

**Athens Institute for Education and Research
ATINER**



**ATINER's Conference Paper Series
ENV2015-1662**

**Hydrogen Production from Renewable
Resources**

**Radostina Palcheva
Associate Professor
Bulgarian Academy of Sciences
Bulgaria**

**Barbara Pawelec
Associate Professor
Institute of Catalysis and Petrochemistry
Spain**

**Eric Gaigneaux
Professor
Catholic University of Louvain
Belgium**

**Jose Luis Fierro
Professor
Institute of Catalysis and Petrochemistry
Spain**

**Sonia Damyanova
Professor
Bulgarian Academy of Sciences
Bulgaria**

An Introduction to
ATINER's Conference Paper Series

ATINER started to publish this conference papers series in 2012. It includes only the papers submitted for publication after they were presented at one of the conferences organized by our Institute every year. This paper has been peer reviewed by at least two academic members of ATINER.

Dr. Gregory T. Papanikos
President
Athens Institute for Education and Research

This paper should be cited as follows:

Palcheva, R., Pawelec, B., Gaigneaux, E., Fierro, J. L. and Damyanova, S.
(2015). "**Hydrogen Production from Renewable Resources**", Athens:
ATINER'S Conference Paper Series, No: **ENV2015-1662**.

Athens Institute for Education and Research
8 Valaoritou Street, Kolonaki, 10671 Athens, Greece
Tel: + 30 210 3634210 Fax: + 30 210 3634209 Email: info@atiner.gr URL:
www.atiner.gr

URL Conference Papers Series: www.atiner.gr/papers.htm

Printed in Athens, Greece by the Athens Institute for Education and Research. All rights reserved. Reproduction is allowed for non-commercial purposes if the source is fully acknowledged.

ISSN: 2241-2891

27/10/2015

Hydrogen Production from Renewable Resources

Radostina Palcheva

Barbara Pawelec

Eric Gaigneaux

Jose Luis Fierro

Sonia Damyanova

Abstract

The effect of ceria loading on the structure and catalytic performance of CeO₂-Al₂O₃-supported Ni catalysts for CO₂ reforming of methane was studied. The physicochemical properties of the samples were determined by N₂ adsorption-desorption isotherm, XRD, TPR and XPS. XPS results revealed the presence of Ni²⁺ and Ni⁰ on the surface of reduced Ni/xCe-Al (x = 0, 1, 3, 6, 12 wt %) catalysts. It was shown that Ni catalysts supported on ceria-alumina oxides exhibit higher CH₄ conversion compared to that of Ni supported on alumina. The most active catalyst in dry reforming of CH₄ was Ni/6Ce-Al due to the specific electron interaction between ceria and Ni species.

Keywords: Biogas reforming, Ceria-alumina oxides, Characterization, Hydrogen production, Nickel catalysts

Acknowledgments: The authors gratefully acknowledge the project FNI (E02/16) for financial support, as well as to the bilateral collaboration of the Institute of Catalysis with the Instituto de Catálisis y Petroleoquímica (Madrid, Spain) and with the Université catholique de Louvain (Louvain la Neuve, Belgium) for some physicochemical characterization.

Introduction

A very attractive and promising issue is the conversion of waste biomass into energy or raw material as biogas via anaerobic digestion. For the successful reforming of biomass derived biogas or bioethanol to hydrogen highly effective catalysts have to be developed. Among several technologies, biogas and bio-ethanol reforming processes to hydrogen have increasing attention and become important industrial processes. As a transition metal, Ni-based catalysts exhibit a high activity in reforming processes to hydrogen (Wang et al., 1998; Yang et al., 2010; Damyanova et al., 2003) and are cost-effective in comparison with noble metal-based catalysts. However, Ni catalysts undergo a fast deactivation caused by coke formation and the sintering of the active phase. Modified supports have been studied in order to improve the stability and the carbon resistance of catalysts (Bellido et al., 2009). CeO₂ - containing oxides such as CeO₂-Al₂O₃, CeO₂-ZrO₂ and/or CeO₂-La₂O₃-Al₂O₃ have been applied as supports for Ni based catalysts (Kambolis et al., 2010; Kumar et al., 2008). It has been suggested that these materials decrease the active metal-alumina interaction, by avoiding the formation of the metal aluminate spinel species. CeO₂-ZrO₂ oxides display better redox properties than ZrO₂, high surface area and good thermal stability (Damyanova et al., 2008). An addition of a small amount of CeO₂ (1 wt%) improved the activity and stability of Pt/Al₂O₃ in the reforming process, due to the increase of the metal-support interface area, caused by the higher Pt dispersion (Damyanova et al., 2003).

The objective of the present work was to explore the effect of the CeO₂ content on the structure, surface properties and the catalytic performance of Ni/*x*Ce-Al catalysts. Different techniques were used for physicochemical the characterization of the samples: N₂ adsorption-desorption isotherms, X-ray diffraction (XRD), temperature programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS). The test reaction was CH₄ reforming with CO₂ carried out at an atmospheric pressure and reaction temperature of 550°C and CH₄/CO₂ ratio of 1/1.

Experimental

Sample Preparation

Mixed *x*CeO₂-Al₂O₃ (*x*Ce-Al) oxides were obtained by the impregnating of alumina ($S_{\text{BET}} = 248 \text{ m}^2/\text{g}$) with an aqueous solution of (NH₄)₃[Ce(NO₃)₆] with an appropriate CeO₂ concentration (*x*=1-12 wt%), followed by drying and calcination at 100° and 600°C, respectively. Supported Ni catalysts were synthesized by impregnation of alumina and *x*Ce-Al supports using an aqueous solution of Ni(NO₃)₂·6H₂O. The samples were dried at 100°C and calcined at 550°C for 12 and 4 h, respectively. The Ni content was 10 wt%. The samples were denoted as Ni/*x*Ce-Al, where *x* is the CeO₂ content.

Sample Characterization

N₂ adsorption-desorption isotherms of the samples were recorded at 77 K with a Micromeritics TriStar 3000 apparatus. The samples were previously out-gassed under vacuum at 150°C for 24 h. The surface area was calculated according to the BET method. An XRD analysis was performed with a Seifert 3000 diffractometer, Ni-filtered CuK α ($\lambda=0.15406$ nm) radiation and a PW 2200 Bragg-Brentano $\theta/2\theta$ goniometer (Pawelec et al., 2006). The TPR was conducted on Micromeritics 2900 provided with a TCD. The samples were reduced under a flow of 10% H₂/Ar up to 1000 °C with a total flow rate of 50 ml/min and a heating rate of 15 K/min. XPS of reduced samples were obtained with a Surface Science Instruments SSX-100 model 206 spectrometer equipped with a monochromatized microfocused Al X-ray source, operating at 10 kV and 12 mA (Damyanova et al., 1997). The base pressure in the analysis chamber was about 10⁻⁸ Torr. The binding energy (BE) scale of the spectrometer was calibrated with respect to the Au 4f_{7/2} peak and the BE's of O 1s, Al 2p, Ni 2p and Ce 3d electrons were referenced to the C1s band at 284.8 eV. The peak decomposition was performed using the Casa XPS program (Casa Software, UK), assuming a 85/15 Gaussian/Lorentzian product function. The reduction of the Ni/xCe-Al samples (200-500 μm) before XPS measurement was performed ex-situ under H₂/He flow (60 cm³/min) at 550°C for 1 h. After reduction, the reactor was cooled down to room temperature under 10% H₂/He and transported to the XPS apparatus under iso-octane.

Catalytic Test

The catalytic experiments in the reaction of CH₄ reforming with CO₂ were conducted at atmospheric pressure in a fixed bed continuous flow reactor consisting of a quartz tube. The catalyst sample (m = 0.05 g) with a particle size fraction of 0.2–0.25 mm was diluted with a quartz (1:9 ratio). Prior to each catalytic test the sample was reduced in situ in a flow of 10% H₂/N₂. The temperature was increased from 350°C to 550 °C for 40 min and kept at this temperature for 1 h. A reactant gas CH₄/CO₂/N₂ (40/40/60) mixture was used. The reaction was conducted at a temperature of 550°C and CH₄/CO₂ of 1. The reaction products were analyzed in a gas chromatograph equipped with a 3 m HayeSep D 100/120 (SUPELCO) column and a TCD (Damyanova et al., 2012, Pawelec et al., 2007). Conversions of CH₄ and CO₂, and yields of CO and H₂ were calculated by the following equations: $X_{\text{CH}_4}, \% = (C_{\text{CH}_4, \text{in}} - C_{\text{CH}_4, \text{out}}) / C_{\text{CH}_4, \text{in}} \times 100$, $X_{\text{CO}_2}, \% = (C_{\text{CO}_2, \text{in}} - C_{\text{CO}_2, \text{out}}) / C_{\text{CO}_2, \text{in}} \times 100$, $\text{Yield H}_2, \% = C_{\text{H}_2, \text{out}} / 2C_{\text{CH}_4, \text{in}} \times 100$, $\text{Yield CO}, \% = C_{\text{CO}, \text{out}} / (C_{\text{CH}_4, \text{in}} + C_{\text{CO}_2, \text{in}}) \times 100$.

Results and Discussion

The textural properties of Ni/xCe-Al samples are listed in Table 1. The lower surface area of the Ni/Al sample compared to that of Al₂O₃ can be related to a blockage of the alumina pores by Ni oxide species. The S_{BET} of Ni

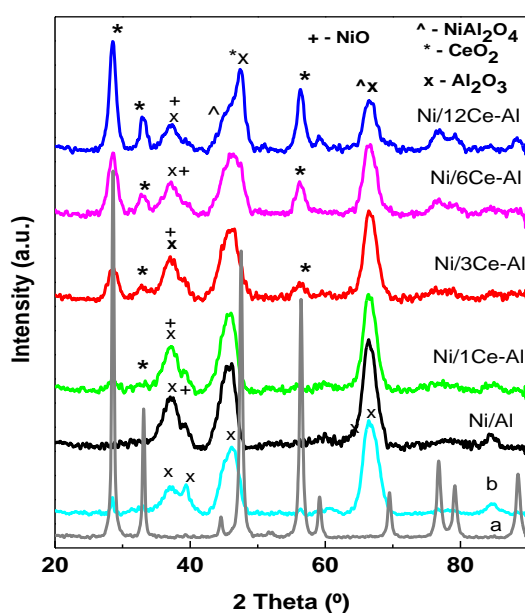
catalysts supported on alumina modified with 1 and 3 wt% CeO₂ is higher compared to that of Ni/Al. The values of the pore volume of the Ni/xCe-Al (x=1, 3 and 6 wt %) samples are also higher than that of Ni/Al. It was reported (Wang et al., 1998) that the increase of S_{BET} can be related to the influence of the low and medium ceria amount on alumina thermal stability.

Table 1. Textural Properties and Crystallite Size (D_{XRD}) of CeO₂ for Calcined Ni/xCe-Al Samples

Sample	S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	Pore diameter (nm)	D _{XRD} (nm)
γ-Al ₂ O ₃	248	0.92	14.6	-
Ni/Al	187	0.55	11.7	-
Ni/1Ce-Al	193	0.66	13.2	-
Ni/3Ce-Al	190	0.70	13.6	5.0
Ni/6Ce-Al	173	0.65	14.2	6.2
Ni/12Ce-Al	158	0.48	12.1	9.3

Indeed the mean pore size of Ni/xCe-Al catalysts is higher than that of Ni/Al (Table 1). This is probably related to the presence of particles with larger pores and a possible blockage of the pores with low diameter, by cerium oxide species (Bereketidou et al., 2012), being confirmed by the pore size distribution of the samples.

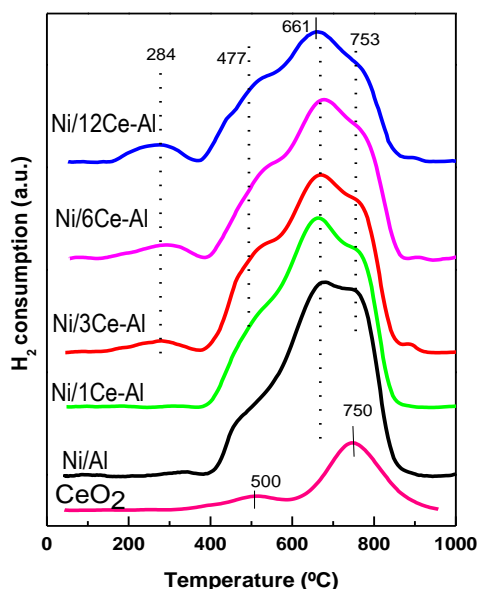
Figure 1. XRD Patterns for CeO₂ (a), Alumina (b) and Calcined Ni/xCe-Al Catalysts



The XRD patterns of pure alumina and calcined Ni/xCe-Al samples are shown in Figure 1. Peaks at $2\theta = 28.2^\circ$, 32.3° , 47.4° and 56.5° , the characteristic of the CeO_2 phase with the fluorite structure, are detectable for all CeO_2 -containing samples. The XRD patterns of poorly crystalline $\gamma\text{-Al}_2\text{O}_3$ ($2\theta = 37.2^\circ$, 47.4° , 66.7°) and/or NiO and NiAl_2O_4 like species ($2\theta = 37.2^\circ$, 43.3° , 45.8° , 66.4° , 76.5° and 79.2°) are observed for the supported Ni samples (Figure 1). The crystallite average size (D_{XRD}) of CeO_2 included in Table 1 is estimated by the $2\theta = 28.6^\circ$ reflection and the application of the Scherrer equation. The D_{XRD} of CeO_2 particles increases with increasing the CeO_2 content due to the ceria capacity to form aggregates (Damyanova et al., 2002).

The TPR profiles of CeO_2 , Ni/Al and Ni/xCe-Al samples are shown in Figure 2. According to the reduction mechanism of the bulk CeO_2 proposed by (Piras et al., 2000) the outermost layers of the smaller crystalline, CeO_2 are first reduced at a lower temperature, due to the lower enthalpy of reduction and then the reduction of bulk ceria occurs. The broad reduction profile of the Ni/Al sample could be divided into three components. According to the literature data (Richardson, et al., 1998), the reduction peak at ca. 465°C should be attributed to the reduction of the small NiO particles in a weak interaction with alumina support whereas, the reduction peaks appearing at higher temperatures of 661°C and 753°C that are related to the reduction of bigger NiO particles and nickel oxide species in a strong interaction with alumina, respectively. Probably, the last peak is due to the reduction of surface non-stoichiometric nickel aluminate spinel (Scheffer et al., 1989).

Figure 2. TPR Profiles of Bulk CeO_2 and Ni/xCe-Al



The addition of a small amount of CeO₂ to Ni/Al, practically, does not change the reductive properties of the sample. However, the intensity and the relative proportion of the peaks change with the increase of the ceria loading (≥ 3 wt%). A new peak at a lower temperature of 285°C, which is more intensive at higher CeO₂ loading, appears. This one could be ascribed to the reduction of the NiO-CeO₂ species (Wang et al., 2008).

The XPS atomic Ni/ (Ce+Al) and Ce/Al ratios of reduced samples are given in Table 2. All calcined samples show the main line of the Ni 2p_{3/2} core electrons at 855.8 eV, indicating the presence of the Ni²⁺ species. The BE value Ni 2p_{3/2} is close to that of the nickel aluminate (856.1 eV) (Jun et al., 2008). The BEs values of Ni 2p_{3/2} at 852.3 and 856.1 eV characterize Ni⁰ and Ni²⁺ ions, respectively. The XPS percentage of metallic nickel on the surface increases in the following order: Ni/12Ce-Al < Ni/6Ce-Al < Ni/3Ce-Al < Ni/1Ce-Al < Ni/Al. It can be concluded that the highest Ni⁰ amount is observed for Ni/Al. A lower BE value of Ni⁰ is observed for the Ni/6Ce-Al sample (851.8 eV), due to a more intimate contact between the ceria and Ni species.

Table 2. XPS Atomic Ratios of Reduced Supported Ni Catalysts, CH₄ Conversions (%) and H₂/CO Ratio in Dry Reforming of Methane at 120 min ($T_{\text{reac.}} = 550$ °C)

Samples	CeO ₂ (wt%)	Ni/(Al+Ce)	Ce/Al	CH ₄ conv. (%)	H ₂ /CO
Ni/Al	-	0.03	-	43.5	0.63
Ni/1Ce-Al	1	0.04	0.007	53.2	0.65
Ni/3Ce-Al	3	0.04	0.009	51.4	0.64
Ni/6Ce-Al	6	0.06	0.009	57.5	0.65
Ni/12Ce-Al	12	0.06	0.010	50.2	0.62

It should be noted that all the reduced samples reveal the XPS Ni/Al ratio values lower than those of the calcined ones caused by the sintering of the surface Ni species. However, the XPS ratio of the samples increases with increasing the CeO₂ loading. This suggests that the reduced/unreduced nickel species has a good surface exposition and a high dispersion on the support surface, thanks to a ceria addition (Table 2). After the reduction of the supported Ni samples at 550°C by 10% H₂/He the fraction of Ce³⁺ species on the support surface is about 25-35 %. In addition, the Ce/Al ratios of reduced samples decrease in comparison with those of the calcined samples.

The values of the CH₄ conversion that over supported the Ni catalysts at a reaction temperature of 550°C are given in Table 2. It is seen that all Ni/xCe-Al catalysts display a higher CH₄ conversion value (~ 50-53 %) than that of Ni/Al (~44 %) at 120 min reaction. Methane conversion follows the sequence: Ni/Al < Ni/12Ce-Al < Ni/3Ce-Al ~ Ni/1Ce-Al < Ni/6Ce-Al. The most active catalyst is Ni/6Ce-Al. The catalytic activity of the Ni/xCe-Al catalysts remains

relatively stable with time on stream. However, a fast deactivation is observed for alumina-supported Ni catalyst.

It has been reported that a loading of 2-5 wt % for a rare earth oxide would be optimum for catalyst activity (Slagtern et al., 1997). A large amount of promoters generally leads to a decrease of catalytic activity due to the coverage of active sites. The catalyst promoted with the highest amount of CeO₂ (12 wt%) has the lowest CH₄ conversion value, as well as the lowest H₂/CO ratio (Table 2). Some covering of the metallic nickel species by cerium oxide species is possible to occur. The results from a physicochemical characterization of the samples show that there is a difference in the amount of metallic Ni species on the catalyst surface with the change of CeO₂ content due to the change in the dispersion and reducibility of supported species (Table 2).

The high activity and stability of the Ni/*x*Ce-Al catalysts in the dry reforming of CH₄ can be related to the redox property of CeO₂-based materials, the high Ni dispersion and the electronic interaction between the ceria and nickel species. It is observed, that the H₂/CO ratios of the catalysts are lower than the stoichiometric one (1:1). The latter is caused by the occurrence of the reverse water - gas shift reaction (CO₂ + H₂ → CO + H₂O).

Conclusions

The results showed that the different nature of Ni - support the interaction in Ni/Al and in modified Ni/*x*Ce-Al catalysts causes a different dispersion and reducibility of nickel, oxide and CeO₂. It was concluded that the optimal interaction between the active metal Ni particles and the oxygen vacancies of the surface of mixed *x*Ce-Al oxides is responsible for the high catalyst activity and stability as a result of the enhanced dispersion of the active metal phase and the resistance to coke formation. The most active Ni/6Ce-Al catalyst with a H₂/CO ratio of 0.65 also showed a high stability with time on stream in CO₂ reforming of CH₄ at 550°C, a high dispersion and specific electron interaction between CeO₂ and Ni particles.

References

- Bellido J.D.A, Assaf E.M. (2009). Effect of the Y₂O₃-ZrO₂ support composition on nickel catalyst evaluated in dry reforming of methane. *Appl. Catal. A: Gen.* 352, 179-187.
- Bereketidou O.A., Goula M.A. (2012). Biogas reforming for syngas production over nickel supported on ceria-alumina catalysts. *Catal. Today* 195, 93-100.
- Damyanova S., Bueno J.M.C. (2003). Effects of CeO₂ loading on the surface and catalytic behaviors of CeO₂-Al₂O₃ supported Pt catalysts, *Appl. Catal. A: Gen.* 253, 135-150.
- Damyanova S., Grange P., Delmon B. (1997). Surface Characterization of Zirconia-Coated Alumina and Silica Carriers. *J. Catal.* 168, 421-430.

- Damyanova S., Perez C.A., Schmal M., Bueno J.M.C. (2002). Characterization of ceria-coated alumina carrier. *Appl. Catal. A: Gen.* 234, 271-282.
- Damyanova S., Pawelec B., Arishtirova K., Huerta M.V.M., Fierro J.L.G. (2008). Study of the surface and redox properties of ceria-zirconia oxides. *Appl. Catal. A: Gen.* 337, 86-96.
- Damyanova S., Pawelec B., Arishtirova K., Fierro J.L.G. (2012). Ni-based catalysts for reforming of methane with CO₂. *Int. J. Hydrogen Energy* 37, 15966-15975.
- Jun J., Dhayal M., J-Shin H., Han Y.H., Getoff N. (2008). Surface chemistry and catalytic activity of Ni/Al₂O₃ irradiated with high-energy electron beam. *Appl. Surf. Sci.* 254, 4557-4564.
- Kambolis A., Matralis H., Trovarelli A., Papadopoulou Ch., (2010). Ni/CeO₂-ZrO₂ catalysts for the dry reforming of methane. *Appl. Catal. A: Gen.* 377, 16-26.
- Kumar P., Sun Y., Idem R.O. (2008). Comparative study of Ni-based mixed oxide catalyst for carbon dioxide reforming of methane. *Energy&Fuels* 22, 3575-3582.
- Pawelec B., La Parola V., Navarro R.M., Murcia-Mascaros S., Fierro J.L.G., (2006). On the origin of the high performance of MWNT-supported PtPd catalysts for the hydrogenation of aromatics. *Carbon* 44, 84-98.
- Pawelec B., Damyanova S., Arishtirova., Fierro J.L.G., Petrov L., (2007). Structural and surface features of PtNi catalysts for reforming of methane with CO₂. *Appl. Catal. A:* 323, 188-201.
- Piras A., Trovarelli A., Dolcetti G. (2000). Remarkable stabilization of transition alumina operated by ceria under reducing and redox conditions. *Appl. Catal. B* 28, 77-81.
- Richardson J.T., Twigg M.V. (1998). Reduction of impregnated NiO/ α -Al₂O₃ association of Al³⁺ ions with NiO. *Appl Catal A: Gen.* 167, 57-64.
- Scheffer B., Molhoek P., Moulijn J.A. (1989). Temperature-programmed reduction of NiO-WO₃/Al₂O₃ catalysts. *Appl. Catal.* 46, 11-30.
- Slagtern A., Olsbye U., Blom R., Dahl I.M. (1997). The influence of rare earth oxides on Ni/Al₂O₃ catalysts during CO₂ reforming of CH₄. *Stud. Surf. Sci. Catal.* 107, 497-502.
- Wang, S., Lu G.O. (Max) (1998). Role of CeO₂ in Ni/CeO₂-Al₂O₃ catalysts for carbon dioxide reforming of methane. *Appl. Catal. B: Envir.* 19, 267-277.
- Wang Y., Zhu A., Zhang Y., Au C.T., Yang X., Shi C. (2008). Catalytic reduction of NO by CO over NiO/CeO₂ catalyst in stoichiometric NO/CO and NO/CO/O₂ reaction. *Appl. Catal B: Envir.* 81, 141-149.
- Yang, R., Xing, C., Lv, C., Shi, L., Tsubaki, N. (2010). Promotional effect of La₂O₃ and CeO₂ on Ni/ γ -Al₂O₃ catalysts for CO₂ reforming of CH₄. *Appl. Catal. A: Gen.* 385, 92-100.