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Research paper

Ni/CeO$_2$-thin ceramic layer depositions on ceramic monoliths for syngas production by Oxy Steam Reforming of biogas

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ABSTRACT

Ni-CeO$_2$ catalysts (metals load equal to 7.5 wt.%) as thin oxide layers on ceramic monoliths have been obtained by support dip-coating into acid-free stable catalyst dispersion. Ni-based catalysts were prepared by precipitation-dry-impregnation method or solution combustion synthesis and characterized by XRD, BET, CO-Chemisorption, TPR, TEM and SEM-EDX techniques.

Coating load (15–20 wt.%) was controlled by multiple depositions on the basis of the slurry rheological behavior. Procedure goodness was evaluated in terms of coating load and adhesion performance. Homogeneous and well adherent layers of ca. 10–20 μm were found. The performance of final structured systems was evaluated towards biogas oxy-steam reforming (OSR) reaction, highlighting the influence of morphological and structural properties of synthesized Ni-based powders on the catalytic activity. Catalytic tests demonstrated superior performances of solution combustion synthesized Ni/CeO$_2$ catalyst washcoated on monolith, especially at high space velocity.

1. Introduction

Hydrogen is expected to be one of the main clean energy carrier in the 21st century [1–3]. At present, the commercial production of hydrogen is mostly based on steam reforming of fossil fuels, primarily natural gas [4,5]. However, from the standpoint of fossil fuels limitations and global climate changes, alternative ways are under investigation in order to replace fossil hydrocarbons with renewable sources. In this contest, biogas represents a clean and environment friendly fuel that is typically generated from anaerobic degradation of biomass [6–8]. Moreover, hydrogen production from biogas is expected to promote the recycling process in society [5,9,10].

Among the various biogas reforming options, the Oxy Steam Reforming (OSR) process, which consists in a combination of Dry Reforming (DR), Steam Reforming (SR) and Partial Oxidation (CPO) of methane in a single step, appears to be a valuable route [11,12]. The presence of steam promotes SR and water gas shift (WGS) reactions, limiting the problem of carbon deposition which occurs in DR reaction. Besides, the addition of O$_2$ compensates the endothermic reforming reactions, reducing significantly energy requirements by the endothermic process (DR and SR) [2,12]. Moreover, OSR process offers several advantages compared to other reforming alternatives: small unit size, lower energy requirements, lower operational temperature, easier start-up, and a wider choice of materials, coupled with the possibility to regulate the H$_2$/CO molar ratio by changing the inlet gas composition [13,14].

Ni-based systems have been widely investigated by many researchers, showing good catalytic performances towards the reforming processes [15–19]. Nevertheless, catalytic activities gradually decrease as a result of carbon deposition and sintering of active metals. A key issue for successful application of Ni-based catalysts consists in the solving the deactivation phenomenon [15,20]. 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 [21–23]. In addition, the adopted preparation method affects the morphology of synthesized catalysts (namely crystallinity, homogeneity and particle size), determining, in turn, catalytic activity and stability towards reforming processes [2,24].

Structured catalysts and reactors for process intensification have received large interest due to their peculiar characteristics, including high geometric surface area and small pressure drop [5,25]. Structured systems with active components supported on different configurations (foams, honeycombs, gauze, microchannels) demonstrated many advantages, providing an efficient heat and mass transfer compared to conventional packed bed reactors [26]. In particular, monoliths have been proposed for hydrogen production processes from biogas [25,27,28]. One of the most critical issues for the fabrication of structured catalytic beds is the deposition of suitable active layers on the carrier, capable to withstand critical reaction conditions (oxidative environment,

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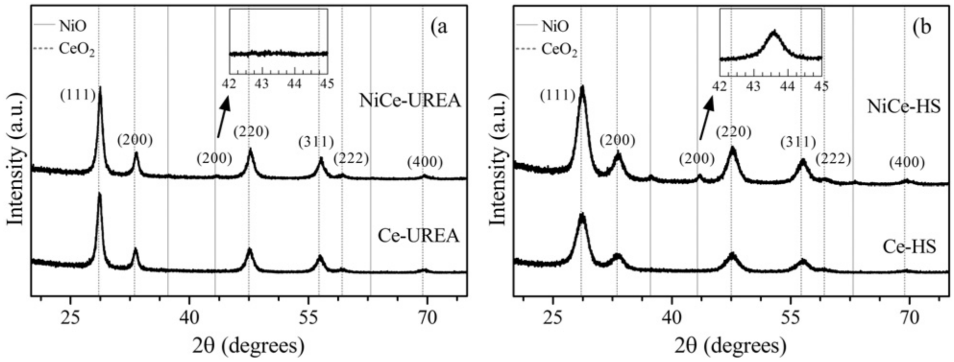

Fig. 1. Catalyst powder XRD analysis: precipitation/dry impregnation (a) and solution combustion synthesis (b).

high temperature) and, in some cases, mechanical vibrations. Among different deposition methods, dip-coating into a solution or a dispersion is widely considered the best procedure in order to washcoat geometrical supports [29–33], constituting the best compromise among costs, time and efficiency [34].

The dip-coating process is based on the immersion of the morphological substrate into a liquid phase, which contains the catalytic active phase precursor. Once substrates void are filled, the withdrawing process allows to create an homogeneous film on support surface, thanks to the balance between the gravitational force, which attract the film downward, and the viscous force which hinders its sliding [35,36]. On these basis, rheological behavior and withdrawal speed are the most important parameters in order to properly control coating layer formation [37]. 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. As a matter of fact, low viscosity slurries usually lead to low loads and high adhesion, while high viscosity formulations promote high washcoat load but poor adhesion [36,37]. Dispersion stabilization and rheological properties are the major concerns in slurry coating. Usually, acidic solutions are used in order to obtain stable dispersions. Powder surface is covered by H^+ ions and, thus, stability is achieved by surface charging [37]. Unfortunately, this method is not effective both in case of low surface area and chemically inert powders. Moreover, some active phases or supports may be altered in case of acidic solution [38]. For these reasons, organic compounds have been investigated as alternative dispersants [39].

In this work, new Ni-based structured catalysts were prepared for the production of syngas by reforming processes. Ceramic monoliths were used as structured supports (500 cpsi, diameter 1 cm, length 1.5 cm), in which Ni/CeO_2 (metals load equal to 7.5 wt.%) catalyst was deposited by support dip-coating into acid-free stable catalyst dispersion. Powder dispersion stabilization was achieved by means of a novel organic bases solution, which was obtained by mixing water, glycerol and polyvinyl alcohol. The latter formulation was used as alternative dispersion medium with respect to the commonly used acidic solutions. Ni/CeO_2 catalysts were prepared using two different preparation methods (i.e. the two-steps precipitation-dry-impregnation method and the single-step combustion synthesis) and characterized by XRD, BET, CO-Chemisorption, TPR, TEM and SEM techniques. Washcoating quality was evaluated in terms of coating load and adhesion performance. Therefore, the performance of the final structured systems was evaluated towards the biogas oxy-steam reforming (OSR) reaction.

Table 1
Main textural and structural properties of synthesized catalysts.

Sample	BET Surface area (m^2/g)	X-ray			Metal dispersion[b] (%)	Ni Particle size[c] (nm)
		CeO_2 size[a] (nm)	CeO_2 lattice parameter[a] (Å)	NiO size[a] (nm)		
Ce-HS	90	4.8	5.410	–	–	–
NiCe-HS	80	5.5	5.409	15.2	1.0	30–60
Ce-UREA	14	11.4	5.394	–	–	–
NiCe-UREA	10	11.3	5.380	–	2.2	3–5

[a] Calculated from X-ray diffraction: CeO_2 crystallite size from Scherrer's equation of CeO_2 (111) reflection; Lattice parameter (α) from relation $\alpha = \sqrt{h^2 \cdot k^2 \cdot l^2} \cdot (\lambda/2 \cdot \sin\theta)$.
[b] Determined by CO-pulse chemisorption.
[c] Determined by TEM analysis.

2. Experimental

2.1. Catalyst preparation

Catalyst powders were produced according to two different preparation routes, namely the combined precipitation-dry-impregnation process and the solution combustion synthesis. In both cases a Ni content of 7.5 wt.% was fixed. Ni content in the catalytic powder was confirmed by chemical analysis (ICP/OES).

2.1.1. Precipitation-dry-impregnation

It is a double steps process where the support is first obtained via precipitation reaction and then it is impregnated by incipient wetness technique with a precursor of Ni active phase. A conventional precipitation procedure was applied to obtain the Ce-based support [40]. Accordingly, $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich) was dissolved in water (1 M) and CeO_2 was precipitated by adding a $(NH_4)_2CO_3$ (Sigma-Aldrich) water solution (2.6 M) under magnetic stirring at room temperature. The obtained slurry was filtered and the solid was washed until neutral pH. The resulting solid (reported as Ce-HS) was dried at 120 °C overnight and finally calcinated at 500 °C for 3 h (2 °C min^{-1} of heating rate). Incipient wetness technique [41] was applied to obtain the final Ni-based catalyst (reported as NiCe-HS). $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich) was used as precursor for the metal active phase. The impregnated powder was dried overnight at 120 °C and subsequently it was fired at 500 °C for 10 h (2 °C min^{-1} of heating rate). All the heat treatments were carried out in air.

2.1.2. Solution combustion synthesis

In a typical experiment, stoichiometric amount of Ni precursor ($Ni(NO_3)_2 \cdot 6H_2O$ from Sigma Aldrich) and Ce precursor ($Ce(NO_3)_3 \cdot 6H_2O$ from Alfa Aesar) were dissolved in the minimum quantity of distilled water (~100 ml) with the suitable quantity of fuel (CH_4N_2O, urea from Sigma Aldrich) [24]. The amount of fuel was determined by the so-called fuel-to-oxidant ratio and calculated using the total oxidizing (O) and reducing (F) valencies of the components in order to have an equivalence ratio equal to one ($\phi = O{:}F = 1$), corresponding to a maximum release of energy. The obtained solution was introduced into a