

Proceedings



# Coke-Resistant Rh and Ni Catalysts Supported on γ-Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> for Biogas Oxidative Steam Reforming <sup>+</sup>

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**Abstract:** The depletion of fossil fuels and the growing concerns related to the environmental impact of their processing has progressively switched the interest towards the utilization of biomassderived materials for a large variety of processes. Among them, biogas, which is a CH<sub>4</sub>-rich gas deriving from anaerobic digestion of biomass, has acquired a lot of interest as a feedstock for reforming processes. The main issue in employing biogas is related to the carbon deposition and active metal sintering, which are both responsible for the deactivation of the catalyst. In this work, bimetallic and monometallic Rh- and Ni-based formulations were supported on alumina and ceria with the aim of evaluating their activity and stability in biogas oxidative steam reforming. The Rh addition to the monometallic Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> formulation enhances its catalytic performances; nevertheless, this induces a higher coke deposition, thus suggesting a preferential coke formation on Rh sites. The initial activity of the CeO<sub>2</sub>-supported catalysts was found to be lower than the Al<sub>2</sub>O<sub>3</sub>supported catalysts, but the 5%Ni/CeO<sub>2</sub> sample showed a very good stability during the test and, despite the lower activity, 0.5%Rh-5%Ni/CeO<sub>2</sub> did not show coke deposition. The results suggest that the promotion of Ni/CeO<sub>2</sub> catalysts with other active metals could lead to the selection of a highly stable and performing formulation for biogas oxidative steam reforming.

Keywords: biogas oxidative steam reforming; Rh-Ni catalysts; deactivation study

## 1. Introduction

Biogas is a key component of green technologies which has acquired a growing importance in the renewable energy sources scenario. It is produced via anaerobic digestion of organic matter and its composition strictly depends on the original biomass nature: it is a methane-rich gas, with CH<sub>4</sub> typically in the range 55–65%, also containing CO<sub>2</sub> (35–45%) and trace gases (0–1%), among which H<sub>2</sub>S is one of the main impurities [1]. Due to its composition, it finds a good application as a methane substitute in several processes, first of all methane reforming. However, the presence of CO<sub>2</sub> determines some difficulties and, in particular, it induces a fast and early deactivation of the catalyst. Biogas can be employed in the dry reforming reaction (Equation (1)), but it has several drawbacks such as high endothermicity and a high tendency to coke deposition because of the large number of side equations which can occur [2]. Addition of water and oxygen to the reaction system leads to the biogas oxidative steam reforming reaction, also called tri-reforming of biogas, in which Equations (1)–(3) occur simultaneously.

$$CH_4 + CO_2 \rightleftharpoons 2CO + H_2$$
  $\Delta H_{298K}^o = 247.4 \ kJ \ mol^{-1}$  (1)

$$CH_4 + H_2 \mathbf{0} \leftrightarrow C\mathbf{0} + 3H_2 \qquad \qquad \Delta H_{298K}^o = \mathbf{206} \ kJ \ mol^{-1} \tag{2}$$

$$CH_4 + 1/2 \ O_2 \rightleftharpoons CO + 2H_2 \qquad \Delta H^o_{298K} = -35.6 \ kJ \ mol^{-1}$$
 (3)

The presence of water and oxygen allows regulating the H<sub>2</sub>/CO ratio and, even more importantly, it mitigates the carbon deposition, thus improving the process efficiency and increasing the catalyst lifetime [3,4].

As it is well known, nickel is by far the most employed active metal in catalysts for methane steam reforming: for this reason, its application to biogas reforming processes is a natural consequence. It is a general opinion that high-metal content catalysts undergo deactivation extremely more easily, and for this reason, low-metal content formulations are always preferred; despite that, the activity of low-content Ni catalysts towards the reaction is limited [5]. For this reason, Mg is frequently used as a promoter, while CeO<sub>2</sub> and ZrO<sub>2</sub> or mixed oxides are employed as dopants or supports [6]. In recent studies, rhodium has been selected as a promising promoter for biogas dry reforming (DR) and oxidative dry reforming (ODR) [7,8], while Moral et al. reported that low-content Rh-based catalysts outperformed Pt-based catalysts in the ODR of biogas, thus selecting Rh as the most active noble metal towards the reaction [9].

This work reports the investigation of Al<sub>2</sub>O<sub>3</sub>- and CeO<sub>2</sub>-supported catalysts in which Ni, Rh or their combination are employed as active species in biogas oxidative steam reforming. The work aims to fill the gap in the literature, reporting a detailed study on the activity and stability of mono- and bimetallic formulations, in which the effect of the Rh addition to low-content Ni catalysts is highlighted.

#### 2. Materials and Methods

#### 2.1. Catalysts Preparation and Characterization

In this work, six catalysts were prepared and tested in the biogas oxidative steam reforming reaction. Commercial Al<sub>2</sub>O<sub>3</sub> (provided by Sasol) and CeO<sub>2</sub> (provided by Rhodia) were employed as supports and preventively calcined at 850 °C before the active species deposition. Ni and Rh were deposited via wet impregnation, by preparing a solution of the precursor salt in bi-distilled water: Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and RhCl<sub>3</sub> (both provided by Sigma-Aldrich) were, respectively, employed. For achieving the complete dissolution of RhCl<sub>3</sub> in water, the solution was acidified with HCl until reaching a pH value of 2. Once complete salt dissolution was achieved, the calcined support was added, and the solution was kept stirring until complete evaporation of the solvent; then, the catalyst was dried overnight and calcined at 850 °C for 3 h. In the bimetallic catalysts' preparation, Ni and Rh were deposited in this order in two separate impregnation steps; a calcination step between the first and second wet impregnations was performed. The prepared catalysts with the corresponding nominal loadings are listed in Table 1.

The prepared catalysts were characterized by means of SSA analysis (B.E.T. method), ED-XRF, XRD and TPO. The SSA analysis was performed with a Costech International Sorptometer 1040 by N2 dynamic adsorption at –196 °C. The metal loading of the catalysts was evaluated by an ARL<sup>TM</sup> QUANT'X Thermo Scientific<sup>TM</sup> ED-XRF spectrometer, with a fundamental parameters method: the analyses were performed with the powder catalysts compacted in a pill form (300 mg). The TPO was performed in situ in the reactor at the end of the stability test, with an oxidizing stream (500 Ncc/min, 5% O<sub>2</sub> in N<sub>2</sub>) heating the system up to 1000 °C with a heating rate of 10 °C/min.

#### 2.2. Experimental Apparatus and Procedures

The activity and stability tests were conducted in a tubular reactor (stainless-steel AISI 310, 400 mm long and with an internal diameter of 12 mm), horizontally located in an electric furnace for heat supply. A K-type thermocouple was employed to monitor the temperature at the outlet of the

catalytic bed; in the inlet section, the reactor was equipped with an internal coil for water vaporization. For both the activity and stability tests, 0.5 g of catalysts (particles' dimensions in the range 180–355  $\mu$ m) was loaded in the middle of the reactor, diluted with quartz spheres (500–710  $\mu$ m) up to a volume of 2 cm<sup>3</sup> and held between two quartz wool disks. The product stream was dehydrated in a cold trap (2 °C) and then sent to a mass spectrometer (Hiden Analytical) for a continuous analysis.

The activity tests were carried out a constant temperature (850 and 750 °C) with the feed molar ratios  $CH_4/CO_2 = 1.5$ ,  $O_2/biogas = 0.1$  and  $H_2O/biogas = 0.4$  (where  $biogas = CH_4 + CO_2$ ); space velocity (SV, defined as the ratio between the biogas flowrate and the catalyst mass) was set to 60 NL h<sup>-1</sup>g<sup>-1</sup>. Before each catalytic test, the sample was reduced in situ with a reducing stream (500 Ncc/min, 5%H<sub>2</sub> in Ar), increasing the temperature with a heating rate of 10 °C/min up to 850 °C. Stability tests (time-on-stream, TOS) were carried out at 750 °C with the same feed condition for 24 h. Methane conversion and hydrogen yield were evaluated, respectively, as Equations (4) and (5). TPO experiments were conducted at the end of the TOS tests. With these results, the tendency to form coke for each catalyst was evaluated in terms of coke yield and average rate of coke production (defined as carbon formation rate, CFR), which were evaluated, respectively, according to Equations (6) and (7).

$$X_{CH_4} = \frac{mol_{CH_4,in} - mol_{CH_4,out}}{mol_{CH_4,in}}$$
(4)

$$Y_{H_2} = \frac{mol_{H_2,out}}{mol_{BIOGAS}}$$
(5)

$$Y_C = \frac{mol_C}{mol_{C,fed}} \tag{6}$$

$$CFR = \frac{mass_{coke}}{mass_{catalyst} \cdot mass_{c,fed} \cdot time} \cdot 100$$
(7)

#### 3. Results and Discussion

#### 3.1. Characterization

The specific surface area and metal loading obtained, respectively, via SSA measurement with B.E.T. calculation and ED-XRF analysis are reported in Table 1. From the results of the SSA analysis, it is possible to see the marked difference between ceria- and alumina-supported catalysts; furthermore, a reduction in the surface area is observed when the active metal is deposited on the support. These results were expected, but a peculiar reduction in SSA was observed for Rh-based catalysts: in fact, despite the Rh low loading, its addition determined a strong reduction in the SSA of the samples; this might be due to the acidification of the solution, which could have determined a structural modification of the support.

Table 1. Physical properties for the catalysts and bare supports (all samples calcined at 850 °C).

	Nominal Metal Loading		ED-XRF wt% <sup>b</sup>		SSA m²/g	Yc ⁰∕	CFR
Label	wt% ª						
	Ni	Rh	Ni	Rh		70	(Ingcoke/gcat·gC,ted·II)
10%Ni/Al2O3	10	-	7.897	-	93		
5%Ni/Al2O3	5	-	4.010	-	104	0.010	0.0046
0.5%Rh/Al2O3	-	0.5	-	0.423	96	0.230	0.2629
0.5%Rh-5%Ni/Al2O3	5	0.5	4.125	0.402	91	0.095	0.0793
5%Ni/CeO2	5	-	4.067	-	31		
0.5%Rh-5%Ni/CeO2	5	0.5	4.102	0.399	15		
Al <sub>2</sub> O <sub>3</sub>					113		
CeO <sub>2</sub>					40		

<sup>a</sup>Nominal metal loading is intended as %wt of metal with respect to the support mass. <sup>b</sup>Metal loading from ED-XRF analysis is the %wt with respect to the whole sample mass.

For what concerns the coke production, it is possible to see that 0.5%Rh/Al<sub>2</sub>O<sub>3</sub> was the catalyst which showed the highest and also the fastest coke deposition, followed by 0.5%Rh-5%Ni/Al<sub>2</sub>O<sub>3</sub> and 5%Ni/Al<sub>2</sub>O<sub>3</sub>.

#### 3.2. Activity Tests

The activity tests results are reported in Figure 1. What emerges is that Al<sub>2</sub>O<sub>3</sub>-supported catalysts have a remarkably higher initial activity than CeO<sub>2</sub>-supported catalysts: this requires two separate considerations.

In general, Al<sub>2</sub>O<sub>3</sub>-supported catalysts resulted to be very active and with a good approach to the equilibrium value, with the only exception for the 10%Ni/Al<sub>2</sub>O<sub>3</sub> sample, whose catalytic performances are remarkably far from equilibrium, especially at 750 °C. Nevertheless, comparing the results of the CH<sub>4</sub> conversion and H<sub>2</sub> yield, it is clear that all catalysts showed an almost unitary selectivity at 850 °C and a selectivity exceeding 90% at 750 °C, which are good achievements. The order of activity, which is obtainable from both the CH<sub>4</sub> conversion and the H<sub>2</sub> yield trend, is 10%Ni <5%Ni <0.5%Rh <0.5%Rh <0.5%Rh. Thus, the noble metal has not only a higher activity than Ni, but also contributes to enhance the activity in the bimetallic formulation. The reason for the lower activity of the 10%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst might be addressed to the relatively low specific surface area of the sample (compared to the other Al<sub>2</sub>O<sub>3</sub>-supported catalysts): as a matter of fact, its SSA is comparable to the value obtained for the 0.5%Rh sample, but with a metal loading 20 times higher.

For what concerns the CeO<sub>2</sub>-supported catalysts, the reduced activity can be addressed to the marked low specific surface area, which surely caused a bad dispersion of the active metal on the support surface. Furthermore, the activity even showed a worsening in catalytic activity with the addition of Rh to the formulation. Considering that Rh demonstrated to be a very active metal towards the reaction when supported on alumina, this result has to be necessarily related to the HCl addition to the precursor salt solution during preparation. In fact, the 0.5%Rh-5%Ni/CeO<sub>2</sub> catalyst reported the lowest SSA value, thus leading to a very bad dispersion of the active metals and consequently a poor number of active sites for the reaction.



**Figure 1.** Activity tests results for the Al<sub>2</sub>O<sub>3</sub>-based samples. Operating conditions: SV = 60 NL  $h^{-1}g^{-1}$ ; CH<sub>4</sub>/CO<sub>2</sub> = 1.5, O<sub>2</sub>/biogas = 0.1 and H<sub>2</sub>O/biogas = 0.4.

#### 3.3. Deactivation Study

All catalysts, except for 10%Ni/Al<sub>2</sub>O<sub>3</sub>, were tested in a 24-h time-on-stream experiment in order to evaluate their resistance over time and the eventual coke formation during the reaction. The results of these tests are reported in Figure 2 in terms of methane conversion and pressure drop. The latter was evaluated continuously by means of a pressure indicator, and it gives preliminary information on coke deposition: in fact, an increase in pressure drop means the formation of a solid product, which decreases the void fraction in the catalytic bed. As it is possible to see, 5%Ni/Al<sub>2</sub>O<sub>3</sub> showed a marked deactivation during the test, reaching a stable condition after 12 h with a loss in H<sub>2</sub> yield of

about 26% of the initial value; nevertheless, the unvaried pressure drop suggests a negligible coke deposition on the catalyst. On the other hand, 0.5%Rh/Al<sub>2</sub>O<sub>3</sub> catalysts showed almost constant hydrogen production, but, at the same time, a strong rise in the pressure drop signal after 12 h of reaction: as discussed before, this could be ascribed to the deposition of a consistent amount of coke; in fact, in correspondence to this sharp rise, it was possible to observe a decrease in H<sub>2</sub> yield. The bimetallic sample 0.5%Rh-5%Ni/Al<sub>2</sub>O<sub>3</sub> showed intermediate behavior: an appreciable rise in the pressure drop was observed, but it was not so marked as 0.5%Rh/Al<sub>2</sub>O<sub>3</sub>; and a slight decrease in the catalytic activity was observed, about 4% of the initial value.

The CeO<sub>2</sub>-supported catalysts showed an unvaried pressure drop signal all throughout the experimental test, thus indicating a null coke formation. Nevertheless, the 5%Ni/CeO<sub>2</sub> sample showed a constant activity during the TOS test, while the 0.5%Rh-5%Ni/CeO<sub>2</sub> catalyst showed a consistent deactivation after 8 h. In addition to what was observed for the 5%Ni/Al<sub>2</sub>O<sub>3</sub> sample, also in this case, the deactivation is ascribable to sintering phenomena, which are even more likely to occur considering the very low SSA of the sample. Comparing the behavior of the 5%Ni/CeO<sub>2</sub> at the end of the TOS test, thus indicating that the alumina-supported catalyst is not thermally stable and so the difference observed in the initial activity does not correctly describe the catalytic behavior of the samples.



**Figure 2.** Stability test results for the Al<sub>2</sub>O<sub>3</sub>-based samples. Operating conditions: SV = 60 NL  $h^{-1}g^{-1}$ ; CH<sub>4</sub>/CO<sub>2</sub> = 1.5, O<sub>2</sub>/biogas = 0.1 and H<sub>2</sub>O/biogas = 0.4; T = 750 °C.

The results of the TPO experiments are reported in Figure 3 for the alumina-supported catalysts: CeO<sub>2</sub>-supported samples did not produce CO<sub>2</sub> during the TPO experiment, thus confirming the lack of coke deposition in the catalytic bed; for this reason, these latter profiles are not shown below. As it is possible to see, the results are in agreement with the hypotheses made when observing the pressure drop trends: the sample 0.5%Rh/Al<sub>2</sub>O<sub>3</sub> induced the highest coke formation, while a smaller production was observed on 0.5%Rh-5%Ni/Al<sub>2</sub>O<sub>3</sub>; and a very small quantity of coke was gasified during TPO on the 5%Ni/Al<sub>2</sub>O<sub>3</sub> sample, thus again suggesting metal sintering as a different reason for the catalyst deactivation. Furthermore, these results suggest that coke deposition occurs preferentially on Rh sites rather than Ni ones.



Figure 3. TPO results for the Al<sub>2</sub>O<sub>3</sub>-supported catalysts.

### 4. Conclusions

In this work, a comparative study was performed on Ni- and Rh-based catalysts supported on Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. The experimental results show that the Al<sub>2</sub>O<sub>3</sub>-supported catalysts demonstrated to have a higher catalytic activity towards the reaction; despite that, they are not stable over time because of coke deposition or sintering phenomena. On the other hand, CeO<sub>2</sub>-supported catalysts showed a lower activity but the 5%Ni/CeO<sub>2</sub> sample displayed a very good stability in the TOS test. Due to its good stability and the absence of coke formation, the 5%Ni/CeO<sub>2</sub> sample actually represents a promising catalyst to be promoted with the addition of a second metal, also considering Rh promotion with the employment of a different precursor salt.

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#### References

- Kathiraser, Y.; Wang, Z.; Ang, M.L.; Mo, L.; Li, Z.; Oemar, U.; Kawi, S. Highly active and coke resistant Ni/SiO<sub>2</sub> catalysts for oxidative reforming of model biogas: Effect of low ceria loading. *J. CO<sub>2</sub> Util* 2017, *19*, 284–295, doi:10.1016/j.jcou.2017.03.018.
- Tanios, C.; Bsaibes, S.; Gennequin, C.; Labaki, M.; Cazier, F.; Billet, S.; Tidahy, H.L.; Nsouli, B.; Aboukaïs, A.; Abi-Aad, E. Syngas production by the CO<sub>2</sub> reforming of CH<sub>4</sub> over Ni–Co–Mg–Al catalysts obtained from hydrotalcite precursors. *Int. J. Hydrog. Energy* 2017, 42, 12818–12828, doi:10.1016/j.ijhydene.2017.01.120.
- 3. Song, C.; Pan, W. Tri-reforming of methane: A novel concept for catalytic production of industrially useful synthesis gas with desired H<sub>2</sub>/CO ratios. *Catal. Today* **2004**, *98*, 463–484, doi:10.1016/j.cattod.2004.09.054.
- 4. Chein, R.Y.; Hsu, W.H. Analysis of Syngas Production from Biogas via the Tri-Reforming Process. *Energies* **2018**, *11*, 1075, doi:10.3390/en11051075.
- Izquierdo-Colorado, A.; Dębek, R.; Da Costa, P.; Gálvez, M.E. Excess-methane dry and oxidative reforming on Ni-containing hydrotalcite-derived catalysts for biogas upgrading into synthesis gas. *Int. J. Hydrog. Energy* 2018, 43, 11981–11989, doi:10.1016/j.ijhydene.2018.04.237.
- Zhao, X.; Ngo, H.T.; Walker, D.M.; Weber, D.; Maiti, D.; Cimenler, U.; Petrov, A.D.; Joseph, B.; Kuhn, J.N. Tri-reforming of surrogate biogas over Ni/Mg/ceria–zirconia/alumina pellet catalysts. *Chem. Eng. Comm.* 2018, 205, 1129–1142, doi:10.1080/00986445.2018.1434162.
- Luneau, M.; Gianotti, E.; Meunier, F.C.; Mirodatos, C.; Puzenat, E.; Schuurman, Y.; Guilhaume, N. Deactivation mechanism of Ni supported on Mg-Al spinel during autothermal reforming of model biogas. *Appl. Catal. B Environ.* 2017, 203, 289–299, doi:10.1016/j.apcatb.2016.10.023.

- Roy, P.S.; Song, J.; Kim, K.; Kim, J.; Park, C.S.; Raju, A.S.K. Effects of CeZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> support composition of metal-foam-coated Pd–Rh catalysts for the steam-biogas reforming reaction. *J. Ind. Eng. Chem.* 2018, 62, 120– 129, doi:10.1016/j.jiec.2017.12.050.
- 9. Moral, A.; Reyero, I.; Alfaro, C.; Bimbela, F.; Gandía, L.M. Syngas production by means of biogas catalytic partial oxidation and dry reforming using Rh-based catalysts. *Catal. Today* **2018**, *299*, 280–288, doi:10.1016/j.cattod.2017.03.049.

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