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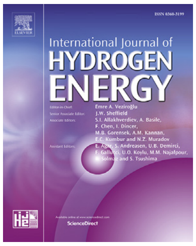

Cermets Ni/($Ce_{0.9}Ln_{0.1}O_{1.95}$) (Ln = Gd, La, Nd and Sm) prepared by solution combustion method as catalysts for hydrogen production by partial oxidation of methane

Consuelo Alvarez-Galvan [a],[*], Horacio Falcon [b], Vanessa Cascos [c], Loreto Troncoso [c], Susana Perez-Ferreras [a], Maricarmen Capel-Sanchez [a], Jose M. Campos-Martin [a], Jose Antonio Alonso [c], Jose L.G. Fierro [a]

[a] *Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, E-28049, Madrid, Spain*
[b] *Centro de Investigación y Tecnología Química (CITeQ), Universidad Tecnológica Nacional-Facultad Regional Córdoba, X5016ZAA, Córdoba, Argentina*
[c] *Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049, Madrid, Spain*

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ABSTRACT

Catalysts based on Ni/($Ce_{0.9}Ln_{0.1}O_{1.95}$) (Ln = Gd, La, Nd and Sm) have been developed and tested for hydrogen production by partial oxidation of methane. The synthesis method (SCS, solution combustion synthesis) produces macroporous composite materials composed of ceramic (cer, $Ce_{0.9}Ln_{0.1}O_{1.95}$) and metallic (met, Ni) phases, without the need of an activation stage prior to the catalytic reaction. The catalysts have been characterized by different techniques: X-ray diffraction, N_2 adsorption-desorption, Hg porosimetry, Scanning Electron Microscopy, Temperature Programmed Reduction, H_2 and O_2 pulse chemisorption, X-ray photoelectron spectroscopy and Raman spectroscopy. With the exception of the lanthanum-loaded catalyst, the catalysts are highly active, selective and stable; being the one doped with gadolinium the most efficient. Correlations structure-activity point out that the excellent catalytic performance is related to the high catalytic surface area per unit mass of catalyst and to an appropriate balance of nickel dispersion to oxygen vacancies of the support.

Introduction

There is a great economic incentive in developing efficient catalysts for the conversion of natural gas into valuable products. Natural gas is found in many locations around the world (more distributed than oil reserves) and avoids dependence from oil producer countries; however the main drawback to use methane as a source of chemicals and fuels is the relatively low cost of oil coupled with the high cost of natural gas storage and transportation from remote reservoirs. So far, the only economically available route for the conversion of methane into more valuable chemicals is via syngas production [1].

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[*] *Corresponding author.*
E-mail address: c.alvarez@icp.csic.es (C. Alvarez-Galvan).

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Thus, there is a great motivation in developing efficient catalysts for the conversion of natural gas into syngas (suitable for methanol and Fischer-Tropsch syntheses) or for hydrogen production. Among the existing technologies employed to reform natural gas: steam reforming (SRM), dry reforming (DRM) and partial oxidation of methane (POM), the POM reaction presents some advantages compared to the conventionally used, highly endothermic, methane steam reforming such as energy saving, since it is a mild exothermic reaction and leads to a H_2/CO ratio ~ 2 (suitable for Fischer-Tropsch or methanol syntheses). The thermodynamics indicates that methane conversion and selectivity to syngas is enhanced at high temperature, being necessary the use of a catalyst with thermal stability at high temperatures (around 700–800 °C). Their main problems are the formation of hot-spots in the catalytic bed and, in some cases, the need of an oxygen separation plant [2].

Supported Ni catalysts were found to be active for the former process, but suffer from deactivation caused by coke formation as well as sintering of Ni particles. In comparison, noble metal catalysts exhibit higher activity and stability; however, they are much more expensive and less readily available.

On the other hand, the support has also a role in the catalyst efficiency, changing the adsorption and reactivity of reactant molecules, decreasing carbon formation by their basicity or by the formation of carbonates, containing oxygen vacancies and enhancing oxygen mobility and tuning the dispersion of the supported active phase by the different interaction with the support. The use of rare earths as supports results in efficient catalysts for oxidation reactions, increases the oxygen storage/release capacity oxidizing deposited carbon and produces a strong interaction with active phase, decreasing sintering [3–7].

Considering the advantages of both metal and support phases, Ni-ceria supported catalysts have been successfully used as catalysts for catalytic partial oxidation of methane (CPOM). It was found that oxygen mobility in the support is enhanced by metal-support interaction, which is influenced by the preparation method [8]. The influence of the amount of nickel on catalytic performance has been also investigated [9] and, very importantly, the effect of Zr incorporation in the ceria lattice on the redox properties was identified, finding that the catalytic behavior is related to the metal dispersion and the surface oxygen mobility, promoting carbon elimination [10–14].

Although there is not a general consensus on the reaction mechanism, for a medium-high space velocity reaction, it is assumed that the reaction would proceed in two-stages: the first includes a combustion reaction and the second involves reforming reactions leading to CO_2 and H_2O, being necessary to favor heat transfer in order to facilitate these last endothermic reactions. The supported metallic phase would act by dissociating methane, followed by reaction with oxygen species from the support (in a Mars van Krevelen mechanism) to form syngas. Supported active particles with a higher oxidation state would facilitate a deeper oxidation [15].

Among various methods employed for catalysts preparation, solution combustion synthesis (SCS) is well suited for the synthesis of metal oxides of homogeneous, porous and finely particulate compositions. These are critical points in these materials, helping to improve heat and mass transfer and to decrease the formation of hot-spots [16,17].

Inspired by the latest developments in ceria-supported Ni catalysts [9,18,19], we focused on the preparation by the SCS method of nickel supported on mixed cerium oxides, doped with different lanthanides (Gd, La, Nd and Sm), in order to analyze the formation of oxygen vacancies and oxygen mobility, which would have an influence on oxygen adsorption and carbon gasification and their possible role in POM reaction.

Experimental

Preparation method

In this study, cermets $(Ni)_{0.1}(Ce_{0.9}Ln_{0.1}O_{1.95})_{0.9}$ (Ln = Gd, La, Nd and Sm) (coded NCG, NCL, NCN and NCS) were prepared by the SCS method. In a typical procedure, stoichiometric amounts of the corresponding nitrates are dissolved in distilled water, and then a certain amount of glycine is added [20]. The mixture is heated on a hot plate up to 310 °C. Upon the evaporation of water, a viscous gel is produced. Then a self-igniting or autocombustion process is produced, leading, in a single step, to a finely particulate powder consisting of nickel metal particles supported on the corresponding doped-ceria mixed oxide [17].

Characterization

The phase identification was performed by X-ray diffraction (XRD) analysis using a X'Pert Pro PANalytical equipment. XRD patterns were recorded using a CuKα radiation (λ = 1.5406 Å, 45 kV, 40 mA). The mean particle size was then estimated from X-ray line broadening using the Scherrer equation. Width was taken as the full width at half maximum intensity of the most intense and least overlapped peak of the doped-ceria support ($2\theta = 28.4°$). XRD data were analyzed by the Rietveld method [21] with the FULLPROF program [22]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final run: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates and isotropic thermal factors for all the atoms.

Specific surface areas were calculated using the BET method from the nitrogen adsorption isotherms recorded at 196 °C using a Micromeritics ASAP 2420 automatic instrument. The total pore volume, total pore area and pore size distribution were determined using mercury porosimetry (Micromeritics AutoPore IV 9510).

Temperature-programmed reduction (TPR) experiments were carried out in an automatic Micromeritics TPD/TPR 2900. The catalyst was pretreated under helium at 110 °C for 15 min. The TPR profile was recorded by heating the sample from room temperature to 800 °C at a rate of 10 °C min^{-1} under a H_2/Ar (10% v/v) flow.

Metallic nickel surface area of the catalysts and the amount of chemisorbed oxygen for the supports were

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