

Low Temperature Methane Steam Reforming: Catalytic Activity and Coke Deposition Study

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Low temperature steam reforming combined with hydrogen-selective membrane offers significant advantages in terms of energy conservation, reduction of GHG emissions and low cost operation. In this study, Ni supported on La/CeO₂-ZrO₂ is evaluated under steam reforming at temperature <550 °C. The catalyst is highly active in steam reforming of methane and water gas shift reaction. Stability test at simulated biogas steam reforming was conducted and the catalyst showed extremely stable performance for long time on stream (90 h) and very low amount of carbonaceous deposits, as determined by TPO and TPH. The above characteristics demonstrate that this catalyst is a potential candidate for use in membrane reactors operating at low temperature for the one-step production of pure hydrogen.

1. Introduction

The increasing hydrogen demand in crude oil refinery and its growing use as energy carrier and storage medium, make its production an important subject in the present and future energy policy. The main route for hydrogen production is steam reforming of natural gas. The conventional process is consisted of a reforming reactor operating at temperature 800 - 1,000 °C followed by a WGS reactor and products separation, resulting in high operation cost and GHG emissions.

An alternative process is proposed, which is based on low-temperature steam reforming (400 - 550°C). As renewable and C-free heat source, concentrating solar power (CSP) plants can be used in conjunction with a mixture of molten nitrates as a heat transfer and storage medium. The utilization of CSP plant as an external heat supplier results in the reduction of GHG emissions (Piemonte et al. 2010) and the molten salts up to 550 °C with a heat storage device can ensure constant-rate solar heat supply for an energy demanding industrial chemical process like the steam reforming of methane (Giaconia et al. 2008). Furthermore, the compact small-scale process proposed offers flexibility to use as primary fuel natural gas, biogas or bioethanol according to local availability. Reforming reactions are carried out in a low-temperature operating reactor, where conversion is enhanced by the use of a hydrogen selective membrane. Thus, H₂ is separated with high purity from the reaction products, and at the same time the shift of the reforming reaction is favoured (Lægsgaard-Jørgensen et al. 1995).

The milder operating conditions of the reforming reactor offer significant advantages since a lower amount of energy is required and as a result operation cost is decreased. Furthermore, compared to the conventional high temperature steam reforming, this low temperature process ensures quick start-up and does not require a CO shift.

The role of catalyst is very important at membrane reforming when hydrogen permeation is faster than the kinetics of the catalyst (Sørensen 2005). Experimental studies of methane steam reforming (Tong and Matsumura 2006) showed that catalytic activity affects methane conversion in a membrane reactor much greater than in a conventional reactor. In addition, the catalyst should be highly active as well as resistant to deactivation factors (Halabi et al. 2010). Carbon formation is favoured at low temperature but also

preferential oxidation (mainly for Ni catalysts) readily occurs and has an even stronger deactivating effect than carbon formation (Matsumura and Nakamori 2004). The latter is enhanced in the presence of a membrane, where H₂-poor and at the same time H₂O-rich gas is in contact with the catalyst. Heat transfer properties of the catalyst are also important to maintain the reactor temperature as high as possible, while pressure drops should be minimized in order to drive the hydrogen permeation through the membrane. In the proposed system pressure drop is minimized and heat transfer is enhanced by the employment of an open foam structure as a support for the catalytic material.

It is well known that both the metal type and the support can contribute to the above characteristic properties of an ideal reforming catalyst (Rostrup-Nielsen et al. 2002). CeO₂ has been applied widely as support for steam reforming of methane and its wide application is attributed not only to the satisfactory thermal and mechanical resistance but mostly to the high oxygen storage capacity. The latter is considered crucial contributing to the removal by oxidation of the carbonaceous deposits formed on the support surface. Under steam reforming conditions, the catalyst is in reduced state which means that oxygen vacancies are present on the surface of ceria. The addition of lanthana into ceria-zirconia mixed oxides enhances the thermal stability of the catalyst (Kundakovic and Flytzani-Stephanopoulos 1998).

Our recent studies in steam reforming of light oxygenates demonstrated that ceria-zirconia support especially when doped with lanthana can result to the minimization of coking deposition thanks to the unique property of ceria to provide active oxygen for the oxidation of carbonaceous deposits (Vagia and Lemonidou 2010). In this study, the performance of Ni catalyst supported on La/CeO₂-ZrO₂ is investigated in low temperature steam reforming. The stability of the catalyst was examined at simulated biogas steam reforming at high pressure and the carbon depositions on the catalyst surface was measured via temperature programmed techniques.

2. Experimental

The wet impregnation method was applied for the catalyst's preparation. Ceria and lanthana doped zirconium oxide (78 % ZrO₂, 17 % CeO₂ and 5 % La₂O₃) provided by Mel Chemicals (XZO1768) was used as the support. Ni(NO₃)₂·6H₂O was used as a precursor for nickel (10 wt%). The aqueous solution of the precursor was mixed with the support particles and stirred for 1 h at 70 °C. The solvent was removed via evaporation under mild vacuum conditions and the sample was dried overnight at 110 °C. The catalytic material was calcined in air flow at 800 °C for 5 h. The catalytic material is referred to as Ni(x)CeZrLa (where x is the metal wt%).

X-ray diffraction and nitrogen adsorption isotherm techniques were used for the identification of crystal phases and the determination of the surface area. Temperature Programed Reduction (TPR) experiments were performed in a gas flow system using a U-tube reactor connected online with a quadrupole mass analyzer (Omnistar). The catalyst sample (100 mg) was placed in the reactor and pretreated for 0.5 h at 250 °C followed by cooling at room temperature in He flow. The temperature was then raised from ambient to 800 °C at a rate of 10 °C/min in a 10% H₂/He flow (50 mL/min).

The metal dispersion was measured with H₂ temperature-programed desorption (TPD-H₂). Using the same flow system as mentioned above the catalysts (200 mg) were treated at 500 °C for 0.5 h under 20 % O₂/He and then reduced with 20 % H₂/He for 1.5 h at the same temperature. After reduction, the sample was heated at 600 °C in He flow to desorb any H₂ that might have been spilled over the support. A flow of 10 % H₂/He was applied as the temperature decreased to ambient and remained under these conditions for 0.5 h, followed by He flow for another 0.5 h. The TPD analysis was carried out from room temperature to 800 °C in a heating rate of 10 °C/min. In order to calculate the amount of H₂ desorbed, the peak area was compared to that obtained when known amount of H₂ was pulsed.

The catalytic evaluation experiments were performed at atmospheric pressure in a laboratory unit equipped with a mass flow-controlled system for gases admission, a fixed bed quartz reactor, and an online gas chromatograph. An UFLC pump (Shimadzu) was used for the feeding of water to the reactor through a preheater. The fixed bed reactor was heated electrically by a tubular furnace, with three independently controlled temperature zones. The temperature in the middle of the catalytic bed was measured with a coaxial thermocouple. The hot gases exiting the reactor were cooled to condense the unreacted steam. The gas phase products were analyzed with an online gas chromatograph (Agilent Technologies 7890A) equipped with a TCD. The reaction tests were conducted at temperatures from 400 to 550 °C with GHSV in the range 30,000 - 70,000 h⁻¹ and pressure 0.1 MPa. Undiluted feed of CH₄ and H₂O at 1/3 molar ratios were admitted to the catalyst bed. The time on stream activity of the catalyst was also tested in experiments conducted for 5, 50 and 90 h at 500 °C and 0.7 MPa. This test was performed using as feed simulated biogas in a molar ratio H₂O/CH₄/CO₂ of 3/1/1 and GHSV of 30,000 h⁻¹.

Coke depositions after long time on stream tests were characterized in the flow system equipped with the mass analyzer via temperature programmed oxidation and hydrogenation. In both techniques, 30 mg of the used catalyst were pretreated at 250 °C for 0.5 h in He flow and allowed to cool. The samples were heated in the rate of 10 °C/min to 850 °C in a flow of 15 mL/min of oxidation gas (20 % O₂/He) or hydrogenation gas (80 % H₂/He). Quantification analysis of the carbonaceous species was realized by the amount of produced CO₂ and CH₄.

3. Results and Discussion

The characteristic properties of the prepared catalyst are shown in Table 1. The impregnation of the metal on the support does not affect the specific surface area which decreases from 54.9 m²/g to 37.2. The dispersion of Ni is very low, probably due to the strong metal-support interaction (Biswas and Kunzru 2007) and the high content on the catalyst.

Table 1: Characteristic properties of the catalysts.

Catalyst	Metal Loading (wt %)	Support Composition	Specific Surface Area (m ² /g)	Metal Dispersion (%)
ZrCeLa (support)	-		54.9	-
Ni(10)ZrCeLa	Ni-10	78% ZrO ₂ 17% CeO ₂ 5% La ₂ O ₃ ,	37.2	0.75

The diffraction pattern of the catalyst is shown in Figure 1. The characteristic peaks of the Zr_{0.84}Ce_{0.16}O₂ crystal phase of the support are present, while no peaks for La₂O₃ are observed implying that it is finely dispersed or in an amorphous state. NiO characteristic peaks are also present.

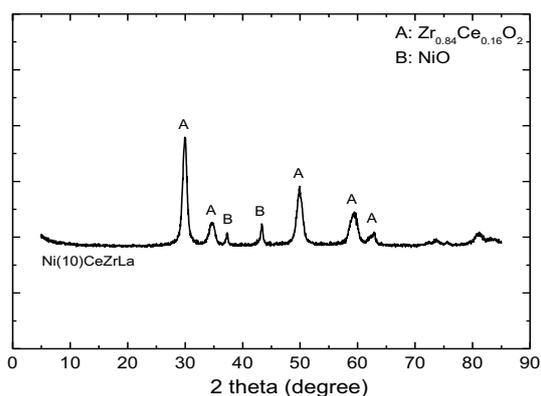


Figure 1: X-Ray diffraction pattern of Ni(10)CeZrLa.

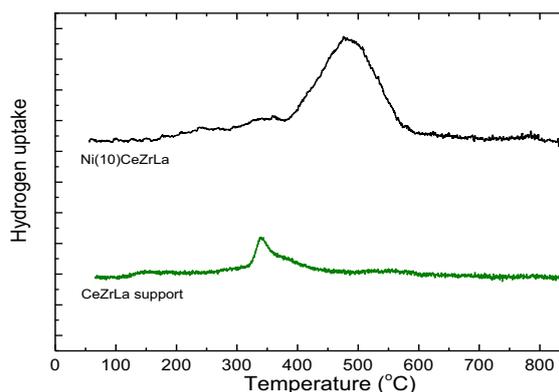


Figure 2: TPR profiles of Ni(10)CeZrLa, and the support.

Figure 2 depicts the results of the temperature programmed reduction of the support and the Ni-based catalyst. In the TPR profile of the support maximum H₂ consumption occurs at 340 °C which is attributed to the partial reduction of CeO₂ of the CeO₂-ZrO₂ mixed oxide. In the TPR profile of the Ni-based catalyst, a main reduction peak is observed with maximum H₂ consumption at 445 °C, which stands for the reduction of NiO species to metallic Ni. In addition, a shoulder in the temperature range of 300 - 400 °C is observed probably due to the reduction of the support. It should be emphasized that in low temperature operating systems, the ability of the catalyst to be reduced in the same temperature range, offers significant advantage since no further heating of the reactor is required.

The catalyst after reduction was tested in steam reforming at the temperature range of 400 - 550 °C applying CH₄ and steam in molar ratio of 1/3. The composition on dry basis of the reactor exit stream is presented in Figure 3. It is clear that the catalyst is very active in methane reforming even at such low temperatures. For the space velocity of 30,000 h⁻¹ and temperatures higher than 450 °C the composition agrees with the thermodynamic equilibrium (dashed lines). Higher space velocities as expected remove the system from equilibrium.

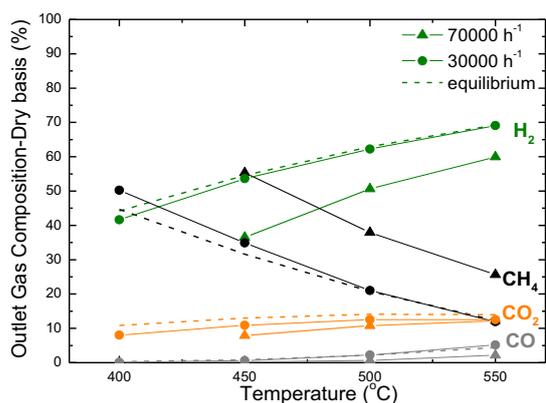


Figure 3: Activity tests over Ni(10)CeZrLa. Methane feed, $P=0.1$ MPa, $H_2O/CH_4=3$

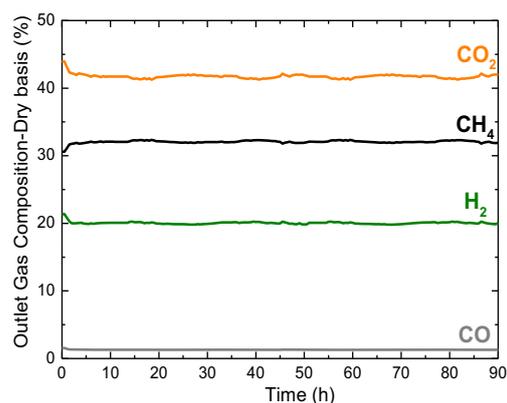


Figure 4: Stability of Ni(10)CeZrLa. Simulated biogas feed, $P=0.7$ MPa, $H_2O/CH_4/CO_2 = 3/1/1$.

More specifically, at GHSV of $70,000\text{ h}^{-1}$ and temperature of $450\text{ }^\circ\text{C}$, a conversion of 15.2 % (50 % of equilibrium predicted) is obtained. In these conditions, the turnover frequency is calculated as 2.57 s^{-1} . Very few studies of the reforming of methane at low temperature in the literature report the turnover frequencies of the reaction. Ligthar et al. (2011) studied methane steam reforming at $500\text{ }^\circ\text{C}$ over Rh/Ce_{0.25}Zr_{0.75}O₂ and the turnover frequency was found 11.5 s^{-1} , while no respective value was found for Ni-based catalyst. As evidenced by the very low concentration of CO in the reactor exit stream (<5 % CO), the catalyst is also very active in WGS reaction. As a result the catalyst reported in this work is promising candidate for application in membrane reactor, since CO is the most important poison of the membrane.

The stability of the catalyst was checked under steam reforming conditions of simulated biogas ($H_2O/CH_4/CO_2 = 3/1/1$) at $500\text{ }^\circ\text{C}$ and 0.7 MPa for 5, 50 and 90 h. No loss in activity even after 90 h TOS (Figure 4) was observed. The stability can be ascribed to lanthana dopant, known for its thermal stabilization effect, and to the low affinity for coking. The high mobility of oxygen formed from the decomposition of H_2O and/or CO_2 on the support surface and its diffusion through ceria facilitates the oxidation of any carbonaceous deposits formed (Vagia and Lemonidou 2010).

In order to investigate further the carbon deposition, the used samples of the Ni-based catalyst after the stability tests described above at different reaction time were analyzed by Temperature Programmed Oxidation (TPO) and Hydrogenation (TPH) techniques. The amount of coke was calculated based on the CO_2 and CH_4 produced respectively and the results are tabulated in Table 2.

Table 2: Quantification of deposited carbon determined by TPO and TPH.

TOS (h)	C wt% on catalyst (TPO)	C wt% on catalyst (TPH)
5	0.08	0.08
50	0.12	0.08
90	0.05	0.06

The results of the two techniques are in perfect agreement. The total amount of carbon on the catalyst surface was 0.08 % wt during the first 5h on stream and was maintained at such low level even after 90 h on stream. The fact that the amount of carbon deposited is not increased with the reaction time indicates that the carbon species formed are active and their production and consumption rates are equilibrated as the reaction proceeds.

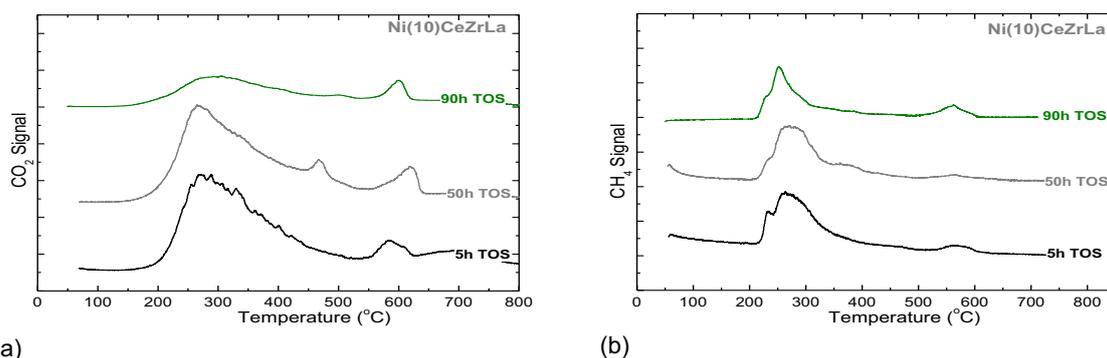


Figure 6: Removal of carbon species by temperature programmed techniques. (a) TPO and (b)TPH

The TPO and TPH profiles of the used samples are presented in Figure 6 (a) and (b) respectively. Both techniques confirm that not only the amount of carbon formed remains unchanged with the increase in reaction time, but its nature as well. Two main peaks are observed, in both techniques, which are attributed to two types of carbon species with different reactivity towards the reaction gas. The first type, which corresponds to more than 85 % of the total carbon, is oxidized at the temperature range of 200 - 500 °C ($T_{\text{max,ox}} = 300$ °C) and hydrogenated at the temperature range of 200 - 400 °C ($T_{\text{max,hyd}} = 270$ °C). The reactivity of this type of carbon at low temperature implies its oligomeric nature (Rostrup-Nielsen, Sehested & Nørskov 2002). The second type is oxidized at the temperature range of 550 - 650 °C ($T_{\text{max,ox}} = 600$ °C) and hydrogenated at 530 - 610 °C ($T_{\text{max,hyd}} = 580$ °C). This type of carbon species could be formed through Boudouard reaction.

Of great interest for an industrial application is the fact that during hydrogenation (using part of the H₂ production stream) more than 85 % of the deposited carbon is removed at temperature below 500 °C and at the same time the catalyst is maintained at reduced state. However, in an industrial application the catalyst is exposed to natural gas or biogas, also containing impurities that could significantly affect the performance of the catalyst. The presence of sulfur-containing compounds and higher hydrocarbons in the gas feed will be considered in our future investigations.

4. Conclusions

Nickel supported on lanthana modified ceria-zirconia is very active catalyst for methane steam reforming achieving thermodynamic equilibrium at low reaction temperature <550 °C and very high space velocities. The Ni-based catalyst showed extremely stable performance for long time on stream at simulated biogas steam reforming conditions and the low amount of coke formation demonstrated that this catalyst is a potential candidate for use in membrane reactors operating at low temperature for the one-step production of pure hydrogen.

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