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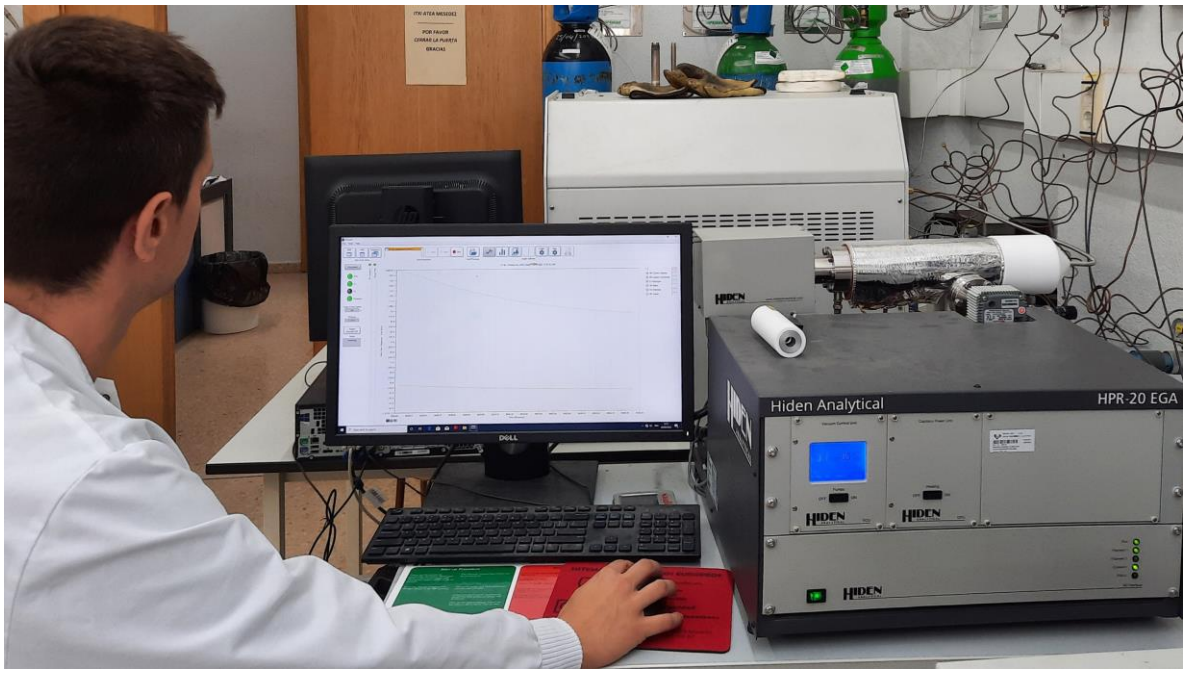
Applicability of $LaNiO_3$-derived catalysts as dual function materials for CO_2 capture and in-situ conversion to methane

Integrated cyclic CO_2 capture and in-situ hydrogenation to CH_4 on dual function materials (DFMs) has attracted increasing interest in recent years, since it eliminates the costly CO_2 purification step that is required for CO_2 methanation on the continuous operation. The conventional DFMs are composed of a CO_2 storage material (such as, Ca, Na, Mg or K) and a metal (mainly Ni or Ru) that assists its methanation. However, Ni presents lower activity and stability than Ru, whereas its high cost is the main limitation of the latter. Considering this background, the aim of this work is to evaluate the applicability of supported $LaNiO_3$ perovskites, as precursors of efficient dual function materials for CO_2 adsorption and in-situ hydrogenation to methane.

Four DFMs, obtained after the controlled reduction of different perovskite-based precursor (30% $LaNiO_3/CeO_2$, 30% $LaNiO_3/Al_2O_3$, 30% $LaNiO_3$/La-Al_2O_3 and $LaNiO_3$), were prepared by combining citric acid and impregnation methods. The physico-chemical properties of the DFMs were determined by N_2 adsorption-desorption, XRD analysis, STEM-EDX images as well as H_2-TPR, H_2-TPD and CO_2-TPD experiments. All temperature programmed experiments were monitored with a **Hiden Analytical HPR-20 EGA mass spectrometer**. CO_2 adsorption and hydrogenation cycles were carried out in a vertical stainless steel tubular reactor inside a 3-zone tube furnace. CO_2, CH_4, CO and H_2O concentrations were continuously monitored by FTIR during the CO_2 storage/capture period (10% CO_2/Ar, 1 min) followed by its hydrogenation/methanation (10% H_2/Ar, 2 min), with an intermediate Ar purge. The experiments were carried out with a flow rate of 1200 ml min^{-1} on the pre-reduced sample (550 or 800°C, 2h), in the 280-520°C temperature range.



The Hiden Analytical HPR-20 EGA Mass Spectrometer in the Laboratory

Results of XRD analysis, STEM-EDX images, H_2-TPD, H_2-TPR and CO_2-TPD experiments reveal that the DFM obtained after reduction of 30% $LaNiO_3/CeO_2$ formulation shows the smallest Ni^0 particle size (7 nm) and the highest medium-strong basic sites concentration. As a result, this DFM widens the operational window with respect to those obtained from 30% $LaNiO_3/Al_2O_3$, 30%

$LaNiO_3/La\text{-}Al_2O_3$ and $LaNiO_3$ formulation. Specifically, the resulting DFM maintains the methane production ranging between 80 and 103 μmol g^{-1} and the selectivity towards methane above 90% in the range of 280-520 °C. Based on characterization results, the best catalytic behaviour is related to a better contact between the different nature basic sites and the homogenously distributed Ni^0 sites, which favours a fast spill-over of dissociated H to nearby CO_2 adsorption sites. Note that these properties are significantly promoted with respect to conventional DFMs. The applicability of this DFM is further evidenced by a highly stable CH_4 production during long-term experiments and a promoted Ni^0/NiO reversibility in the absence/presence of O_2 during the CO_2 adsorption period, which allows a fast and complete recovery of CH_4 production in absence of O_2. These aspects favour a versatile application of the 30% $LaNiO_3/CeO_2$-based DFM formulation to convert CO_2 outlet streams from combustion flue gases of different nature.

Project summary by:

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Hiden Product:

HPR-20 EGA