

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

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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.

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

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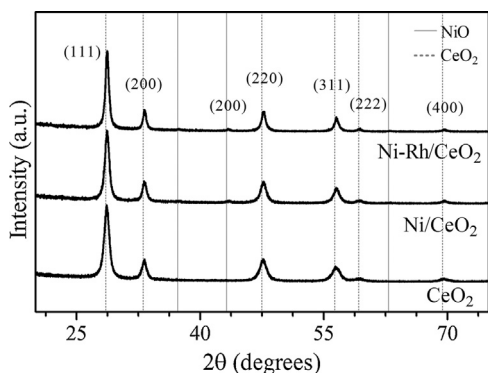


Fig. 1. XRD spectra of synthesized CeO₂, Ni/CeO₂ and Ni-Rh/CeO₂ powders.

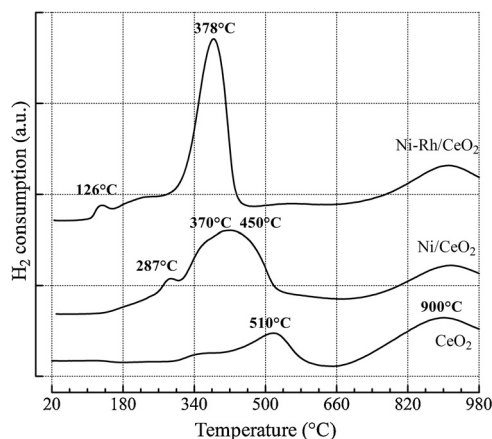


Fig. 2. H₂-TPR patterns of CeO₂, Ni/CeO₂ and Ni-Rh/CeO₂ powders.

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 wash-coat 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

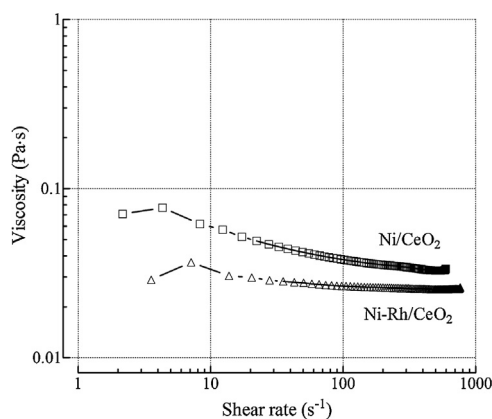


Fig. 3. Rheological properties of catalytic HGP-based slurries.

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)

crystallographic structures, respectively. CeO₂ lattice parameter (α) was obtained from the related pattern at low scan rate.

Catalyst reducibility was studied by H₂ Temperature Programmed Reduction (TPR) using a *Micromeritics ChemiSorb 2750* instrument. A continuous flow of 5% H₂/Ar (30 NmL/min) was passed over the catalyst and temperature was raised up to 1000 °C with a 20 °C/min rate. Before measurements, all catalyst samples were treated in situ at 500 °C for 30 min under O₂ flow. The H₂ consumption was monitored by a thermal conductivity detector (TCD) and the response was quantitatively calibrated from the TPR area of known amounts of CuO. The degree of reduction of CeO₂, NiO and Rh₂O₃ was calculated by taking the ratio of actual H₂ consumption to theoretical H₂ requirement to reduce all the metal oxides present in the sample, by assuming constant degree of reduction of support material.

2.2. Washcoating procedure

Catalyst powders (Ni/CeO₂ and NiRh/CeO₂) were washcoated on both cordierite monolith and alumina open cell foam. Monoliths (500 cpsi, diameter 1 cm, length 1.5 cm) were supplied by Chauger Honeycomb Ceramics (Taiwan), while foams (30 ppi, diameter 1 cm, length 1.5 cm) were provided by Lanik company (Czech Republic). Powders dispersions were obtained according to a procedure reported elsewhere [43,44]. Glycerol (87% w/w water solution, Sigma-Aldrich) was used as dispersant and distilled water was used as solvent/diluent. Glycerol/powder ratio of 1.9 and water/powder ratio of 1.5 were used, respectively. 2 wt.% of polyvinyl alcohol (PVA) (Mowiol from Sigma-Aldrich) related to water-glycerol mixture was used as rheology modifier. In a typical experiment, the dispersion medium (HGP) was produced by dissolving PVA in distilled water and then by adding glycerol under magnetic stirring at 85 °C. Catalyst powder was thus added to the HGP medium and the resulting slurry was ball-milled using ZrO₂ spheres (1 cm diameter and mass ratio with respect to powder equal to 7) as grinding bodies for 24 h at 50 rpm in a polyethylene jar. At the end of milling process, a sonication treatment was performed for 30 min on the slurry in order to reduce foaming. A dynamic stress device (*Rheometrics*) was used to assess slurry rheological properties. Parallel disc plate geometry (40 mm diameter) was chosen; dynamic viscosity was evaluated in the 1–10³ s⁻¹ shear rate range at 25 °C. Structured supports were washed in acetone by ultrasound bath for 30 min before deposition process. Slurry deposition was carried out by dip-coating, at constant withdrawal rate of 13 cm min⁻¹ for both dipping and withdrawal steps. Multiple dippings were performed in order to obtain a coating load of 15–20 wt.%. After each dipping, samples were flash dried in air for 6 min at 350 °C in a sealed oven. In order to obtain the final coated catalysts, a 10 h calcination process was performed at 800 °C (2 °C min⁻¹ heating rate).

Gravimetric analysis was performed after each flash drying step and after the final calcination process, in order to control weight evolution and to assess washcoat load. Final washcoat load was determined by weight, as difference between the bare and the coated support.

Coating adhesion was determined by sonication for 30 min in petroleum ether bath, according to literature [43,44].

SEM investigation of structured catalysts was obtained using a *FEI XL 30* microscope that was equipped with a field emission gun. Optical microscope (*Olympus, SZ-CTV microscope*) was used to assess coating homogeneity.

In the following, the obtained structured systems will be identified as Ni-MO, NiRh-MO, Ni-FO and NiRh-FO as a function of the catalytic formulation (Rh and NiRh for Ni/CeO₂ and NiRh/CeO₂ catalysts, respectively) and the support (MO and FO for monolith and foam, respectively).

2.3. Catalytic tests

Biogas SR and OSR experiments were carried out in a quartz fixed-bed reactor (i.d.=1 cm) that is inserted into a PID temperature controlled furnace. Prior to reaction, structured catalysts were reduced by 50% H₂/N₂ stream (30 NmL/min) at 450 °C for 1 h. Then, catalytic performance was studied feeding a mixture of methane, carbon dioxide, steam and/or oxygen. SR experiments were conducted feeding reagents with CH₄:CO₂:H₂O:N₂ = 1.0:0.67:3.0:0.2 molar ratios, while OSR experiments were carried out at CH₄:CO₂:H₂O:O₂:N₂ = 1.0:0.67:0.3:0.1:0.1 molar ratios. High purity gases (99.999%, from RIVOIRA) were used in the experiments, keeping constant flow rates by using mass flow-controllers (*Brooks Instrument Smart Mass Flow*). Steam was fed using an isocratic pump (Agilent 1100 Series) and a specially designed evaporator. Tests were carried out varying temperature (700–800 °C) and weight space velocity (WSV = 70,000–350,000 NmL g_{cat}⁻¹ h⁻¹), defined as volumetric flow rate of the reactants at 0 °C and 1 bar per gram of catalytic layer. Reaction temperature (T_{SET}) was measured at the center of catalyst bed, between the catalytic system and the tubular quartz reactor, using a chromel/alumel thermocouple. Moreover, two thermocouples were positioned at the inlet (T_{IN}) and at the outlet (T_{OUT}) of the catalytic bed respectively to measure the temperature gradient that is generated by reactions. The duration of each test was set to 6 h. Reagents and products compositions were determined using an on-line gas chromatograph (*Agilent 6890 Plus*) that was equipped with thermal conductivity (TCD) and flame ionization (FID) detectors. CH₄, which was revealed in both detectors, was used as reference compound, while N₂ was used as internal standard for mass balance calibration.

The experimental results were compared with the thermodynamic equilibrium values calculated by a commercial steady state simulation package named Aspen Plus[®] by AspenTech, based on the minimization of Gibbs free-energy of each of the existing species (CH₄, O₂, H₂O, CO₂, CO, H₂, solid carbon). The calculation was carried out at the reaction temperature (T_{SET}) and at the maximum temperature recorded at the outlet (T_{OUT}) of the catalytic bed [34].

3. Results and discussion

3.1. Catalyst characterization

The main textural and structural characteristics of the synthesized Ni/CeO₂ and Ni-Rh/CeO₂ catalysts are included in Table 1 and they are compared with those of CeO₂ carrier that was prepared by the same route. The synthesized powders exhibited specific surface area varying in the range of 10–15 m²/g. XRD patterns of the systems are shown in Fig. 1. All systems were characterized by a typical cubic fluorite structure of ceria, corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2) and (4 0 0) planes (reference JCPDS 4–593). The average particle size of the samples, that was calculated by Scherrer equation (Table 1), indicated a particles size of 10.9 nm for the CeO₂ carrier, that slightly increased to 13.1 and 16.9 nm for Ni/CeO₂ and Ni-Rh/CeO₂ catalysts, respectively. No clear evidence of Ni active phase can be noticed; this is a signal of the presence of small and well distributed particles. However, the small reflection at 2 θ = 43.33° could be attributed to the presence of nickel oxide (reference JCPDS 4–835), which corresponds to NiO particles size of ca. 13.1 and 17.8 nm. Besides, rhodium identification is probably hampered in view of its small amount, that falls below the detection limit. In addition, the lattice contraction (5.385–5.387 Å compared to 5.394 of CeO₂) indicated the partial incorporation of smaller Ni²⁺ ions ($r_{\text{Ni}^{2+}} = 0.81\text{Å}$) and probably of Rh³⁺ ions ($r_{\text{Rh}^{3+}} = 0.68\text{Å}$) into the lattice of ceria Ce⁴⁺ ($r_{\text{Ce}^{4+}} = 0.97\text{Å}$) to form a solid solution [46].

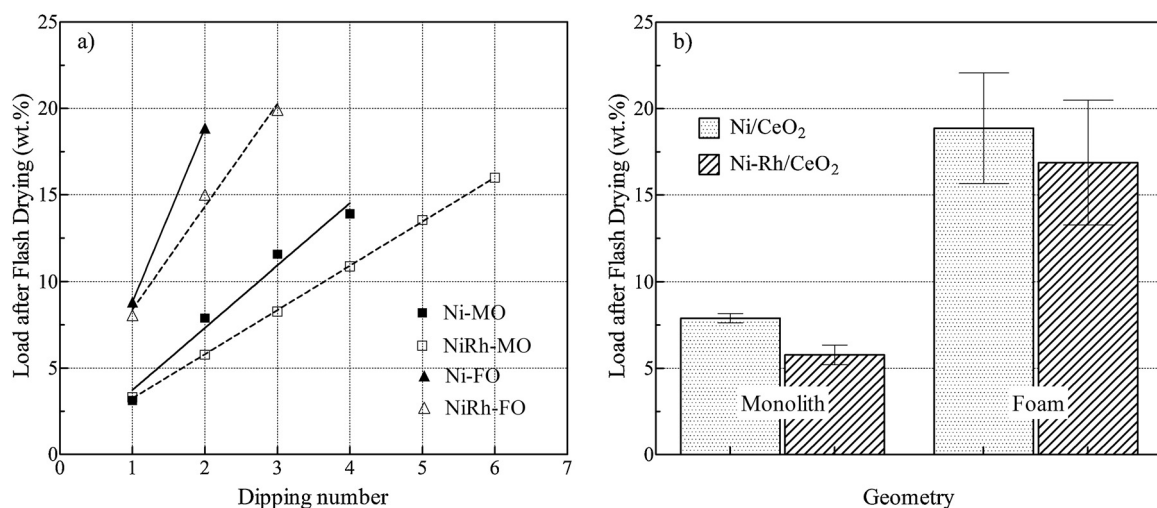


Fig. 4. Washcoat load evolution (a) after flash drying (a) as function of the dipping number and (b) after two dippings. Effect of catalytic sample and support geometry.

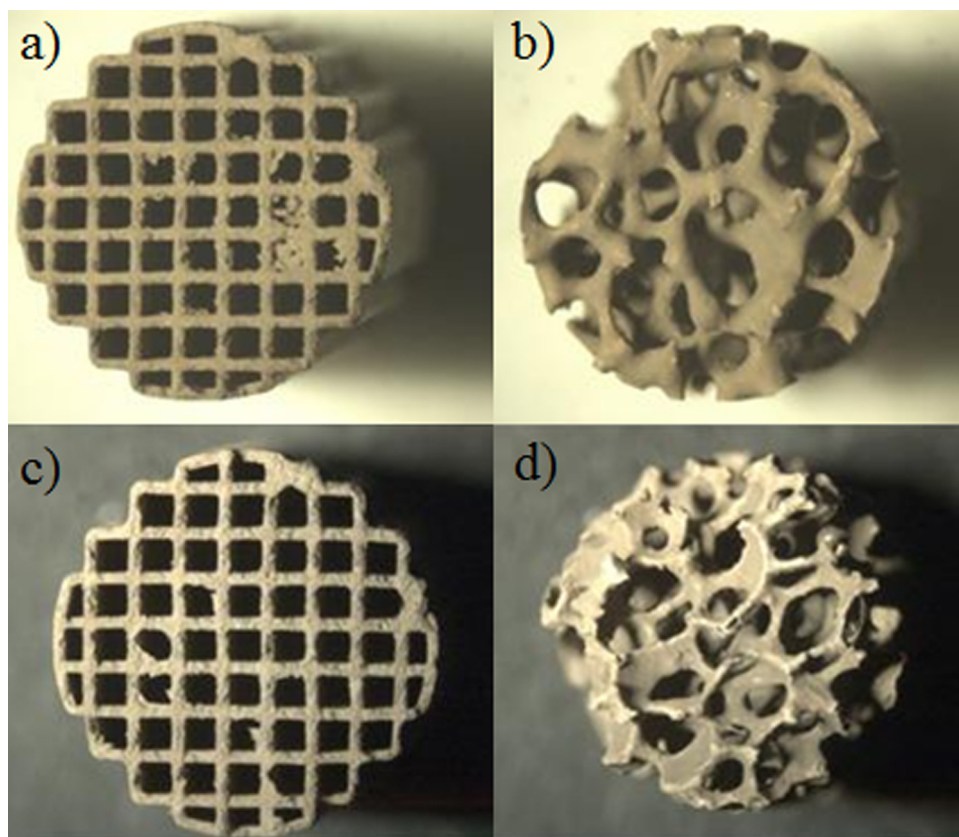


Fig. 5. Optical microscope characterization of Ni/CeO₂ based samples (top, a–b) and Ni-Rh/CeO₂ based samples (bottom c–d) supported on monolith (right) and foam (left).

Table 1
Main textural and structural properties of synthesized CeO₂, Ni/CeO₂ and Ni-Rh/CeO₂ powders.

Sample	BET Surface area (m ² /g)	X-ray		
		CeO ₂ size ^a (nm)	CeO ₂ lattice parameter ^a (Å)	NiO size ^a (nm)
CeO ₂	15	10.9	5.394	–
Ni/CeO ₂	11	13.1	5.387	11.7
Ni-Rh/CeO ₂	10	16.9	5.385	17.8

^a Calculated from X-ray diffraction: CeO₂ particle size from the Scherrer's equation of the CeO₂ (111) reflection; lattice parameter (α) from the relation $\alpha = \sqrt{h^2 \times k^2 \times l^2} / (\lambda / 2 \times \sin\theta)$.

Table 2
Geometric properties of bare supports (monolith and foam).

Sample	Characteristics size $d_{p(mm)}$	Wall/Strut thickness t (mm)	Bed density (kg/m ³)	Bed porosity (%)	Open frontal area ε	Geometric surface area GSA (m ² /m ³)
Cordierite monolith	0.83	0.32	771	72.5	0.52	2529
Alumina foam	1.40	0.43	383	83.6	0.86	988

Fig. 2 compares the H₂-TPR profiles of the CeO₂ carrier and the Ni/CeO₂ and Ni-Rh/CeO₂ catalysts. For bare ceria, two main reduction peaks were observed, at 510 and 900 °C, respectively. As reported in literature, the low-temperature peak is due to the reduction of CeO₂ surface oxygen, while the high-temperature peak is due to CeO₂ bulk oxygen reduction [46,47]. The amount of hydrogen consumption of low-temperature peak (510 °C) was 0.6 mmolH₂/g_{cat}, which corresponds to ca. 10% of the reducible CeO₂ species. The catalyst containing Ni showed reduction peaks at 287, 370, 450 and 900 °C, as previously reported [18,20,46]. The low-temperature zone (temperatures range between 130 and 300 °C with a maximum at ca. 287 °C) is ascribed to adsorbed oxygen reduction due to NiO solid solution formation into CeO₂ [46,48,49]. Besides, the contribution of bulk NiO particles reduction without interaction with the ceria support cannot be excluded [50]. In the middle-temperature zone, the peak at 370 °C can be correlated to the reduction of NiO interacting with (but not chemically bound to) the support, while the latter peak (at 450 °C) can be associated to the formation of Ni-Ce solid solution [20,50] and to the reduction of CeO₂ surface oxygen, shifted towards lower temperature than the bare ceria (510 °C) due to the effect of Ni. The high-temperature zone is ascribed to CeO₂ bulk oxygen reduction, which does not seem affected by Ni presence [50,51]. The amount of hydrogen consumed by NiO species at 287, 370 and 450 °C, was 1.2 mmolH₂/g_{cat}, corresponding to a reduction degree of ca. 95%. However, a partial contribution due to the reduction of CeO₂ to Ce₃O₄ cannot be excluded. The catalyst containing both Rh and Ni exhibited a rearrangement of the reduction profile, with two main peaks at 126 °C and 378 °C, which can be ascribed to Rh₂O₃ and NiO reduction, respectively. Similar profile has been reported by Kugai et al. [51]. The degree of reduction of Rh₂O₃ and NiO species was 74 and 96%, respectively, but even in this case it is difficult to estimate the contribution of CeO₂ species reduction. Indeed, surface ceria reduction was facilitated, via hydrogen spillover, by the presence of Rh; hydrogen, after dissociation on metallic Rh, was able to spill over to CeO₂ and to reduce it at lower temperatures, as evidenced by Hou et al. [49].

According to the procedure described in the experimental section, catalyst powders were dispersed in the HGP liquid medium and their rheological behavior was assessed. Results are reported in Fig. 3. Ni/CeO₂ slurry displayed a lightly shear thinning behavior, with a viscosity value of 0.059 Pa s in the typical shear range for dip-coating applications (i.e. about 10 s⁻¹). The addition of rhodium induced some changes on rheological behavior: viscosity decreased down to 0.033 Pa s (at 10 s⁻¹) and the flow curve displayed a quasi-Newtonian behavior, especially at high shear rate values. These small differences could be due to the diverse volume fraction of the powder used for preparing the slurry; in particular, a lower volumetric fraction was used in the case of Ni-Rh/CeO₂ catalyst, due to the presence of heavier rhodium ions.

3.2. Support washcoating

Ni/CeO₂ and Ni-Rh/CeO₂ slurries were deposited on both ceramic monoliths and open cell foams, according to the procedure reported in Section 2.2. The main geometrical characteristics of bare supports are listed in Table 2. The characteristic sizes (d_p) are the channel inner size (monolith) and the pore diameter (foam) [52].

Monolith channel inner size (d_p) and wall thickness (t) were microscopically determined by using 30 different supports. Foam pore diameter (d_p) and strut thickness (t) were microscopically determined by using ca. 500 features of 30 different supports. Bed density was calculated by using bed weight and volume. Bed porosity was determined by helium pycnometry. The open frontal area (ε) of monolithic support was calculated from channel inner size (d_p) and wall thickness (t) by equation $\varepsilon = d_p^2 / (d_p + t)^2$ [53]. Foam open frontal area was calculated from the relative density (ρ_A/ρ_B) by the equation $\varepsilon = 1 - \rho_A/\rho_B = 1 - [2.59 \times (t/t + d_p)^2]$ [54]. Monolith geometric surface area (GSA) was calculated according to Cybulski and Moulijn [55], while the tetrakaidecahedron model of Buciuman and Kraushaar-Czarnetzki [56] was used for the foam.

Results in terms of washcoat load after flash drying as a function of dipping number are reported in Fig. 4a. A linear trend between coating load and dipping number was clearly manifest in both samples. From the observation of the load-dipping curves, also a good washcoat process reproducibility was detected: almost the same coating load was deposited after each dipping step. Washcoat load appears to be dependent on the complexity of the structured supports. As a matter of fact, honeycomb monoliths, that have straight and parallel channels, display always a lower washcoat load with respect to foams. Indeed, after two dippings, foam coating amount was almost twice the load of the monolith; this behavior can be ascribed to the surface area per unit volume (GSA), which is higher in ceramic foam than in monolith (Table 2). Not surprisingly, also the rheological behavior influences washcoat load: higher loads were obtained by using Ni/CeO₂ slurry, that is the sample with the highest slurry viscosity. These behaviors are better clarified in Fig. 4b, where the average load after two dippings is reported as a function of support geometry and catalytic formulation. Indeed, the final coating load can be managed with a multiple-dipping process up to the final load required for the application. In this case, the final washcoat of 15–20 wt.% was reached after 2–6 dipping steps, depending on the sample, or more precisely on the slurry rheological behavior, and on the support geometry. In addition, washcoat load was evaluated dividing coating mass by morphological support surface area. For both systems (i.e. MO and FO), washcoat load with respect to morphological support surface area unit was found to be ca. 0.06 g/cm². This is a first indication of the fact that, regardless structured support shape, similar washcoat layers thickness are expected. Fig. 5 shows the images of the structured systems obtained by means of optical microscope. In all cases, very good washcoat homogeneity was found. Honeycomb channels as well as foam pores were almost open and no pore clogging was detected. Therefore, the slurry was only deposited onto the external surface, as a “skin layer” of the geometrical support.

Adhesion tests results pointed out sufficiently good coated layers adhesion, with average losses of 25 wt.% and 18 wt.% for Ni/CeO₂ and Ni-Rh/CeO₂ samples respectively, in case of washcoat on foam supports. Better results were obtained for monolithic supports, that are characterized by losses lower than 10 wt.%. Weight losses are referred to washcoat load before and after the tests and they are in line with results obtained for other geometrical supports and similar washcoat compositions [29,37,38]. It has to be considered that ultrasound tests are particularly stronger if compared to the stresses experienced by washcoat inside a reactor [35,38].

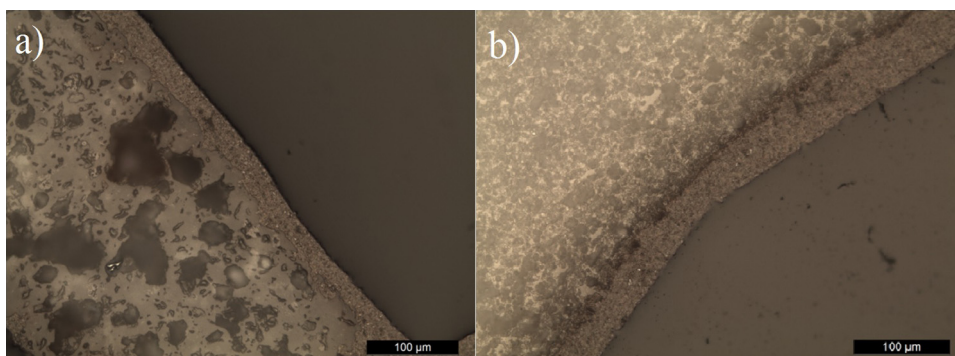


Fig. 6. SEM analysis of NiRh-MO (a) and NiRh-FO (b) coating thickness.

Table 3
Biogas SR activity results on Ni/CeO₂ and Ni-Rh/CeO₂ catalysts washcoated on monolith and foam at different temperature (700–800 °C) and space velocity (WSV = 250,000–350,000 Nml g_{cat}⁻¹ h⁻¹).

Catalyst	WSV (Nml g _{cat} ⁻¹ h ⁻¹)	T _{SET} (°C)	T _{IN} (°C)	T _{OUT} (°C)	χ _{CH4} (%)	χ _{CO2} (%)	H ₂ /CO	Products composition (%) [*]			
								CH ₄	CO ₂	H ₂	CO
Ni-MO	250,000	800	883	904	97.6	-3.0	3.13	0.53	14.63	64.28	20.56
	350,000	800	902	879	97.3	-4.4	3.18	0.59	14.96	64.24	20.21
NiRh-MO	250,000	800	801	822	99.9	-2.1	3.12	0.02	14.82	64.51	20.65
	350,000	800	804	822	99.9	-3.5	3.12	0.03	14.81	64.47	20.69
NiRh-FO	250,000	800	806	825	99.9	-1.9	3.06	0.03	14.58	64.38	21.01
	350,000	800	824	839	99.9	-1.4	3.08	0.02	14.65	64.41	20.92
Ni-MO	250,000	700	785	795	83.1	-29.0	4.14	3.90	19.29	61.86	14.95
	350,000	700	806	770	77.2	-27.1	4.13	5.59	20.23	59.72	14.46
NiRh-MO	250,000	700	712	729	96.7	-21.9	3.71	0.70	17.26	64.62	17.42
	350,000	700	716	723	92.3	-20.8	3.70	1.65	17.77	63.44	17.14
NiRh-FO	250,000	700	713	725	98.6	-19.1	3.60	0.29	16.90	64.81	18.00
	350,000	700	727	731	98.6	-19.3	3.63	0.30	16.93	64.91	17.86

^{*} Dry and N₂-free basis.

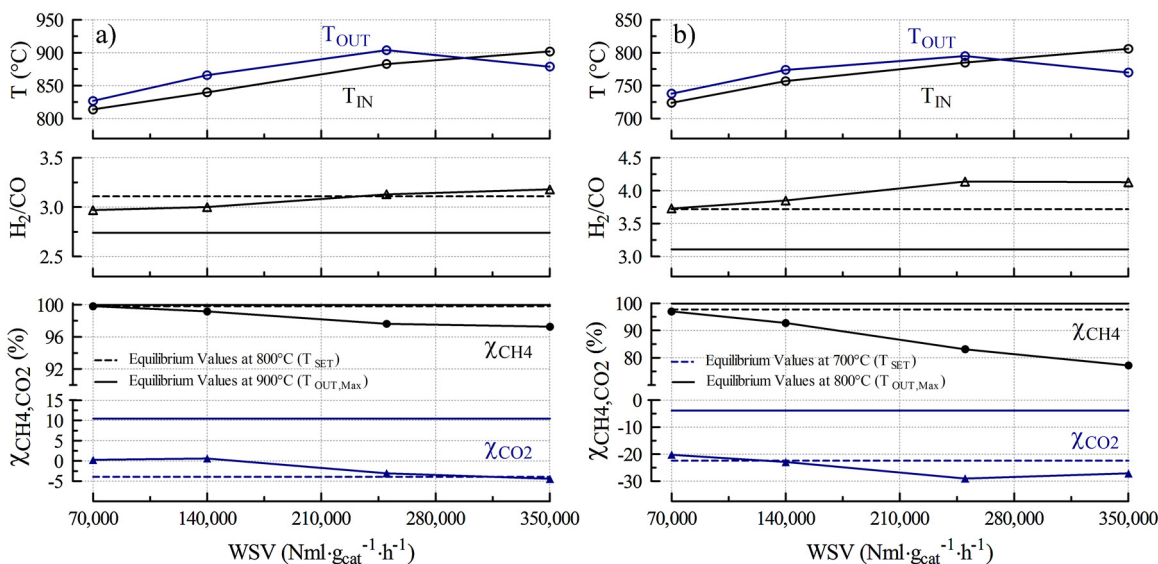


Fig. 7. Biogas SR activity results on Ni/CeO₂ catalyst washcoated on monolith: effect of space velocity (WSV = 70,000–350,000 Nml g_{cat}⁻¹ h⁻¹) at 800 (a) and 700 °C (b).

Coating thickness was evaluated by SEM measurements, resulting ca. 20–30 μm, as reported in Fig. 6 for NiRh-MO and NiRh-FO systems.

3.3. Activity tests

3.3.1. SR and OSR activity of Ni/CeO₂ on monoliths

Ni-MO catalyst performance was first evaluated in SR reaction of biogas at atmospheric pressure and H₂O/CH₄ ratio of 3. The effect

of weight space velocity (WSV = 70,000–350,000 Nml g_{cat}⁻¹ h⁻¹) at different temperatures (700–800 °C) was addressed and results are shown in Fig. 7 in terms of methane (χ_{CH4}) and carbon dioxide (χ_{CO2}) conversion and H₂/CO molar ratio. Recorded temperatures at the inlet (T_{IN}) and at the outlet (T_{OUT}) of the catalytic bed are also reported. At the WSV of 70,000 Nml g_{cat}⁻¹ h⁻¹, CH₄ conversion approached equilibrium values at both investigated temperatures (T_{SET}, 800–700 °C, at the center of the catalytic bed). CO₂ conversions were found to be slight higher than the equilibrium values

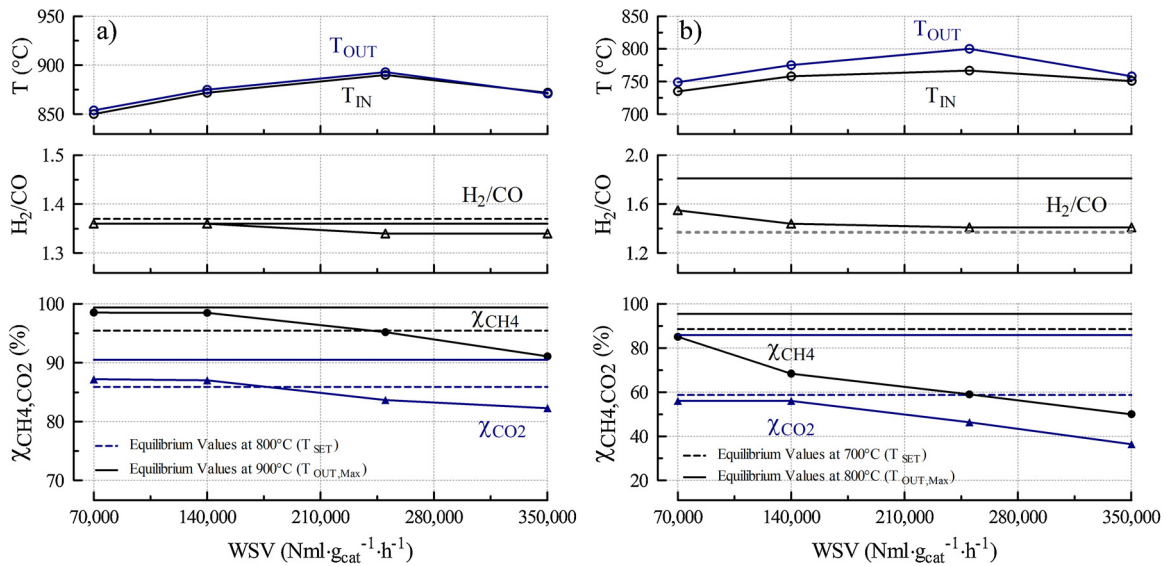


Fig. 8. Biogas OSR activity results on Ni/CeO₂ catalyst washcoated on monolith: effect of space velocity (WSV = 70,000–350,000 Nml g_{cat}⁻¹ h⁻¹) at 800 (a) and 700 °C (b).

Table 4

Biogas OSR activity results on Ni/CeO₂ and NiRh/CeO₂ catalysts washcoated on monolith and foam at different temperature (700–800 °C) and space velocity (WSV = 250,000–350,000 Nml g_{cat}⁻¹ h⁻¹).

Catalyst	WSV (Nml g _{cat} ⁻¹ h ⁻¹)	T _{SET} (°C)	T _{IN} (°C)	T _{OUT} (°C)	χ _{CH4} (%)	χ _{CO2} (%)	H ₂ /CO	Product composition (%) [*]			
								CH ₄	CO ₂	H ₂	CO
Ni-MO	250,000	800	890	893	95.2	83.7	1.34	1.24	3.11	54.80	40.85
	350,000	800	872	871	91.1	82.3	1.34	2.34	3.27	54.06	40.33
NiRh-MO	250,000	800	867	869	95.8	85.5	1.37	1.07	2.63	55.69	40.61
	350,000	800	872	873	92.1	83.6	1.37	2.06	3.01	54.89	40.04
NiRh-FO	250,000	800	846	848	96.8	87.3	1.36	0.83	2.27	55.88	41.02
	350,000	800	864	864	94.7	84.2	1.37	1.38	2.91	55.41	40.30
Ni-MO	250,000	700	800	767	59.0	46.4	1.43	14.73	12.54	42.81	29.92
	350,000	700	758	751	50.0	36.4	1.41	19.49	16.29	37.58	26.64
NiRh-MO	250,000	700	753	742	73.3	61.7	1.34	7.99	8.29	47.95	35.77
	350,000	700	770	748	65.4	55.3	1.34	11.12	10.13	45.12	33.63
NiRh-FO	250,000	700	738	726	77.4	66.9	1.36	6.74	6.83	49.85	36.58
	350,000	700	749	726	69.0	56.4	1.35	9.90	9.80	46.19	34.11

^{*} Dry and N₂-free basis.

calculated at reaction temperatures. This could be due to the measured T_{IN} and T_{OUT} that were always higher than T_{SET} and that were probably affected by the heat transferred from the furnace to the catalytic bed, which supports the endothermic steam reforming reaction [20,34,35]. Increasing the WSV, catalytic performances decreased as was expected, in terms of both CH₄ (from 99.8 to 97.3 at 800 °C) and CO₂ conversion. The decrease in catalytic activity was more pronounced at low temperature (700 °C), where methane conversion decreased from 97.0 to 77.2%. Moreover, CO₂ was produced by SR and water gas shift (WGS) reactions, that are both favored by the high steam content in the reactants stream (S/C = 3.0), resulting in low CO₂ conversion [57].

Fig. 8 shows the effect of WSV at 800 (Fig. 8a) and 700 °C (Fig. 8b) on Ni-MO catalytic activity towards the OSR reaction. A reactant mixture poor in steam and oxygen (S/C and O₂/C molar ratios equal to 0.3 and 0.1, respectively) was selected for OSR experiments. Thus, a prevalence of methane dry reforming with respect to steam and partial/total oxidation of methane can be predicted. At 800 °C (Fig. 8a), Ni-MO catalysts showed almost constant catalytic activity in all the investigated WSV range, leading to CH₄ and CO₂ conversion of 98.5 and 87.2%, respectively, at WSV of 70,000 Nml g_{cat}⁻¹ h⁻¹. However, a slight decrease down to 91.1% (CH₄ conversion) and 82.3% (CO₂ conversion) was evidenced at high space velocity. An almost constant H₂/CO molar ratio (1.34–1.36) was also recorded. At 700 °C (Fig. 8b), catalytic activity rapidly

decreased with increasing space velocity: CH₄ and CO₂ conversions were 50.0 and 36.4, respectively, at WSV of 350,000 Nml g_{cat}⁻¹ h⁻¹. In addition, H₂/CO molar ratio (1.41–1.55) was always lower than equilibrium values calculated at T_{SET} of 700 °C, probably due to the higher T_{IN} and T_{OUT}. Moreover, the occurrence of reverse water gas shift reaction (RWGS) cannot be excluded [58].

It is widely reported [59,60] that syngas production by reforming reactions in presence of oxygen proceeds by a two steps path:

- (i) methane combustion that produces H₂O and CO₂, followed by
- (ii) methane reforming reactions (with H₂O and CO₂) that produce syngas. Besides, in the first part of the catalytic bed, partial oxidation of nickel species (with high activity for combustion reaction) occurs [61]. After total oxygen oxidation, in the second part of the bed reforming reactions prevail. The good balance between the oxidation-reforming zones determines catalyst reforming activity. The occurrence of oxidation zone could be confirmed by the high temperature that was recorded as T_{IN}, while the high recorded temperature at the exit of the catalytic bed (T_{OUT}) is due to the heat provided by the furnace for supporting endothermic steam and dry reforming reactions [34, 59, 60].

3.3.2. Effect of catalytic formulation and support geometry on the SR and OSR activity

The catalytic activity of Ni-MO, NiRh-MO and NiRh-FO systems was investigated towards biogas SR (Table 3) and OSR (Table 4), at

different temperatures (700–800 °C) and weight space velocities (WSV = 250,000–350,000 Nml g_{cat}⁻¹ h⁻¹). The comparative analysis of catalytic performance in biogas SR and OSR gave information about catalytic formulation effect on activity. NiRh-based catalyst showed slightly better performance than Ni-based catalyst, especially at low temperatures. This was due to (i) the higher loading of active ingredients in the catalytic formulation and (ii) Rh promoter effect, as reported by several authors [9,21,22].

Meanwhile, from the point of view of catalyst geometry, both monolith and foam are promising for efficient structured catalysts manufacturing for biogas reforming into syngas. Catalytic activity tests showed that foam structured catalysts allowed higher activity with respect to honeycomb structured catalysts. As reported by Ciambelli et al. [29], the random porous network of a foam catalyst carrier may determine an improvement in gas temperature profile and species diffusion. Therefore, the higher performance of Ni–Rh-foam structured system as compared with the same active component on monolith could be explained by the presence of a more efficient mass transfer, making the catalytic phase more accessible to reagents.

4. Conclusions

In this work, structured ceramic honeycomb monolith and open cell foam were employed as Ni(7.5 wt.)/CeO₂ and Ni(7.5 wt.)/Rh(0.5 wt.)/CeO₂ catalysts support for biogas steam reforming and oxy-steam reforming reactions. Catalytic powders (previously prepared by solution combustion synthesis) were washcoated by means of support dip-coating into acid-free catalyst dispersion. A catalysts comparative analysis was reported on the basis of their performance in different operating conditions (reactants mixture composition, temperature and space velocity), highlighting the effect of catalytic formulation and support geometry on activity towards reforming processes.

Coating load was controlled by multiple depositions depending on the sample, or, more precisely, on slurry rheological behavior and on support geometry. Homogeneous and well adherent layers of ca. 20–30 μm were found.

Good catalytic activity was obtained on Ni/CeO₂-based structured catalysts, but it decreased with increasing space velocity. NiRh-based catalysts showed slightly better performance than Ni-based systems, especially at low temperatures and high space velocity, mainly due to Rh promoter effect. Regarding the catalyst geometry, both monolith and foam were found to be promising for efficient structured catalysts manufacturing for biogas reforming into syngas. The higher performance of foam supported Ni-Rh catalyst was explained by more efficient heat and mass transfer phenomena, due to the random porous network of foam support.

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