Ammonia decomposition over 3D-printed CeO₂ structures loaded with Ni

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Abstract

Binder-free ceria pastes have been formulated and used to prepare ceria structures with a woodpile arrangement of microchannels through 3D printing. After loading them with nickel, these catalytic structures have been tested for ammonia decomposition to obtain hydrogen, and their performance has been compared with those of conventional Ni/CeO₂ powder catalysts and with that of a conventional cordierite honeycomb washcoated with Ni/CeO₂. Samples have been characterized by N₂ physisorption, inductively coupled plasma optical emission spectrometry (ICP-OES), X-Ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy. At the same reaction temperature and flow rate to catalyst weight ratio (F/W), the 3D-printed ceria structures show a catalytic activity much higher than that of the cordierite honeycomb on a reactor volume basis. Additive manufacturing represents a valuable tool to prepare customized ceria-based catalytic structures for practical application with a variety of geometries not attainable with conventional methods.

Key words: 3D printing, additive manufacturing, ceria-based catalysts, nickel-ceria, ammonia decomposition.

1. Introduction

Three-dimensional (3D) printing by robocasting is an additive manufacturing technique in which the desired material is extruded and sequentially deposited in layers to form a three-dimensional object. The advantages of this fabrication method are the high flexibility of materials and shapes, the precise control of the features of the printed object and the low

cost of the set-up [1-3]. Nowadays, 3D printing is considered a powerful technology for the fabrication of structures used in a high number of different applications as in medicine [4], space exploration [5], pharmacy [6], electronics [7] and industry [8], among others. For catalysis, 3D printing techniques have been used for different purposes: to print catalytic reactors [9], to print catalysts on substrates [10], to print molds for catalytic honeycombs [11], to print substrates to support catalysts [12], or to print honeycombs and microchanneled structures made entirely of the desired catalyst [13-18]. The 3D-printed structure can be coated with another catalytic component or used directly as-printed [19,20]. In the robocasting method, a model is first created through computer-aided design (CAD) and sliced into cross-sectional layers, which are printed from a paste by extrusion through a nozzle of diameter between, typically, 100 and 2000 μm . Then, the as-prepared structure is dried and sintered to produce the final object [21,22]. The sintering of the printed structure is needed to eliminate possible organic binders used in the paste formulation and to enhance the mechanical strength of the object. This is usually attained by temperature treatments at about 1000 $^{\circ}\text{C}$, or even higher. However, for catalysis purposes, thermal sintering should be avoided to maintain high porosity and exposed surface area of the resulting catalytic structure. In this work, we have developed a binder-free ceria paste formulation and a chemical sintering method in a way that a calcination temperature of only 500 $^{\circ}\text{C}$ is required to create the final solid structure. We have recently reported a similar approach for the preparation of 3D-printed titania structures for photocatalytic applications [23].

Ceria is a well-known catalyst or catalyst component in many applications due to its particular redox properties, oxygen storage, and its capacity to disperse metal nanoparticles and prevent metal sintering through robust metal-support interactions [24-27]. Therefore, the possibility of using 3D-printed ceria structures as catalytic support is appealing because additive manufacturing provides with additional design parameters (i.e. 3D channeling and

channeling with variable cross-section) that, for instance, conventional honeycomb structures cannot afford. Based on our previous results with ceria-based catalysts for the decomposition of ammonia to yield hydrogen, $2\text{NH}_{3(g)} \rightleftharpoons \text{N}_{2(g)} + 3\text{H}_{2(g)}$ [28], here we have prepared for the first time 3D-printed ceria structures, impregnated them with Ni, and compared their catalytic performance in the ammonia decomposition with those of powder catalysts as well as that of a conventional cordierite honeycomb washcoated with Ni/CeO₂.

Ammonia is nowadays considered as an interesting alternative to direct hydrogen storage because it liquefies at low pressure (8.6 bar at 20°C), so its transport and storage is much easier than that of hydrogen [29]. Ammonia has higher hydrogen content (17.8% by weight and a volumetric density of 121 kg H₂ m⁻³ at 10 bar) than other chemicals that can be used to produce hydrogen on-site, such as metal hydrides, hydrocarbons or alcohols. On a volume basis, ammonia has a volumetric energy density of 13.6 GJ m⁻³, a value that falls between those of hydrogen and gasoline [30-32]. With respect to safety concerns, ammonia has a narrow combustion range of only 16-25% in air, while for hydrogen it is of 4-75%. Furthermore, ammonia concentrations higher than 5 ppm can be detected simply by smell [33]. A considerable number of works have been published in recent literature related to catalytic ammonia decomposition to obtain hydrogen [34-55]. Ruthenium has shown to be the most active metal for this reaction [34-39]. Ganley *et al.* tested different metals supported on Al₂O₃ pellets and their activity followed the trend Ru>Ni>Rh>Co>Ir>Fe>Pt>Cr>Pd>Cu [40]. Liu *et al.* studied various metals supported on SiO₂ using high throughput techniques and the performance of the most active metals followed a similar trend: Ru>Ni>Co>Ir>Ag [41]. Ceria has been used as a promoter in silica-supported Ni [42], alumina supported Ni [43] and Co-Mo supported on carbon nanotubes [44]. Nickel has demonstrated to be a valid option due to its low cost compared to ruthenium and good ammonia conversion [35]. To increase its catalytic activity, several bimetallic compositions containing Ni have been

studied, but with limited success: Ni-Ir [45], Ni-Pt [46], Ni-Mo [47,48], Ni-Pd [49] and Ni-Fe [50]. Nickel has been used supported on silica, alumina, manganese oxide and in a few cases on carbon substrates, including graphene [42,51-54]. The highest ammonia conversion has been achieved when Ni is supported on aluminum oxide and ceria as a promoter [42], and good stability has been obtained by adding La to the alumina support [51]. In our recent work, we have demonstrated the excellent performance of ceria as a support for ammonia decomposition in Ni/CeO₂ catalyst [28] in terms of catalytic activity and stability with respect to Ni/Al₂O₃. Regarding reactor engineering for the decomposition of ammonia, several approaches have been reported, being catalytic honeycomb reactors, microreactors and membrane reactors those showing the best results [34,55]. In general, catalytic honeycomb reactors have several advantages, such as low pressure drop, high geometric surface area and good mass transfer properties [56–59]. Recently, different catalytic structures have been prepared by 3D-printing in order to modulate geometric characteristics [60] and have been used in various processes to produce hydrogen [61-64], but no ceria honeycombs prepared by additive manufacturing and no 3D-printed structures for ammonia decomposition have been reported so far in the literature.

2. Materials and methods

2.1 Preparation of Ni/CeO₂ powder catalysts

Two different ceria supports were prepared with different particle size, which are named as polycrystalline CeO₂ and nanopolycrystalline CeO₂. Polycrystalline CeO₂ (Ce-p) was prepared by adding a 40 mL solution of 28 vol%. NH₄OH (*Scharlab*) dropwise to a magnetically stirred solution of 12.61 g of Ce(NO₃)₃·6H₂O (*Alfa Aesar*) in 300 mL of distilled water, until the pH reached a value between 9 and 10. The precipitate was filtered, washed with water (three times), dried at 100 °C for 24 h and calcined at 500 °C for 4 hours (5 °C

min⁻¹). Nanopolycrystalline CeO₂ (Ce-np) was prepared using an ultrasonic atomizer (*Sonozap HTWS30*) and a hydrothermal reactor (*Reactor Chemipress-500*) by following the procedure described in [65]. A solution of 6.07 g of Ce(NO₃)₃·6H₂O (*Alfa Aesar*) in 35 mL of distilled water was atomized over a stirred solution of 2.00 g of NaOH (*Fisher Scientific*) in 245 mL of distilled water at 400-500 rpm. The resulting suspension was stirred for 30 minutes at room temperature and introduced in a Teflon-lined hydrothermal reactor, which was heated at 150 °C for 24 hours. The resulting material was centrifuged (15 min at 10,000 rpm), sonicated and cleaned with distilled water (three times) and ethanol (twice) until a neutral pH was obtained. The solid was dried at 70 °C for 24 h and calcined at 500 °C for 4 hours (2 °C min⁻¹). The CeO₂ powder supports (Ce-p and Ce-np) were impregnated using the incipient wetness (IW) impregnation method from a 0.3 M aqueous solution of Ni(CH₃COO)₂·4H₂O (*Probus*). After impregnation, catalysts were dried at 100 °C for 24 h and calcined at 450 °C for 4 h (5 °C min⁻¹). They were labeled as Ni-Ce-p and Ni-Ce-np, respectively. The nominal Ni content was fixed at 10 wt.%.

2.2 Preparation of 3D-printed CeO₂ and Ni/CeO₂ structures

4.5 g of CeO₂ powder were added to a 1.5 mL solution of 70 vol%. nitric acid (*Fisher Scientific*) and 1 mL of distilled water (pH of -0.9). The mixture was stirred at 300 rpm and heated at 100 °C for 1 min. The as-prepared paste (labeled as Ce-p-PASTE and Ce-np-PASTE according to the precursor) had a viscosity of 4500 Pa s at 20 °C under a shear rate of 0.1 s⁻¹. A modified 3D printer (*BCN3D+*) with a horizontal and vertical positioning accuracy of ±50 and ±100 μm, respectively, was used for the production of the 3D structures. Polypropylene syringes and 580 μm diameter tips were used. The maximum force exerted by the paste extruder was 125 N. Structure designs were carried out with a CAD software, which was used to create G-Code files with the Symplify3D slicing software package. The printed cylindrical ceria structures had a diameter of 20 mm, a height of 8 mm and a filling

of 50% defined by a woodpile arrangement of ceria filaments, which resulted in cylindrical structures of 52 channels. The as-printed ceria structures were dried at ambient conditions and subsequently dried in a furnace using three consecutive heating ramps: 60 °C for 3 h, 90 °C for 3 h and 110 °C for 3 h (0.5 °C min⁻¹). Finally, the structures were calcined at 500 °C for 4 h (2 °C min⁻¹). These samples are labeled as Ce-p-3D and Ce-np-3D according to the starting ceria powder used (Ce-p or Ce-np). After the drying and calcination processes, a shrinkage of the structures was observed, with final dimensions of ca. 14 mm in diameter and 6 mm in height, and the final number of channels was 32. Ni was deposited on the ceria 3D structures by impregnation from a 1 M Ni(CH₃COO)₂·4H₂O (*Probus*) ethanolic solution (2.5 g of ceria in 2 mL). The impregnation method consisted in immersing the ceria structures for 2 hours in the nickel solution. The catalytic structures were dried for two days at ambient conditions, dried at 70 °C for 24 h (2 °C min⁻¹) and calcined at 450 °C for 4 h (2 °C min⁻¹). The concentration of the nickel solution was adjusted to obtain a Ni/Ce surface ratio in the 3D-printed structures similar to that of the powder catalysts, as determined by XPS (see section 3.1).

2.3 Preparation of a cordierite honeycomb coated with Ni/CeO₂

A cordierite honeycomb with square channels and a cell density of 400 cpsi (*Corning Celcor LFA 400/4*) was shaped to have exactly the same dimensions as those of the calcined 3D-printed ceria structures (14 mm in diameter and 6 mm in height). The resulting number of square channels was 88. The Ni/CeO₂ (Ni-Ce-p) catalyst powder was deposited on the cordierite honeycomb by the washcoating method. Briefly, the cordierite substrate was soaked in a suspension containing 0.6 g of Ni-Ce-p in 10 mL of distilled water. The excess liquid was blown away with N₂ and the honeycomb was dried at 120 °C for 10 min in a rotating furnace and calcined at 400 °C for 1 h (10 °C min⁻¹). The washcoating method above

described was repeated several times to load the cordierite substrate with the desired amount of catalyst (0.1 g). This sample was labeled as Ni-Ce-p-CORD.

2.4 Catalyst characterization

Powder X-ray Diffraction (XRD) patterns were recorded with a Siemens D5000 diffractometer using Cu K α radiation (45 kV, 35 mA) in Bragg-Brentano geometry. The diffraction patterns were recorded in steps of 0.02° at 1 s per step. The Debye-Scherrer equation was used to measure the crystallite size. Nitrogen adsorption isotherms were performed at 77 K using a Micromeritics ASAP2020 gas adsorption instrument. The materials were degassed at 500 °C for 10 h prior to the adsorption experiments. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method. Scanning Electron Microscopy (SEM) images were recorded at 5 kV using a Zeiss Neon40 Crossbeam Station instrument equipped with a field emission source. The average particle diameter was calculated from the mean diameter frequency distribution with the formula $d = \sum n_i d_i / \sum n_i$, where n_i is the number of particles with particle diameter d_i in a certain range. High resolution transmission electron microscopy (HRTEM) was carried out with a FEI TECNAI F20 S/TEM instrument equipped with a field emission electron source operated at 200 kV. Samples were prepared by dispersing the catalysts in methanol; a drop of the suspension was then allowed to evaporate on a lacey carbon copper grid. Characterization of the surface was done by X-ray Photoelectron Spectroscopy (XPS) on a SPECS system equipped with a XR50 source operating at 250 W and a Phoibos 150 MCD-9 detector. The pass energy of the hemispherical analyzer was set at 20 eV and the energy step of high-resolution spectra was set at 0.05 eV. The pressure in the analysis chamber was always below 10⁻⁷ Pa. Binding energy (BE) values were referred to the adventitious C 1s peak at 284.8 eV. Data processing was performed with the CasaXPS software. Atomic fractions were calculated using peak areas normalized on the basis of acquisition parameters after background subtraction,

experimental sensitivity factors and transmission factors provided by the manufacturer. Cerium 3d spectra were deconvoluted using six peaks for Ce^{4+} (V, V'', V''', U, U'' and U'''), corresponding to three pairs of spin-orbit doublets, and four peaks (two doublets) for Ce^{3+} (V_0 , V' , U_0 and U'), based on the peak positions reported by Mullins et al. [66], where U and V refer to the $3d_{3/2}$ and $3d_{5/2}$ spin-orbit components, respectively. Nickel 2p spectra were deconvoluted using four peaks and four satellites for Ni^{2+} , corresponding to two pairs of spin-orbit doublets, and two peaks and two satellites for Ni^{3+} [67-70]. Characterization by micro-Raman spectroscopy was carried out using a Renishaw inVia Qontor confocal Raman microscope equipped with a 532.1 ± 0.3 nm laser with a nominal 100 mW output power directed through a specially adapted Leica DM2700 M microscope (x50 magnification). Spectra were acquired in the range $100\text{-}1350\text{ cm}^{-1}$ with an exposure time of 1 s, 1% of laser maximum power and 12 repetitions. Fourier-transform Infrared Spectroscopy (FTIR) was performed with a Nicolet 6700 instrument equipped with a CsI detector. The Ni content of the samples was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) using a Perkin Elmer Optima 3200RL instrument.

2.5 Catalytic tests

The ammonia decomposition reaction was carried out at atmospheric pressure in 316-grade stainless steel tubular reactors with an outer diameter (OD) of 1/4" (powder catalysts) or 5/8" (cordierite honeycomb and 3D-printed structures). The mass of the powder catalysts was 0.1 g, which was diluted with SiC to obtain a fixed bed volume of 0.5 cm^3 . The reactors were placed inside a vertical furnace connected to an external thermal control system to regulate the temperature of the reactor within $\pm 0.1\text{ }^\circ\text{C}$. The reactor effluent was analyzed on-line with a mass spectrometer (OmniStar GSD320 O2). In this study, an uncertainty of $\pm 5\%$ in the mass spectrometer results was considered. The reaction tests of the temperature-dependent catalytic activity were conducted using a total gas flow of 25 mL min^{-1} and an

Ar:NH₃ ratio of 1.3:1 (molar basis) between 350 and 600 °C at steps of 50 °C (30 min at each temperature). Stability tests were conducted for 100 h at 450 °C (25 mL min⁻¹, Ar:NH₃=1.3:1 molar basis). Catalytic tests under different F/W values were carried out at 500 °C maintaining a constant Ar:NH₃ ratio of 1.3:1 (molar basis) using different total gas flows: 25, 50, 75 and 85 ml min⁻¹. The catalysts reached fast steady-state regime under all reaction conditions. The TOF values were calculated at 500 °C under differential conditions using a gaseous mixture of Ar:NH₃=1.3:1 and F/W values of 257-543 L h⁻¹ g_{Ni}⁻¹. Catalysts were activated at 300 °C for 1 h with 10% H₂ in Ar (80 mL min⁻¹, 10 °C min⁻¹). Ammonia conversion, NH₃ conv, is defined by equation 1, where $\dot{Q}$ is the molar flow rate of ammonia (mol NH₃ s⁻¹).

$$\text{NH}_3 \text{ conv} = \frac{\dot{Q} \text{NH}_3 \text{ initial} - \dot{Q} \text{NH}_3 \text{ final}}{\dot{Q} \text{NH}_3 \text{ initial}} \times 100 \quad (\text{eq. 1})$$

3. Results and discussion

3.1 Characterization

Figure 1 illustrates representative SEM images of Ce-np (A), Ni-Ce-np (B), Ce-p (C), and Ni-Ce-p (D) powders. Both Ce-p and Ce-np supports showed a cluster-of-grape morphology with rounded ceria particles with an average size of 10 and 6 nm, respectively. The BET surface areas of both of them were in the range 70-80 m² g⁻¹. The analysis by SEM of the corresponding Ni/CeO₂ samples confirmed that the morphology and size of the ceria particles remained unaltered with respect to those of the bare supports. Figure 2 shows SEM images of the cordierite honeycomb loaded with the Ni-Ce-p catalyst. As expected from the washcoating method, the surface of the cordierite channels was homogeneously covered by catalyst particles and their size was preserved at about 10 nm.

Figure 1. SEM images of Ce-np (A), Ni-Ce-np (B), Ce-p (C) and Ni-Ce-p (D) and ceria particle size histograms.

Figure 2. SEM images of Ni-Ce-p-CORD (A,B).

Figure 3 shows photographs of the 3D-printed structures as-prepared (A,B) and after loading with Ni (C,D). In all cases the 3D-printed structures showed well-developed geometries and a homogeneous appearance, as deduced also from the SEM images recorded with secondary electrons (E) and with a combination of secondary and backscattered electrons (F). Although the geometry was not perfect, the resulting ceria filaments showed a mean diameter of 550 μm and the channels measured about 980 μm wide after calcination.

Several attempts to improve the geometry were carried out by changing the calcination temperature and calcination ramp, but they were unsuccessful.

Figure 3. Photographs of the Ce-p-3D (A,B) and Ni-Ce-p-3D (C,D) samples. SEM images of the Ni-Ce-p-3D catalytic structure recorded with secondary electrons (E) and with a combination of secondary and backscattered electrons (F).

The SEM images reported in Figure 4 correspond to the surface of the 3D-printed structures at high magnification. They are constituted by well-packed and notably homogeneous ceria particles. The size of the ceria particles in the 3D-printed structures increased with respect to the initial size in the powder samples, from approximately 10 nm in Ce-p to 20 nm in Ce-p-3D, and from 6 nm in Ce-np to 14 nm in Ce-np-3D. Therefore, it can be safely concluded that the sintering of the initial ceria particles was moderate during the 3D printing procedure and the post-processing of the catalytic structures. Moreover, SEM and HRTEM analyses of the post-reacted 3D catalytic structures (which were tested up to 600 °C, see section 3.2) showed that the average particle size of ceria remained unaltered. Regarding nickel, SEM did not allow for a proper evaluation of the Ni particle size. However, the absence of contrast

in the SEM images recorded with backscattered electrons suggested that Ni was well dispersed and below 5 nm. Ni particle size was determined by HRTEM and will be discussed in section 3.2.

Figure 4. SEM images of Ni-Ce-np-3D (A,B), and Ni-Ce-p (C,D) recorded with secondary electrons (A,C) and backscattered electrons (B,D) and ceria particle size histograms.

Samples Ce-p, dry Ce-p-PASTE and Ce-p-3D, which were obtained during the different steps in the preparation of the 3D-printed ceria structure Ce-p-3D, were studied by FTIR, Raman spectroscopy and XRD (Figures 5 and 6). The FTIR spectrum of the Ce-p sample is dominated by absorption bands at about 1523 and 1342 cm^{-1} (Figure 5), which correspond to surface carbonate species [71-75]. This is commonly observed as a result of the reaction of the surface basic sites of ceria with atmospheric CO_2 . The band due to the Ce-O stretching appears below 770 cm^{-1} in the FTIR spectrum [76] and it is not visible in the range studied, but in the Raman spectrum the intense peaks at 462, 600 and 1167 cm^{-1} (Figure 6A) are characteristic of the CeO_2 structure. Also, the XRD pattern of the Ce-p sample (Figure 6B) shows the characteristic diffraction peaks of fcc CeO_2 . In addition to the

carbonate bands, the FTIR spectrum of the dry Ce-p-PASTE (Figure 5) shows new bands at 1440, 1176 and 995 cm^{-1} , which are ascribed to the partial dissolution of ceria by the addition of nitric acid and the concomitant formation of surface cerium nitrate groups [77]. These surface nitrate groups likely act as linkers between adjacent ceria particles and originate the viscosity of the paste. Accordingly, cerium nitrate is also recognized in the Raman spectrum of the dry Ce-p-PASTE (Figure 6A) at 741, 1046 and 1300 cm^{-1} [78]. In addition to the nitrate bands, the presence of a broad band at about 3500 cm^{-1} accompanied by a well-defined band at 1631 cm^{-1} in the FTIR spectrum indicates the presence of adsorbed water and/or surface hydroxyl groups. However, both the Raman spectrum and the XRD pattern of the Ce-p-PASTE (Figure 6) show the bulk presence of ceria, which is a clear indication that dissolution of ceria particles only occurs at the surface. Finally, the FTIR and Raman spectra of the 3D-printed structure, Ce-p-3D, show the disappearance of the nitrate bands after calcination. On the other hand, the FTIR spectrum of Ce-p-3D shows, in addition to weak surface carbonate bands similar to the starting Ce-p powder, a prominent band at about 3400 cm^{-1} . This band is a clear indication of the presence of surface hydroxyl groups, which are likely formed from the partial surface dissolution of ceria by nitric acid followed by drying and calcination. This process (that we call “chemical sintering”) confers the necessary mechanical strength to the 3D-printed ceria structures, while keeping a low sintering, as can be deduced from the SEM analysis discussed above. As expected, the XRD pattern of Ce-p-3D shows the characteristic peaks of crystalline CeO_2 (Figure 6B) and, also in agreement with the SEM observations, the mean crystallite size determined by the Scherrer equation is about 20 nm.

Figure 5. FTIR spectra of powder Ce-p, dry Ce-p-PASTE and Ce-p-3D printed structure.

Figure 6. Raman spectra (A) and XRD patterns (B) of powder Ce-p, dry Ce-p-PASTE and Ce-p-3D printed structure.

Figure 7 shows the XRD patterns of the ceria powder samples before and after loading with Ni and those of the catalytic 3D-printed structures loaded with Ni. All the patterns show the characteristic peaks of the CeO₂ fcc phase. Additional peaks of NiO [79] are observed in the powder catalysts prepared by IW impregnation (9.4 wt.% Ni determined by ICP-OES). In the 3D-printed ceria structures, the peaks of NiO are not visible due to the low weight content of NiO with respect to CeO₂ (0.7 wt.% Ni determined by ICP-OES). Figure 8 shows the Raman spectra of the samples as well as the spectrum of unsupported NiO prepared following the same methodology. Given the surface/sub-surface sensitivity of Raman spectroscopy, now the presence of NiO in all of the Ni/CeO₂ samples (powder and 3D-printed) is seen at 411, 494, 539 and 1050 cm⁻¹ [80] in addition to the bands corresponding to ceria at 462, 600 and 1167 cm⁻¹ [81].

Figure 7. XRD patterns of the powder samples before (Ce-p and Ce-np) and after Ni loading (Ni-Ce-p and Ni-Ce- np) and the catalytic 3D-printed structures impregnated with Ni (Ni-Ce-p-3D and Ni-Ce-np-3D).

Figure 8. Raman spectra of NiO, Ni/CeO₂ powder catalysts and 3D-printed structures.

The Ce 3d and Ni 2p X-ray photoelectron spectra (XPS) of the Ni/CeO₂ samples (powders and 3D-printed) are shown in Figure 9 and the corresponding surface atomic ratios and Ni binding energy values are reported in Table 1. As explained in section 2.2, the impregnation conditions of the ceria 3D-printed structures with Ni were varied until their surface atomic composition was comparable to that of the powder catalysts to ensure a reliable comparison of the catalytic performance. As reported in Table 1, the amount of Ce(III) and the distribution of the Ni species in powder and 3D-printed samples were similar, around 20-30% of Ce(III) and about 80-90% of Ni(II). Also, similar binding energy values were recorded for Ni.

Figure 9. XPS spectra of the Ce 3d and Ni 2p regions of Ni-Ce-np (A), Ni-Ce-np-3D (B), Ni-Ce-p (C) and Ni-Ce-p-3D (D).

Table 1. XPS surface atomic composition and Ni binding energy values of Ni/CeO₂ catalysts.

Catalyst	% Ni	% Ce(III)/Ce	% Ni(II)/Ni	Ni 2p _{3/2} binding energy (eV)	
				Ni(III)	Ni(II)
Ni-Ce-np	53	31	82	855.6	854.0, 856.1
Ni-Ce-p	55	27	88	855.7	854.1, 856.3
Ni-Ce-np-3D	41	23	89	855.2	854.0, 856.4
Ni-Ce-p-3D	46	32	90	855.4	854.1, 856.1

3.2 Catalytic tests

Figure 10 shows the variable-temperature ammonia conversion of the Ni/CeO₂ powder catalysts, the Ni/CeO₂ cordierite honeycomb, the 3D-printed Ni/CeO₂ structures, that of a 3D-printed structure of bare CeO₂ (Ce-p-3D) and a blank run of the reactor employed for comparative purposes. In all cases, the only products detected according with the stoichiometric decomposition of ammonia were hydrogen and nitrogen in a H₂:N₂ molar ratio of ca. 3:1. The ammonia conversion increased with temperature and the catalytic activity of all nickel catalysts was remarkably higher than that of Ce-p-3D and that of the blank run, as expected. On the other hand, as deduced from the slope of the S-shape curves (ammonia conversion vs. temperature), the 3D-printed structures showed more severe mass transfer limitations at high values of ammonia conversion, where the performance of the catalytic devices is governed by diffusion regime, with respect to the powder catalysts. In contrast, the sample Ni-Ce-p-CORD was less active but showed better mass transfer characteristics. This is ascribed to the large open area of the cordierite honeycomb, which facilitates external mass transfer at the expense of catalytic efficiency. Overall, the ammonia decomposition activity followed the trend Ni-Ce-np~Ni-Ce-p>Ni-Ce-np-3D>Ni-Ce-p-3D>>Ni-Ce-p-CORD. It should be noted that the catalytic performance of the 3D-printed structures was much better than that of the cordierite honeycomb, which clearly indicates that the woodpile arrangement of the microchannels of the 3D-printed catalysts confers advantages with respect to the conventional structured catalytic wall geometry of cordierite honeycombs. Therefore, the 3D printing technique emerges as a valuable tool for the preparation of ceria-based catalytic wall reactors, which can lead to a significant advance in process intensification.

Figure 10. Ammonia conversion at different temperatures. Total flow 25 ml min⁻¹, Ar:NH₃=1.3:1, 1 atm, GHSV of 3000 h⁻¹ (powder catalysts and cordierite honeycomb) and 7500 h⁻¹ (3D-printed structures).

Considering that similar atomic surface Ni/Ce ratios were recorded for all Ni/CeO₂ samples tested (Table 1), it is possible to make an adequate comparison of their catalytic performance by comparing the specific rates of hydrogen production per reactor volume for each of them at different F/W ratios at the same reaction temperature (Figure 11). The comparison of specific rates of hydrogen production against F/W is mandatory since both the ammonia flow rate and the amount of Ni is different for the different samples (see sections 2.1, 2.5 and 3.1). Interestingly, the specific rates of hydrogen production are very similar for the powder catalysts and for the 3D-printed catalytic structures, since they define a similar linear trend up to an F/W ratio of approximately 300 L h⁻¹ g_{Ni}⁻¹. In addition, in this range, specific production rates of hydrogen are fully proportional to the increase in F/W, which indicates that the samples are capable of efficiently processing the ammonia load. In contrast, the specific rates of hydrogen production recorded on the catalytic cordierite honeycomb, Ni-Ce-p-CORD, are much lower with respect to the powder catalyst and the

3D-printed catalytic structures. Therefore, the catalytic efficiency of the ceria 3D-printed structures is remarkably higher than that of conventional honeycomb. We ascribe this behavior to a better flow distribution and enhanced contact between catalyst and reactants in the 3D-printed ceria woodpile structures with respect to the 2D cordierite honeycomb geometry. Overall, the specific hydrogen production rates at 500°C and similar F/W ratios follows the trend Ni-Ce-p~Ni-Ce-p-3D~Ni-Ce-np-3D>>Ni-Ce-p-CORD.

Figure 11. Specific hydrogen production rates normalized per reactor volume under different F/W ratios at 500 °C, Ar:NH₃=1.3:1, 1 atm.

Long-term (100 h) stability tests were conducted over Ni-Ce-p, Ni-Ce-p-3D and Ni-Ce-p-CORD at 450 °C to study the robustness of the catalysts (Figure 12). The high stability of all catalysts in terms of ammonia conversion after 100 h is remarkable. Interestingly, the catalytic performance of the 3D-printed structure improved over time on stream, which we ascribe to a progressive activation of the sample by reduction of Ni [28].

Figure 12. Ammonia conversion in long-term stability tests of Ni-Ce-p, Ni-Ce-p-3D and Ni-Ce-p-CORD at 450 °C, Ar:NH₃=1.3:1, 1 atm.

The precise size of the nickel particles after the stability tests was determined by HRTEM to calculate the dispersion of the metal and the turnover frequency values (TOF) in order to compare the catalytic performances obtained in this work with those reported in the literature. Figure 13 shows representative HRTEM images of the samples. The 3D-printed ceria samples contain nickel particles with a mean size of 5.9-6.0 nm, while for powdered samples and the catalyst deposited on the cordierite structure the average diameter of the nickel particles is 4.9 nm. The TOF values recorded at 500 °C on the powder catalysts (0.48-0.50 s⁻¹) were slightly higher than those recorded on the catalytic 3D-printed structures and that of the catalytic cordierite honeycomb (0.31-0.40 s⁻¹). These values are similar to the TOF values reported in the literature for nickel-based catalysts for ammonia decomposition. According to Nakamura *et al.* [82], among the various oxides tested as a support for nickel,

zirconia and ceria demonstrated the highest values of TOF under similar reaction conditions, 0.81 and 0.66 s⁻¹, respectively. Zhang *et al.* reported similar TOF values for Ni/Al₂O₃ [83]. Also Zhang *et al.* [84] studied the relationship between the dimensions of the nickel particles supported on multi-walled carbon nanotubes and catalytic performance; the TOF reported for Ni particles of about 5 nm at 500 °C was ca. 0.5 s⁻¹, very similar to our values.

Figure 13. HRTEM images of the catalysts after reaction. a) Ni-Ce-p, b) Ni-Ce-p-CORD, c) Ni-Ce-p-3D and d) Ni-Ce-np-3D.

4. Conclusions

A ceria paste was formulated, characterized and employed in a 3D printer to manufacture ceria catalytic structures with a woodpile geometry of microchannels in a fast and simple way. The ceria paste was easily prepared by the addition of an aqueous solution of nitric acid and did not contain any binder or organic additive. In this way, compact 3D structures after calcination at low temperature (500°C) were obtained. Two sets of 3D-printed ceria structures with ceria filaments of about 550 μm in diameter and channels of about 980 μm wide were prepared from two different ceria powders with different particle size of 6 and 10 nm. After printing and calcining the samples, the ceria particles sintered moderately up to 14 and 20 nm, respectively. The preparation procedure was characterized by SEM, HRTEM, FTIR, XRD, XPS and Raman spectroscopy. The 3D-printed ceria structures were impregnated with nickel and tested in the catalytic decomposition of ammonia to obtain hydrogen. The catalytic performance was monitored at different reaction temperatures and F/W ratios and compared with those obtained on Ni/CeO₂ samples directly in powder form (the same ceria particles as those used for the 3D-printed structures) or loaded over conventional cordierite honeycombs (400 cpsi). The 3D-printed Ni/CeO₂ samples showed excellent catalytic performance, comparable to that exhibited by the powder catalysts under the same reaction conditions, and clearly superior to that of the conventional cordierite honeycomb. The ease of preparing ceria supports by means of 3D printing offers new and exciting perspectives for the preparation of more versatile and efficient ceria-based catalytic devices with unprecedented shapes and geometries. This allows a significant improvement of reaction rates on a reactor volume basis.

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