Hydrogen production by chemical looping methane pyrolysis

Luca Consentino[1,2], Francesca Deganello[2], Rut Guil-Lopez[3], Valeria La Parola[2*], Leonarda Francesca Liotta[2], Giuseppe Pantaleo[2]

[1] *Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, V.le delle Scienze Ed. 17, 90128 Palermo, Italy;* [2] *Institute for NanoStructured Materials, Italian National Research Council (ISMN-CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy,* [3] *Instituto de Catálisis y Petroleoquímica, Spanish National Research Council (ICP-CSIC), 28049 Madrid, Spain*

[*] *valeria.laparola@cnr.it*

Significance and Relevance

Chemical looping reforming of methane turned out to be a promising process to produce pure hydrogen via catalytic methane pyrolysis overcoming the problem of the building up of carbon on catalyst surface. In addition, pure CO can be produced by using CO_2 as an oxidant in the oxidation step. Among the studied catalysts, **NiAlCa** mixed oxide, prepared by thermal decomposition of like-hydrotalcite material, showed the best performance and stability.

Preferred and 2nd choice for the topic: H2 storage and transportation, green H2 production, hydrogen vectors; Sustainable and clean energy production and transport.
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred

Introduction and Motivations

The concomitant increase in energy use and CO_2 emission in the atmosphere is of major concern for the environmental equilibrium and earth health of the next future.

Hydrogen is an energy vector with attractive attributes, such as lightness, storability, reactivity, high energy content per unit mass, and easy production at industrial scale. Furthermore, hydrogen can be used without direct emissions of air pollutants or greenhouse gases and can be produced from a diverse range of low-carbon energy sources. Chemical looping technologies can be applied as a valuable approach for hydrogen production, due to the high energy efficiency and inherent CO_2 capture ability[1]. This study concerns the investigation of three types of nickel-based materials active in the decomposition of methane for hydrogen production used in the first step (reduction step) of the chemical looping, followed by a second step (oxidation step) in either Air (CL_AIR) or CO_2 (CL_CO2) for the removal of the carbon accumulated during the reduction step.

Materials and Methods

Three catalysts with Nickel in different environments were prepared: Ni coprecipitated with cerium oxide (**NiCe**), Ni in a **NiAlCa** mixed oxide prepared by thermal decomposition of like-hydrotalcite material, and Ni in **$LaNi_{0.8}Co_{0.2}O_3$** perovskites structure. All samples were characterized by X-ray diffraction (XRD), nitrogen physisorption, temperature programmed reduction (TPR) with diluted H_2 or CH_4 and temperature programmed oxidation (TPO) techniques. Redox stability was checked with multiple REDOX cycles and chemical looping experiments were carried out isothermally, alternating the gas composition every 10 minutes from 15 vol% of CH_4 in N_2 to air or CO_2. The reaction temperature was chosen for each sample based on temperature programmed reduction measurements with methane.

Results and Discussion

The different nickel environments of the three catalysts have been confirmed by XRD and TPR measurements. The redox stability, analyzed by multiple TPR-TPO cycles, indicated that $LaNi_{0.8}Co_{0.2}O_3$ is the most stable material . Both NiCecp and NiCaAl (exHT) modify their profile after the first TPR-TPO cycle by stabilizing the Ni phase. CH_4-TPR allowed us to identify the best temperature of methane decomposition for each material: 680°C for $LaNi_{0.8}Co_{0.2}O_3$, and 600°C for NiCecp and NiCaAl (exHT).

Figure 1 shows two cycles of CL-AIR (lower panel) and CL-CO_2 (upper panel) for the three materials. The catalytic activity for hydrogen production follows the order NiCaAl (exHT)> NiCe (cp)> $LaNi_{0.8}Co_{0.2}O_3$ with all three catalysts showing good stability as evidenced by the hydrogen production after ten cycles. Interestingly the oxidation step (AIR or CO_2) influenced the nature of the active phase and its interaction with the support/matrix. In the case of $LaNi_{0.8}Co_{0.2}O_3$ and NiCe(cp) the repeated reoxidation in CO_2 produced Ni active phase less effective in the activation of methane, essential step for the catalytic methane pyrolysis. On the contrary, NiCaAl(exHT) shows analogous performances both using air and CO_2 as oxidizing agent.

In conclusion, NiCaAl(exHT) is a promising material with good activity and stability for hydrogen production via methane pyrolysis. Its activity in hydrogen production via chemical looping processes is worth of further study to optimize the experimental details for a scale up study.

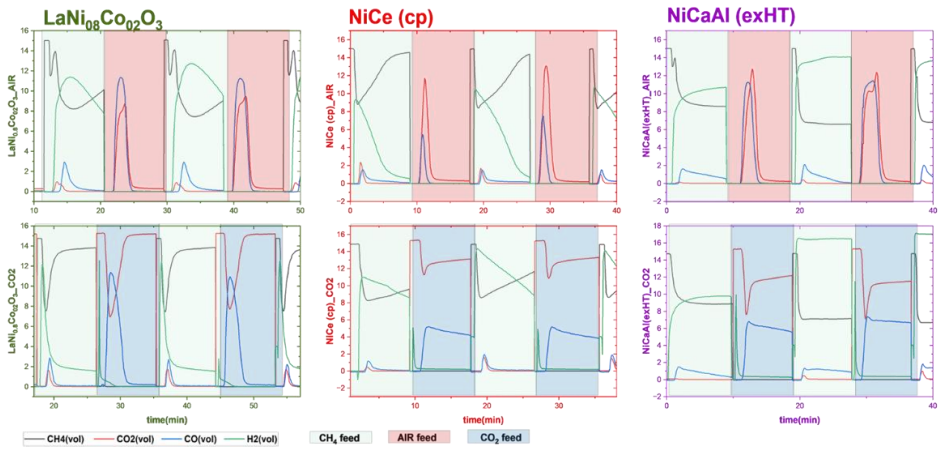

Figure 1 CH_4, CO and CO_2 concentration (ppm) during chemical looping cycle: CL_AIR (upper panel) and CL_CO_2 (lower panel). Enlargement of two cycles.

References

1. Li, L.; Tang, D.; Zheng, Z.; Zhao, C. Catalysts **2018**, 8, 257-269.

Acknowledgements

Project NAUSICA (PON "R&S 2014-2020", grant n. ARS01_00334), Short Term Mobility (STM) 2022 CNR