Journal Pre-proof

Stable NiO-CeO₂ nanoparticles with improved carbon resistance for methane dry reforming

Andrea Cárdenas-Arenas, Esther Bailón-García, Dolores Lozano-Castelló, Patrick Da Costa, Agustín Bueno-López

PII: S1002-0721(20)30472-5

DOI: https://doi.org/10.1016/j.jre.2020.11.020

Reference: JRE 906

To appear in: Journal of Rare Earths

Received Date: 29 July 2020

Revised Date: 10 November 2020

Accepted Date: 23 November 2020

Please cite this article as: Cárdenas-Arenas A, Bailón-García E, Lozano-Castelló D, Da Costa P, Bueno-López A, Stable NiO-CeO₂ nanoparticles with improved carbon resistance for methane dry reforming, *Journal of Rare Earths*, https://doi.org/10.1016/j.jre.2020.11.020.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier B.V. on behalf of Chinese Society of Rare Earths.





Journal Pre-proof

Stable NiO-CeO₂ nanoparticles with improved carbon resistance for methane dry reforming

Andrea Cárdenas-Arenas^a, Esther Bailón-García^a, Dolores Lozano-Castelló^a, Patrick Da Costa^b, Agustín Bueno-López^{a,*}

^aDepartment of Inorganic Chemistry, University of Alicante, Carretera de San Vicente s/n. E03080, Alicante, Spain.*agus@ua.es

^bSorbonne Université, Institut Jean Le Rond d'Alembert, CNRS UMR 7190, 2 place de la gare de ceinture, 78210, Saint Cyr L'Ecole (France).

ABSTRACT. A new NiO-CeO₂ dry methane reforming catalyst (DRM) is presented (8.7 wt% Ni), which consist of high surface area mixed oxide nanoparticles ($122 \text{ m}^2/\text{g}$; 6–7 nm). These nanoparticles showed catalytic stability under the severe conditions of DRM (700 °C), and improved carbon resistance with regard to conventional NiO-CeO₂ catalysts prepared without control of the size. Both the nanoparticles and the reference catalyst compared present high activity and selectivity for DRM, almost reaching the conversion and ratio of products predicted by thermodynamics for the experimental conditions used. Nevertheless, the nanoparticles reduced by 63% the accumulation of carbon during the DRM tests, which is a key feature for this reaction. XPS and H₂-TPR suggest that the improved carbon resistance of the nanoparticles is the better interaction and cooperation between NiO and CeO₂ mixed phases. In nanoparticles, the participation of cerium cations in the redox processes taking place during DRM stabilize cationic species of nickel. On the contrary, the catalyst prepared without control of the size suffered segregation of Ni during DRM reaction, and segregated Ni explains the higher catalytic formation of carbon.

Foundation item: Project supported by the Generalitat Valenciana (Project PROMETEO/2018/076; grant of ACA GRISOLIAP/2017/185; contract of EBG APOSTD/2019/030), MINECO (Project CTQ2015-67597-C2-2-R), MICINN (Project PID2019-105960RB-C22) and European Union FEDER funds

KEYWORDS. Methane dry reforming; nickel; ceria; nanoparticle; rare earths

1. INTRODUCTION

Dry reforming of methane (DRM) has been proposed to diminish emission of greenhouse gases to the atmosphere, catalyzing the reaction between CH_4 and CO_2 to yield a mixture of H_2 and CO (syngas) [1-5]. DRM is an environmental friendly pathway alternative to conventional syngas production by steam reforming. The syngas obtained by DRM can be used for Fischer-Tropsch synthesis of hydrocarbons of different nature, therefore contributing to decrease greenhouse gases emissions producing products with practical interest. DRM has been proposed to valorize waste emissions using biogas as feedstock, as a chemical way to store solar energy, and it has been also proposed to be applied to natural gas with high concentration of CO_2 , among other applications [6, 7].

DRM is endothermic

$$CH_4 + CO_2 = 2CO + 2H_2$$
 $\Delta H_{25 \, \text{°C}} = 247 \, \text{kJ/mol}$

and also presents high activation energy due to the stability of the reactant gases. For this reason, the use of a catalyst is necessary to activate the reaction together with temperatures in the 650–850 °C range.

The most efficient DRM catalysts are supported noble metals (Ru, Rh, and Pt) and certain supported transition metals (Ni and Co) [8]. Noble metal catalysts are more active, more stable against sintering and better carbon resistant than Co and Ni catalysts, but the high price of noble metals limits their practical application. Among suitable catalysts, Ni-based catalysts are the most interesting at industrial level because combine a lower price than noble metals with a suitable catalytic activity [7, 9-11].

The main problem of Ni catalysts is that suffer severe deactivation due to carbon formation under DRM conditions due to side reactions [12-15]. Carbon is a by-product that inhibits the catalyst due to encapsulation of the metal particles and/or blockage of the catalyst porosity [9]. In addition, carbon accumulation on the catalyst could not only lead to deactivation, but can also cause reactor plugging. Carbon is mainly formed by CH₄ decomposition, but hydrogenation of CO and CO₂, and disproportionation of CO can also contribute [9].

$CH_4 = C + 2H_2$	$\Delta H_{25 ^{\circ}\mathrm{C}} = 75 \mathrm{kJ/mol}$
$2CO = C + CO_2$	$\Delta H_{25^{\circ}\mathrm{C}} = -172 \text{ kJ/mol}$
$CO + H_2 = C + H_2O$	$\Delta H_{25^{\rm o}\rm C} = -131 \text{ kJ/mol}$

The nature of the Ni support strongly affects the activity of the catalysts and the carbon resistance, and different supports have been studied, such as ZrO_2 , CeO_2 , ZrO_2 - CeO_2 , Al_2O_3 , MgO, TiO_2, SiO_2, MgAl_2O_4 and ZSM5 among others [16]. Ceria-based supports are among the most efficient, because they promote nickel dispersion and prevent sintering due to the strong metal–support interaction [17]. It is known that DRM requires two type of actives sites on a Ni catalyst, including reduced Ni sites for CH₄ dissociation and basic sites for CO₂ chemisorption and dissociation. It has been also reported that basic supports, like those of ceria, provide efficient sites for such dissociation of CO₂[9] and that the reaction between adsorbed CH₄ and CO with ceria oxygen prevents the formation of carbon on the nickel phase.

It is also well-known that the shape of a catalyst plays a critical role in the catalytic behavior, and ceria nanoparticles have shown high catalytic activity in different reactions,

Stable NiO-CeO2 nanoparticles with improved carbon resistance for methane dry reforming

such as water gas shift [18, 19], photocatalytic water splitting [20] and soot combustion [21, 22] among others.

Taking into account the promising behavior of nickel-ceria catalysts for DRM, and the critical issue of deactivation by carbon formation as undesired by-product, the goal of this study was to improve the carbon resistance of nickel-ceria DRM catalysts. A NiO-CeO₂ DRM catalyst is presented, which consist of mixed oxide nanoparticles. It is demonstrated that these nanoparticles present enough stability under the severe temperatures of DRM, and improved carbon resistance with regard to a counterpart NiO-CeO₂ mixed oxide prepared without control of the size.

2. EXPERIMENTAL

2.1. Catalysts preparation

The nanoparticles catalyst, referred to as NiO-CeO₂ (np), has been prepared by the reversed microemulsion method using Ce(NO₃)₃·6H₂O (99.5%, Alfa Aesar) and Ni(NO₃)₂·6H₂O (Sigma-Aldrich). The amount of Ni and Ce precursors required to obtain 8.5 wt% of Ni in the final catalyst was dissolved in water, and a microemulsion was prepared adding n-heptane, Triton X-100 and hexanol. The precipitation of the oxides was forced adding a similar microemulsion with a base (tetramethylammonium hydroxide) instead of the metal precursors. The mixture was stirred for 24 h and the suspension was

centrifuged to collect the solid, which was washed with ethanol, dried (110 °C) and calcined (500 °C; 1 h).

A reference catalyst (NiO-CeO₂ (ref)) with high catalytic activity, as will be shown afterwards, has been prepared with the same composition but without control of the size. The Ni and Ce precursors were dissolved in water, and citric acid (99%, Sigma-Aldrich) was added in stoichiometric proportion. The solid was dried at 80 °C and calcined at 600 °C.

2.2. Catalytic tests

DRM tests were carried out in a fixed-bed reactor (12 mm diameter) coupled to a gas chromatograph (Agilent Varian GC490, Agilent). The catalysts were reduced in situ before the experiments at 500 °C for 1 h under 100 mL/min of 5% H₂/Ar. DRM experiments were performed afterwards at 700 °C under 100 mL/min of 10% CH₄ + 10% CO₂ with Ar balance. The mass of catalyst was 300 mg (GHSV 24000 h⁻¹).

2.3. Catalysts characterization.

The nickel loading was determined by ICP-OES (Perkin Elmer spectrophotometer, model optima 4300 DV). The extraction was carried out with 2% HNO₃ in water.

TEM images of the catalysts were obtained in a JEOL microscope, model JEM-2010.

 N_2 adsorption-desorption characterization was performed at -196 °C in a volumetric device (QUANTACHROME INSTRUMENT, model AUTOSORB-6). The catalysts were previously degassing for 4 h at 150 °C.

H₂-TPR characterization was carried out in a Micromeritics device (model Pulse Chemisorb 2705) with a TCD detector, using 40 mL/min of 5% H₂/Ar (40 mL/min) and 40 mg of catalyst. CuO was used as standard reference to quantify H₂ consumption. The temperature was raised at 10 °C until 900 °C.

The amount of carbon accumulated on the catalysts during the DRM tests was determined by combustion in a thermobalance (SDT 2960 Simultaneous DSC-TGA; TA Instruments). 10 mg of the used catalysts were heated at 10 °C/min in air (100 mL/min) until 800 °C.

The catalysts were characterized before and after the DRM tests by XRD and XPS. XRD characterization was performed in a Bruker diffractometer (D8-Advance), using Cu K α radiation ($\lambda = 0.1540598$ nm), and XPS in a K-ALPHA Thermo Scientific device, using Al K α radiation (1486.6 eV) and fitting C 1s transition at 284.6 eV to adjust the binding energy scale.

3.- RESULTS AND DISCUSSION.

3.1. Catalysts characterization.

The amount of Ni is near the target (8.5 wt%) in both materials (NiO-CeO₂ (np) 8.7 wt% and NiO-CeO₂ (ref) 8.2 wt%), and ceria fluorite is the main crystalline phase in the diffractograms of both fresh catalysts (Fig. 1), suggesting formation of NiO-CeO₂ mixed oxides, as expected. Tiny peaks of NiO were observed in the diffractogram of fresh NiO-CeO₂ (ref), evidencing few segregation of phases. The peaks broadening of the fresh catalysts indicate that crystallite size of NiO-CeO₂ (np) is smaller to that of NiO-CeO₂ (ref), as expected (data in Table 1).

Figure 1. X-ray diffractograms of the fresh and used catalysts.

The intensity of the XRD peaks increased after the DRM reaction, obtaining much more intense peaks with the reference catalyst NiO-CeO₂ (ref) than with NiO-CeO₂ (np). The reference catalyst additionally shows peaks of metal nickel, confirming the presence of segregated nickel species. The crystallite sizes of ceria have been calculated with the Scherrer's equation using the (111) CeO₂ peak of the diffractograms and values have been compiled in Table 1confirming the smaller crystallite size of NiO-CeO₂ (np) with regard to NiO-CeO₂ (ref) both for fresh and used catalysts.

Stable NiO-CeO2 nanoparticles with improved carbon resistance for methane dry reforming

Catalyst	Ni content	BET specific surface	CeO ₂ crystallite size
-	(wt%)	area (m²/g)	(nm)
NiO-CeO ₂ (np)-fresh	8.7	122	7
NiO-CeO ₂ (np)-used	-	-	19
NiO-CeO ₂ (ref)-fresh	8.2	56	13
NiO-CeO ₂ (ref)-used	-	-	32

Table 1. Ni content, specific surface area and CeO₂ crystallite size of the catalysts.

The smaller crystallite size of fresh NiO-CeO₂ (np), predicted by XRD, is consistent with the results of N₂ adsorption. As expected, the specific surface area of NiO-CeO₂ (np) (122 m^2/g) is higher to that of NiO-CeO₂ (ref) (56 m^2/g) due to the smaller size of the primary particles (see TEM images in Fig. 2).

Figure 2. TEM images of the catalysts. (a) NiO-CeO₂ (np); (b) NiO-CeO₂ (ref).

In this type of materials, the surface area comes from the external area of the primary particles together with the space left among particles, and can be assumed that primary particles are single crystals. For this reason, the smaller the primary particles/crystals the higher the specific surface area. Assuming spherical shape of the primary crystals, it is estimated from surface area values that the primary crystals size is 6-7 nm for NiO-CeO₂ (np), which is consistent with the crystallite size obtained by XRD. This estimation increases to 15 nm for NiO-CeO₂ (ref), but in this case the size of primary crystals is heterogeneous and must be considered as an average value. This is clearly observed in the TEM images of Fig. 2. NiO-CeO₂ (np) image shows smaller crystals with homogeneous

size, being consistent with the estimated size (6–7 nm), while the size of the crystals in the NiO-CeO₂ (ref) image is non homogeneous, and larger crystals can be distinguished.

The formation of nanoparticles also affects the reducibility of the catalyst, as observed in Fig. 3. Both catalysts present H₂ consumption above 700 °C due to the reduction of bulk ceria, and the amount consumed is similar for both catalysts (0.06–0.08 H_2 mole/CeO₂ mole). On the contrary, important differences are noticed in the reduction profiles below 500 °C, where surface reduction events take place. Surface reduction of NiO-CeO₂ (ref) shows a well-defined peak with a small shoulder at low temperature. This is consistent with the formation of a NiO-CeO₂ mixed oxide where Ni^{2+} and Ce^{4+} cations are reduced simultaneously, and the small shoulder is probably due to the low amount of segregated NiO, as deduced from XRD NiO tiny peaks. The surface reduction of NiO-CeO₂ (np) is quite different, with two well defined peaks that evidence the presence of two types of surface species with different reducibility. The maxima of the largest peak at 365 °C is quite similar to that of the surface reduction of NiO-CeO₂ (ref) (350 °C), and the low temperature peak, with onset temperature at 160 °C and maximum at 288 °C, evidences the presence of highly reducible species in the nanoparticles catalyst. In addition, the amount of H₂ consumed for surface reduction of the catalysts is higher for NiO-CeO₂ (np) (147 H₂ mole/ NiO mole) than for NiO-CeO₂ (ref) (121 H₂ mole/ NiO mole). The amounts of H₂ consumed are larger in both cases than the amounts required for NiO reduction to Ni, evidencing simultaneous reduction of ceria.

Figure 3. Temperature programmed reduction experiments with H₂.

Stable NiO-CeO2 nanoparticles with improved carbon resistance for methane dry reforming

In summary, characterization has showed that the NiO-CeO₂ (np) catalyst consists of homogeneously dispersed NiO-CeO₂ mixed oxide nanoparticles (6–7 nm) with higher surface area and improved surface reducibility with regard to the conventional NiO-CeO₂ (ref) prepared without control of the size.

3.2. Catalytic tests.

The nanoparticles catalyst was tested for DRM at 700 °C for 5 h under stoichiometric CH₄/CO₂ conditions, and the conversion curves are plotted in Fig. 4 and compared with those obtained with the reference mixed oxide. Both catalysts reached high conversion values for CO_2 and CH_4 (above 80%), but the nanoparticles catalyst was slightly more active. The CH₄ conversion predicted by thermodynamics for the experimental conditions of these experiments is ~90% [3, 23] and the values obtained with both catalysts are only slightly lower. The conversion values shown in Fig. 4 are high in comparison with those reported in literature for other Ni/CeO₂-based catalysts tested in comparable conditions. For instance, 30% CH₄ conversion was reported for a 12 wt%Ni/CeO₂ catalyst prepared by incipient impregnation and tested at 700 °C with a stoichiometric CO_2/CH_4 mixture, and the catalyst suffered strong deactivation during reaction due to carbon formation [24]. In this case, the performance was significantly improved by optimizing the loading of the active phase on SBA15. In another example, Ni-Co/CeO₂-ZrO₂ catalysts were tested for DRM, and the CH₄ conversion at 700 °C dropped from 35% to 25% approximately after 3 h under reaction conditions due to carbon accumulation [25]. Higher conversion was achieved with a 26 wt% Ni-ceria system prepared by combustion synthesis, reaching 65% CH₄ conversion at 750 °C [26].

The H₂/CO ratio yielded by the catalysts tested in the current study (Fig. 4(c)) is slightly lower to 1, which is the predicted thermodynamic ratio for DRM. Values lower to 1 are obtained due to certain side reactions (CO_x methanation, reversed water gas shift and CH₄ decomposition) taking place together with DRM.

Figure 4. Methane dry reforming experiments. (a) CO_2 conversion; (b) CH_4 conversion; (c) H_2/CO yield. (700 °C; 100 mL/min; 10% CH_4 + 10% CO_2 with Ar balance; 300 mg of catalyst; Pretreatment *in situ* at 500 °C, 1 h, 100 mL/min of 5% H_2/Ar).

In summary, the catalytic tests confirmed that both the nanoparticle catalyst and the reference mixed oxide prepared for comparison are efficient catalysts for DRM, with few room for improvement in catalytic activity and selectivity because both catalysts approached the conversion and selectivity values predicted by thermodynamics. Nevertheless, resistance to carbon accumulation is required for this application, and nanoparticles improved carbon resistance with regard to the reference counterpart catalyst, as deduced from Fig. 5 where thermograms obtained in air with both catalysts after the DRM catalytic tests have been plotted.

Figure 5. Combustion in air in a thermobalance of carbon accumulated on the catalysts during DRM experiments.

The amount of carbon accumulated on the catalysts during DRM was quantified measuring the weight dropped above 450 °C due to the combustion of such carbon. These results reveal that the amount of carbon on the NiO-CeO₂ (np) catalyst is 2.7 times lower to that on the counterpart reference NiO-CeO₂ (ref) catalyst, that is, nanoparticles reduced by 63% the accumulation of carbon during DRM. The average carbon accumulation rate during the catalytic tests is 17 μ g_{carbon}/(h·g_{catalyst}) for NiO-CeO₂ (np) and 45 μ g_{carbon}/(h·g_{catalyst}) for NiO-CeO₂ (ref).

It has been reported that, for Ni/CeO₂-based catalysts, two conditions are relevant to diminish carbon formation [25]. One of them is the strong interaction between the Ni phase and the ceria support and the other one is to ensure high oxygen mobility within the ceria lattice. The NiO-CO₂ contact is expected to be good in mixed oxides, as those prepared in the current study, but certain differences were noticed in XRD and H₂-TPR characterization. These techniques provided evidences about the improved NiO-CeO₂ contact in the catalyst with the best carbon resistance (NiO-CeO₂ (np)) with regard to that in the reference mixed oxide (NiO-CeO₂ (ref)). It has been also proposed that decreasing the particle size of nickel hinders carbon formation if the size is too small for carbon nucleation and growth [25], and therefore, the better formation of the NiO-CeO₂ mixed oxide in the NiO-CeO₂ (np) catalyst and the smaller crystallite size would explain the improved carbon resistance.

3.3. XPS analysis of catalysts before and after the DRM experiments.

The as-prepared catalysts were characterized by XPS, and also after the DRM experiments. The spectra obtained in the Ni_{2p} energy region are included in Fig. 6, showing the most intense band at 851–859 eV with their satellites at 859–866 eV.

Figure 6. XPS spectra recorded in the Ni_{2p} energy region. (a) Fresh catalysts; (b) After the DRM experiments.

There is not general consensus about the assignment of Ni_{2p} peaks, but it has been proposed that the nature of the nickel species can be deduced from the position and deconvolution of the highest intensity peak [27, 28] Peaks of metallic nickel are expected to appear below 852 eV, and above this energy peaks can be assigned to NiO, Ni₂O₃ and Ni(OH)₂ [27, 29–32]. According to this assignment, cationic species of nickel are present on the surface of both fresh catalysts, as expected considering that catalysts were calcined. The ratio of the areas (or intensities) of the main peaks in the spectra is similar for both fresh catalysts, but the binding energies of the maxima are higher for NiO-CeO₂ (np) than for NiO-CeO₂ (ref). This could be related to the better NiO-CeO₂ interaction achieved in the nanoparticles, as deduced from XRD and H₂-TPR. The higher binding energies of nickel cations in NiO-CeO₂ (np) suggest higher interaction between these cations and ceria, that is, this interaction leads to the transfer of negative charge density from NiO to CeO₂.

The intensity of the Ni_{2p} spectra decreased for the used catalysts, and much more noisy spectra were obtained due to the accumulation of carbon on the surface. The position of the most intense Ni_{2p} peak shifts towards higher binding energy after the DRM experiments, indicating changes in the surface of both catalysts that stabilize the oxidized species of nickel. The shift in the position of the Ni_{2p} peaks affects to $NiO-CeO_2$ (ref) in a much higher extent than to $NiO-CeO_2$ (np), that is, the shift for nanoparticles is 1.7 eV while it is higher than 3 eV for the reference catalyst. This is consistent with the important changes detected by XRD for $NiO-CeO_2$ (ref) after the catalytic tests, but XRD predicts the presence of reduced nickel while XPS evidences the formation of nickel cations with high positive charge density. This suggests the segregation of metal nickel during the reaction, but the surface of these segregated nickel particles seems to be highly oxidized.

Figure 7. XPS spectra recorded in the Ce_{3d} energy region. (a) Fresh catalysts; (b) After the DRM experiments.

Changes in the oxidation state of the cerium cations are also detected by XPS before and after the catalytic tests, as deduced from Fig. 7. XPS spectra of cerium combines peaks assigned to Ce^{3+} and Ce^{4+} , as it has been labelled in the figure, and the proportion of Ce^{3+} cations with regard to $Ce^{3+} + Ce^{4+}$ can be estimated as the ratio between the area under the Ce^{3+} peaks and the total area under the spectrum. The estimated Ce^{3+} percentages, compiled in Table 2, predict that the amount of Ce^{3+} in the fresh catalysts is not very different to each other (18% vs 23%). However, the behavior under reaction conditions is very different for each catalyst. While the average oxidation state of cerium cations in NiO-CeO₂ (ref) does not change during the DRM tests (18% before and after the tests), the Ce^{3+} percentage in NiO-CeO₂ (np) drops from 23% to 11%. This suggests that ceria in this catalyst is getting significantly involved in the redox processes taken place under reaction conditions, and probably this participation of ceria explains the higher stability of the nickel species. That is, Ni_{2p} and Ce_{3d} XPS characterization suggests that cooperation between nickel and cerium oxides during DRM is much more efficient in the NiO-CeO₂ (np) catalyst than in the reference material prepared without control of the size.

Table 2. Ce³⁺ percentage determined from XPS analysis.

Catalyst	Ce ³⁺ percentage
NiO-CeO ₂ (np) fresh	23%
NiO-CeO ₂ (np) used	11%
NiO-CeO ₂ (ref) fresh	18%
NiO-CeO ₂ (ref) used	18%

In summary, XPS suggests that the improved carbon resistance of the NiO-CeO₂ (np) catalyst prepared in nanoparticle shape with regard to the counterpart mixed oxide prepared without control of the size is related to the better interaction and cooperation between nickel and cerium cations. The participation of cerium cations in the redox processes taking place during DRM seems to stabilize cationic species of nickel. In a wider outlook of the reaction pathway, it is known nickel active sites are responsible for CH₄ dissociation, leading to CO + H₂ formation throughout the desired DRM reaction mechanism, or catalyzing carbon deposits formation throughout an undesired pathway. The success of the DRM pathway depends on the high interaction between nickel and ceria phases, avoiding segregation of nickel crystals with high enough size to catalyze carbon formation.

4.- CONCLUSIONS

A NiO-CeO₂ DRM catalyst has been presented (8.7 wt% Ni), which consist of mixed oxide nanoparticles (122 m²/g; 6–7 nm). These nanoparticles showed catalytic stability during 5 h under the severe conditions of DRM (700 °C), and improved carbon resistance

with regard to a counterpart NiO-CeO₂ mixed oxide (56 m^2/g ; average 15 nm) prepared without control of the size.

Both the nanoparticles and the reference catalyst present high activity and selectivity for DRM, almost reaching the conversion and ratio of products predicted by thermodynamics for the experimental conditions used. Nevertheless, nanoparticles reduced by 63% the accumulation of carbon.

XPS and H₂-TPR suggest that the improved carbon resistance of the nanoparticles is related to the better interaction and cooperation between NiO and CeO₂ mixed phases. In nanoparticles, participation of cerium cations in the redox processes taking place during DRM seems to stabilize cationic species of nickel. On the contrary, the catalyst prepared without control of the size suffered certain segregation of Ni during DRM reaction (while not the nanoparticles), and the presence of segregated Ni would be responsible of the catalytic formation of carbon.

Acknowledgements

- Generalitat Valenciana: Project PROMETEO/2018/076; grant of ACA GRISOLIAP/2017/185; contract of EBG APOSTD/2019/030.
- MINECO: Project CTQ2015-67597-C2-2-R
- MICINN: Project PID2019-105960RB-C22
- European Union: FEDER funds

REFERENCES

- [1] Usman M, Wan Daud WMA, Abbas HF. Dry reforming of methane: Influence of process parameters—A review. Renew. Sust. Energ. Rev. 2015; 45, 710.
- [2] Aramouni NAK, Touma JG, Tarboush BA, Zeaiter J, Ahmad MN. Catalyst design for dry reforming of methane: Analysis review. Renew. Sust. Energ. Rev. 2018; 82, 2570.
- [3] Wang Y, Yao L, Wu SH, Mao DH, Hu CW. Low-temperature catalytic CO₂ dry reforming of methane on Ni-based catalysts: A review. Fuel Proc. Technol. 2018; 169, 199.
- [4] Abdulrasheed A, Jalil AA, Gambo Y, Ibrahim M, Hambali HU, Hamid MYS. A review on catalyst development for dry reforming of methane to syngas: Recent advances. Renew. Sust. Energ. Rev. 2019; 108, 175.
- [5] Jang W-J, Shim J-O, Kim H-M, Yoo S-Y, Roh H-S. A review on dry reforming of methane in aspect of catalytic properties. Catal. Today 2019; 324, 15.
- [6] Fan MS, Abdullah AZ, Bhatia S. Catalytic technology for carbon dioxide reforming of methane to synthesis gas. ChemCatChem 2009; 12, 192.
- [7] Pakhare D, Spivey J. A review of dry CO₂; reforming of methane over noble metal catalysts. Chem. Soc. Rev. 2014; 4322, 7813.
- [8] Verykios XE. Catalytic dry reforming of natural gas for the production of chemicals and hydrogen. Int. J. Hydrogen Energ. 2003; 28, 1045.
- [9] Abdullah B, Ghani NAA, Vo DN, Recent advances in dry reforming of methane over Ni-based catalysts. J. Clean. Prod. 2017; 162, 170.
- [10] Boukha Z, Kacimi M, Pereira MFR, Faria JL, Figueiredo JL, Ziyad M, Methane dry reforming on Ni loaded hydroxyapatite and fluoroapatite. Appl. Catal. A. Gen. 2007; 317, 299.
- [11] Valderrama G, Kiennemann A, Goldwasser MR. Dry reforming of CH₄ over solid solutions of LaNi_{1-x}Co_xO₃. Catal. Today 2008; 133–135, 142.
- [12] Padi SP, Shelly L, Komarala EP, Schweke D, Hayun S, Rosen BA. Coke-free methane dry reforming over nano-sized NiO-CeO₂ solid solution after exsolution. Catal. Commun. 2020; 138, 105951.
- [13] Juan-Juan J, Román-Martínez MC, Illán-Gómez MJ. Effect of potassium content in the activity of K-promoted Ni/Al₂O₃ catalysts for the dry reforming of methane. Appl. Catal. A. Gen. 2006; 301, 9.

Stable NiO-CeO2 nanoparticles with improved carbon resistance for methane dry reforming

- [14] García-Diéguez M, Pieta IS, Herrera MC, Larrubia MA, Alemany LJ. Nanostructured Pt- and Ni-based catalysts for CO₂-reforming of methane. J. Catal. 2010; 270, 136.
- [15] Wang Y, Li L, Wang YN, Da Costa P, Hu CW. Highly Carbon-Resistant Y Doped NiO–ZrO_m Catalysts for Dry Reforming of Methane. Catalysts. 2019; 9, 1055.
- [16] Barroso-Quiroga MM, Castro-Luna AE. Catalytic activity and effect of modifiers on Ni-based catalysts for the dry reforming of methane. Int. J. Hydrogen Energy. 2010; 35, 6052.
- [17] Laosiripojana N, Sutthisripok W, Assabumrungrat S. Synthesis gas production from dry reforming of methane over CeO₂ doped Ni/Al₂O₃: Influence of the doping ceria on the resistance toward carbon formation. Chem. Eng. J. 2005; 1121-3, 13.
- [18] Fu Q, Weber A, Flytzani-Stephanopoulos M. Nanostructured Au–CeO₂ catalysts for low-temperature Water–Gas Shift. Catalysis Letters 2001; 77, 87.
- [19] Franco P, Martino M, Palma V, Scarpe A, De Marco I. Pt on SAS-CeO₂ nanopowder as catalyst for the CO-WGS reaction. Int. J. Hydrog. Energ. 2018; 43, 25, 19965.
- [20] Primo A, Marino T, Corma A, Molinari R, García H. Efficient Visible-Light Photocatalytic Water Splitting by Minute Amounts of Gold Supported on Nanoparticulate CeO₂ Obtained by a Biopolymer Templating Method. J. Am. Chem. Soc. 2011; 133, 18, 6930.
- [21] Jiu J, Zhao Z, Wang JQ, Xu CM, Duan AJ, Jiang GY, et al. The highly active catalysts of nanometric CeO₂-supported cobaltoxides for soot combustion. Appl. Catal. B-Environ. 2008; 84, 185.
- [22] Guillén-Hurtado N, García-García A, Bueno-López A. Active oxygen by Ce–Pr mixed oxide nanoparticles outperformdiesel soot combustion Pt catalysts. Appl. Catal. B-Environ. 2008; 84, 1–2, 185.
- [23] Cui YH, Zhang HD, Xu HY, Li WZ. Kinetic study of the catalytic reforming of CH₄ with CO₂ to syngas over Ni/ α -Al₂O₃ catalyst: The effect of temperature on the reforming mechanism. Appl. Catal. A. Gen. 2007; 318, 79.
- [24] Wang N, Chu W, Zhang T, Zhao XS. Synthesis, characterization and catalytic performances of Ce-SBA-15 supported nickel catalysts for methane dry reforming to hydrogen and syngas. Int. J. Hydrogen Energy. 2012; 37, 19.
- [25] Djinović P, Osojnikčrnivec IG, Erjavec B, Pintar A. Influence of active metal loading and oxygen mobility on coke-free dry reforming of Ni-Co bimetallic catalysts. Appl. Catal. B Env. 2012; 125, 259.

- [26] Gonzalez-De la Cruz VM, Holgado JP, Pereñíguez R, Caballero A. Morphology changes induced by strong metal–support interaction on a Ni–ceria catalytic system. J. Catal. 2008; 257, 307.
- [27] Grosvenor AP, Biesinger MC, Smart RSC, McIntyre NS. New interpretations of XPS spectra of nickel metal and oxides. Surf. Sci. 2006; 600, 1771.
- [28] Marrani AG, Novelli V, Sheehan S, Dowling DP, Dini D. Probing the redox states at the surface of electroactive nanoporous NiO thin films. ACS Appl. Mater. Interfaces. 2014; 6, 143.
- [29] Xu XL, Li Lin, Yu F, Peng HG, Fang XZ, Wang X. Mesoporous high surface area NiO synthesized with soft templates: Remarkable for catalytic CH₄ deep oxidation. Mol. Catal. 2017; 441, 81.
- [30] Yu GH, Zeng LR, Zhu FW, Chai CL, Lai WY. Magnetic properties and x-ray photoelectron spectroscopy study of NiO/NiFe films prepared by magnetron sputtering. J. Appl. Phys. 2001; 90, 4039.
- [31] Ahmed A, Ali T, Naseem Siddique M, Ahmad A, Tripathi P. Enhanced room temperature ferromagnetism in Ni doped SnO₂ nanoparticles: A comprehensive study. J. Appl. Phys. 2017; 122, 083906.
- [32] Weidler N, Schuch J, Knaus F, Stenner P, Hoch S, Maljusch A et al. X-ray Photoelectron Spectroscopic Investigation of Plasma-Enhanced Chemical Vapor Deposited NiO_x, NiO_xOH_y, and CoNiO_xOH_y: Influence of the Chemical Composition on the Catalytic Activity for the Oxygen Evolution Reaction. J. Phys. Chem. C. 2017; 121, 6455.

Graphical abstract:

High surface area NiO-CeO₂ nanoparticles (122 m^2/g ; 6–7 nm) with improved carbon resistance in dry

methane reforming were prepared.



Journal Pre-proof

Journal Pre-proof



ournal Prert



Journal Pre-proó





Journal Preservo

Journal Pre-proof





- High surface area NiO-CeO₂ nanoparticles have been prepared (122 m²/g; 6-7 nm).
- Nanoparticles showed catalytic stability under the severe conditions of dry reforming of methane (700 °C).
- Nanoparticles reduced by 63% the accumulation of carbon during the DRM tests.

Journal

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: