO_3$ and it produced syngas with a H_2/CO ratio slightly higher than the reference material, indicating that the process of ball-milling was successful.

Palavras-chave: Perovskite, Ball-milling, Dry reforming of methane.

Referências

Silva et al. Perovskite-type catalysts based on nickel applied in the Oxy-CO2 reforming of CH4: Effect of catalyst nature and operative conditions. Catalysis today, vol. 369, p. 19–30, 2021.

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