



Preparation of structured catalysts with Ni and Ni–Rh/CeO₂ catalytic layers for syngas production by biogas reforming processes



C. Italiano^{a,*}, R. Balzarotti^b, A. Vita^a, S. Latorrata^b, C. Fabiano^{a,c}, L. Pino^a, C. Cristiani^b

^a Institute CNR-ITAE, Via Salita S. Lucia sopra Contesse n. 5, S. Lucia, 98126 Messina, Italy

^b Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Piazza Leonardo da Vinci 32, 20133 Milano, Italy

^c Università degli Studi "Mediterranea" di Reggio Calabria, Dipartimento di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali, Salita Melissari, 89124 Reggio Calabria, Italy

ARTICLE INFO

Article history:

Received 27 November 2015

Received in revised form 25 January 2016

Accepted 29 January 2016

Available online 11 February 2016

Keywords:

Structured supports

Monoliths

Foams

Washcoating

Steam reforming

Oxy-steam reforming

Nickel

Rhodium

Bimetallic catalyst

ABSTRACT

Ni(7.5 wt.)/CeO₂ and Ni(7.5 wt.)/Rh(0.5 wt.)/CeO₂ powders (previously prepared by solution combustion synthesis) were washcoated on cordierite monolith and alumina open-cell foam by means of support dip-coating into acid-free catalyst dispersion. Catalytic performances toward the steam reforming (SR) and the oxy-steam reforming (OSR) of biogas were investigated and compared at different temperatures (700–800 °C) and weight space velocities (WSV = 70,000–350,000 Nml g_{cat}⁻¹ h⁻¹). Coating load was controlled by multiple depositions; homogeneous and well adherent layers were found. Catalytic tests demonstrated superior performances of the bimetallic samples (Ni–Rh/CeO₂) compared to the monometallic one (Ni/CeO₂), especially at high space velocity. At the same time, foam showed better performances with respect to the monolithic support toward the SR and OSR processes.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Successive crises in energy and global warming have been increased the study for more efficient technologies and renewable sources of electricity generation [1]. In this context, fuel cells have been developed in the last decades for transportation, as well as for both stationary and portable power generation [2]. Fuel cells, operating using hydrogen or hydrogen-rich fuels (syngas), can potentially contribute to increase distributed energy generation and to reduce pollutants emissions into the environment [3–5]. At present, the commercial production of hydrogen is mostly based on steam reforming of fossil fuels [6]. However, from the standpoint of fossil fuels limitations and also global climate changes, alternative ways are under investigation in order to replace fossil hydrocarbons with renewable sources, such as biogas [7,8]. Thus, reforming technologies (principally Steam Reforming (SR) and Oxy Steam Reforming (OSR)) of biogas for hydrogen/syngas production will play a crucial role in the transition to the “hydrogen based economy” [1,6,9–11].

Biogas reforming catalysts range from noble metals (Rh, Ru, Pt, Pd Ir) [12–15] to base metals (Ni, Co) supported over metal oxides, mixed oxides and perovskites [16–18]. Particular attention is devoted to the development of non-noble metal catalysts, due to high cost and limited availability of noble metals. Nickel-based catalysts are the most investigated catalytic systems despite they may be quickly deactivated by sintering and coking phenomena [19]. Redox support materials, such as ceria-based solid solutions or mixed oxides, have been reported to prevent metal sintering, due to strong metal-support interactions (SMSI). Moreover, they are generally employed to mitigate catalyst deactivation by carbon deposition, due to oxygen storage capabilities [18,19]. In our previous works, it was reported that Ni/CeO₂ catalysts showed high catalytic performance in OSR of biogas [19,20]. The other way to improve catalyst anti-coking property is to introduce a second metal component to form a bimetallic catalyst system [6,9,21]. Several authors reported that a small noble metal addition (Rh, Pt or Pd) can improve catalyst stability [9,21,22]. Among the preparation procedures, Solution Combustion Synthesis (SCS) provides an attractive practical alternative to the conventional preparation methods since it is simple, low-cost, saving in time and energy consumption [23–25], resulting in nanocrystalline oxide

* Corresponding author. Fax: +39090624247.

E-mail address: cristina.italiano@itae.cnr.it (C. Italiano).

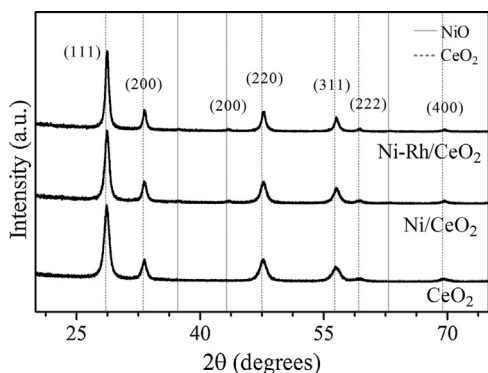


Fig. 1. XRD spectra of synthesized CeO₂, Ni/CeO₂ and Ni-Rh/CeO₂ powders.

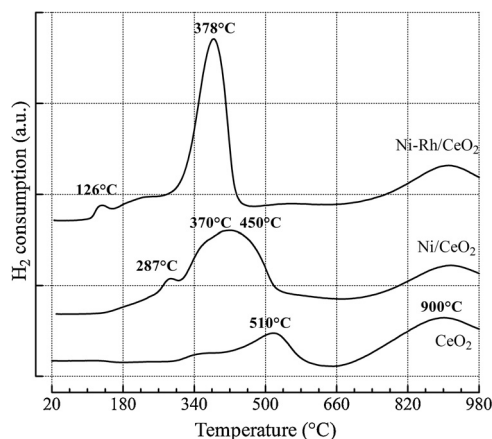


Fig. 2. H₂-TPR patterns of CeO₂, Ni/CeO₂ and Ni-Rh/CeO₂ powders.

powders production with increased homogeneity and reduced size [18,20,26].

Structured catalysts with active components supported on ceramic honeycombs [27–29] and foams [29–32] are well-known to have many advantages, providing an efficient heat and mass transfer compared to conventional packed bed reactors. Good thermal conductivity is especially important in the case of energy-intensive processes to prevent emergence of hot spots/cool zones within the reactor, that could result in a deterioration of catalysts performance [33,34]. Among the many methods available [35], dip-coating into a solution or a dispersion is widely considered the best procedure in order to washcoat geometrical supports [36–39]. Dip-coating process is based on the immersion of the morphological substrate into a slurry containing the catalytic active phase. Once substrates voids are filled, the withdrawing process allows to create an homogeneous film on support surface, thanks to the balance between the gravitational force, attracting the film downward, and the viscous force, which hinders its sliding [40]. On these bases, rheological behavior and withdrawal speed are the most important parameters to be tuned in order to properly control coating layer formation [41]. Slurry rheological behavior depends on a large variety of variables, both from the formulation components (binder, dispersant, solvent) and powder properties (properly sized powder, nature of suspended solids) points of view. All those parameters directly influence viscosity, which is strictly connected to washcoat load/thickness and adhesion properties [41,42]. Suspension stabilization is often achieved by using a water-based acidic solution that allows particle repulsion by means of surface charging [42–44]. Unfortunately, this method shows some limitations as, in some case, an acidic solution may induce significant changes on both chemical and morphological catalyst properties [45].

In this work, Ni/CeO₂ and Ni-Rh/CeO₂ powders (previously prepared by SCS) were washcoated on cordierite monoliths (500 cpsi, diameter 1 cm, length 1.5 cm) and alumina foams (30 ppi, diameter 1 cm, length 1.5 cm) by means of support dip-coating into acid-free catalyst dispersion. Polyvinyl alcohol was used both as rheology modifier and binder: the dependence of coating load, homogeneity and adhesion was evaluated with respect to rheological properties and multiple dip-coating depositions. The catalytic performances of the obtained structured catalysts were investigated toward biogas steam reforming (SR) and oxy-steam reforming (OSR) reactions.

2. Experimental

2.1. Catalyst preparation and characterization

Ni(7.5 wt.%)/CeO₂ and Ni(7.5 wt.%)Rh(0.5 wt.%)/CeO₂ catalysts were prepared by the Solution Combustion Synthesis method (SCS), according to a procedure that was described

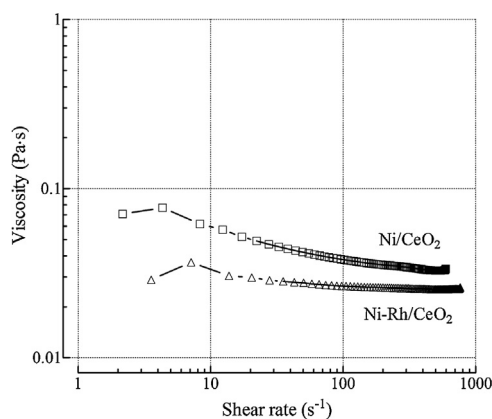


Fig. 3. Rheological properties of catalytic HGP-based slurries.

elsewhere [18,20]. In a typical experiment, stoichiometric amounts of Ce precursor (Ce(NO₃)₃·6H₂O from Alfa Aesar), Ni precursor (Ni(NO₃)₂·6H₂O from Sigma-Aldrich) and Rh precursor (RhCl₃·xH₂O from Sigma-Aldrich) were dissolved in the minimum quantity of distilled water (~100 ml) with the suitable quantity of fuel (urea, CH₄N₂O from Sigma-Aldrich). The amount of fuel was determined by the so-called fuel-to-oxidant ratio and it was calculated using the total oxidizing (O) and reducing (F) valences of the components in order to have an equivalence ratio equal to 1 ($\phi = O:F = 1$); the latter corresponds to a maximum release of energy. The obtained solution was introduced into a preheated muffle furnace (350 °C). In the beginning the solution boils, foams and then undergoes intense flaming combustion with evolution of gases (N₂, CO₂ and H₂O), yielding a very voluminous powder. The resulting powders were calcined at 600 °C for 2 h (heating rate set at 5 °C min⁻¹) to eliminate combustion carbon residues. The Ni and Rh content in the catalytic powders was confirmed by chemical analysis (ICP/OES).

Specific surface area was estimated from adsorption/desorption isotherms at liquid nitrogen temperature (–196 °C) on Micromeritics ASAP 2020 instrument and it was calculated according to the Brunauer–Emmet–Teller (BET) equation.

X-ray diffraction (XRD) analysis of the synthesized catalysts was conducted using a Philips X-Pert 3710 diffractometer that was equipped with a Cu K α radiation at 40 kV and 20 mA. X-ray diffraction patterns were recorded in the scan ranges of $2\theta = 20\text{--}75^\circ$ (1.50°/min), $2\theta = 27\text{--}30^\circ$ (0.06°/min) and $2\theta = 42\text{--}45^\circ$ (0.06°/min). The crystallite size was calculated using Scherrer equation, by using the most intense observed reflection for NiO (2 0 0) and CeO₂ (1 1 1)

Download English Version:

<https://daneshyari.com/en/article/53217>

Download Persian Version:

<https://daneshyari.com/article/53217>

[Daneshyari.com](https://daneshyari.com)