

Composition-activity relationship for Ni-Alkali/Alkaline earth metal unsupported catalysts in the CO₂-SR technology

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Introduction

CO₂-SR technology is a cyclic process that combines the capture and storage of CO₂ with its conversion to high-value compounds through catalyst regeneration with CH₄ [1]. This process involves the use of a dual function catalyst that contains components for CO₂ adsorption based on alkali and alkaline earth metals, as well as redox metal components for CO₂ conversion. This contribution presents the experimental results of the incorporation of Ba, Ca, Sr and K to Ni as unsupported bimetallic catalytic systems, to analyze the structural and physicochemical properties and the effect on the CO₂ storage and regeneration capacity.

Methodology approach

The catalysts were synthesized by an ultrasonic assisted coprecipitation of the heterometallic mixed precursors employing an atomic ratio Ni:Me = 1:1 using colloidal silica as surface area promoting agent and calcined at 800°C in air for 4 h, and an exhaustive characterization was performed. CO₂ adsorption capacity tests were performed feeding 2000 ppm of CO₂ into a fixed-bed reactor connected to a Pfeiffer Mass Spectrometer and an MKS-FTIR Gas Analyzer. Previously, the catalyst was in situ activated in He at 600°C and then reduced in a stream of H₂ (2% in He, 100 mL·min⁻¹) for 1 h followed by a He purge. Oxygen Storage Capacity was carried out by isothermal H₂-He-O₂ alternating cycles (30,000 ppm each one) in TG-coupled to a MS. The performance in the cyclic alternated process of CO₂ storage and in situ regeneration with CH₄ and H₂ was studied. Isothermal alternated cyclic tests were carried out at 600 °C feeding 30,000 ppm pulses of CH₄-He and CO₂-He with He purge on a previously reduced catalyst.

Results and Discussion

The influence of the incorporation of *alkali-alkaline earth metal* in combination with nickel as bimetallic unsupported reference catalysts are summarized in the Table 1. The alkali or alkaline earth metal incorporated into the formulation influences the textural properties of the catalyst, which is related to the adsorption kinetics of the material. Nevertheless, there is not such a significant difference in the overall CO₂ storage capacity when catalyst saturation is reached.

Table 1. Properties of the catalysts.

Catalyst	A _{BET} , m ² ·g ⁻¹	Breakthrough time, s	Ads. Rate, ppm·s ⁻¹	CO ₂ ads Capacity mmolCO ₂ gcat ⁻¹	Ads. Capacity %
NiBa	55	19	31.8	0.17	0.75
NiK	125	37	24.6	0.20	0.87
NiCa	125	15	33.5	0.20	0.86
NiSr	82	10	13.6	0.16	0.70

Oxygen exchange capacity, indicated in the Figure 1, shown that NiBa and NiK presented a better performance; the worse activity registered was for NiSr, while NiCa lost oxygen exchange capacity due to the non-reversible carbonation of catalyst surface.

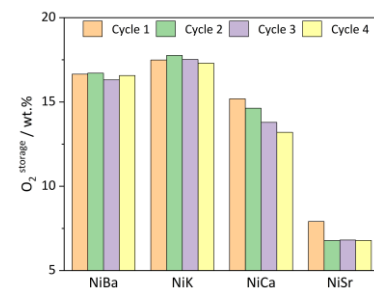


Figure 1. Oxygen Storage Capacity for cycles

For tests carried out at 600°C, NiBa has shown better performance for CO₂-SR technology. Although the CO₂ storage capacity is apparently limited, the NiBa catalyst showed efficient reduction capacity using CH₄ leaving a regenerated surface giving a fuel gas stream containing varying concentrations of CH₄, CO, H₂.

Significance

CO₂-SR is a non-mature technology which enables the valorization of CO₂ by activate storage and the catalyst regeneration using methane in a unique reactor system. It is an emerging strategy to simultaneously reduce emissions of two greenhouse gases (CO₂ and CH₄, GHG) by catalyst with twice functionality to produce an H₂-enriched fuel gas.

References

1. S. Molina-Ramírez, et al. *Journal of CO₂ Utilization* **2020**, 40, 2212-9820.