

Time-on-Stream Stability of New Catalysts for Low-Temperature Steam Reforming of Biogas

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Time-on-stream stability of six different steam reforming catalysts has been tested at 500 °C under a simulated biogas feed. The catalysts are based on different combinations of Ni, Pt and Rh as active species, and CeO₂, ZrO₂ and La₂O₃ as support. In order to perform a conservative analysis, biogas was simulated with a 50 % v/v CO₂-CH₄ mixture; furthermore a steam to methane ratio as low as 2.5 has also been used. All the samples containing CeO₂ in the support proved fairly stable up to 50 h on stream. Therefore, these catalysts are worth being further investigated to assess their activity and determine appropriate reaction rate expressions.

1. Introduction

In the perspective of introducing hydrogen as an energy carrier, existing hydrogen production technologies should be improved or new solution developed in order to accommodate changing patterns in the use of primary energy sources. More specifically, such technologies should be able to operate by using an integrated energy mix, including both renewable and fossil sources.

Steam reforming (SR), which is the most commonly used and mature process for hydrogen production, offers this possibility. Indeed, SR can be carried out both on a fossil fuel such as natural gas, with very high methane content, and a renewable fuel such as biogas, which can contain carbon dioxide up to 50 % on a molar basis.

Conventional steam reforming processes are carried out at temperatures above 700 °C in externally heated tubular reactors. The necessary heat input is provided by placing the reactors inside fossil fuel furnaces. Several economic and environmental advantages could be obtained by lowering the operating temperature below 600 °C; among these are: the use of lower grade materials, reduced overall process heat requirements and the possibility to provide the heat of reaction with carbon-neutral concentrated solar power (CSP) plants, using a low-cost, environmentally friendly mixture of molten salts as heat transfer fluid (Giaconia et al., 2008).

However, several issues must be faced in order to carry out steam reforming processes below the conventional operating temperature range. Firstly, the catalysts used must have a high activity in order to ensure a sufficient reaction rate. Furthermore, especially if biogas SR is considered, lower operating temperatures increase the risk of carbon formation on the catalyst: this can clearly be seen in Figure 1, which shows a map of the conditions leading to coke formation at thermodynamic equilibrium for a CH₄-CO₂-H₂O feed with a molar ratio CO₂/CH₄=1. Carbon formation, together with other phenomena such as preferential oxidation, mainly for Ni catalysts (Matsumura and Nakamori, 2004), can cause catalyst deactivation. It is therefore clear that stability, which is in general a desired feature for a catalyst, becomes even more important when dealing with low-temperature biogas reforming.

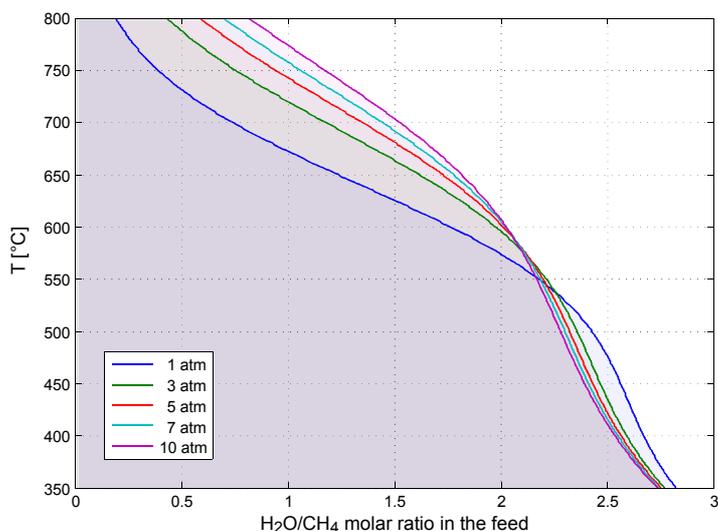


Figure 1: Map of conditions leading to carbon formation at equilibrium for a $\text{CH}_4\text{-CO}_2\text{-H}_2\text{O}$ mixture with molar ratio $\text{CO}_2/\text{CH}_4=1$. The shaded area corresponds to solid carbon formation.

In this work, the time-on-stream stability of six different catalysts has been tested at 500 °C while performing steam reforming of a simulated biogas stream up 50 h. The catalysts that have been analysed are based on different combinations of Ni, Pt and Rh as active species, and CeO_2 , ZrO_2 and La_2O_3 as support.

All the catalysts considered in this work were previously tested for low-temperature methane SR at the same temperature, showing very good activity and stability. However, due to the higher carbon content, biogas is more prone to carbon formation, and therefore catalyst deactivation than methane (Annesini et al., 2007).

In order to perform a conservative analysis, biogas was simulated with a 50 % v/v $\text{CO}_2\text{-CH}_4$ mixture, which can be considered as the maximum CO_2 concentration in biogas; furthermore a steam to methane (S/C) molar ratio as low as 2.5 has also been used.

All the catalyst samples containing CeO_2 in the support showed a fairly constant hydrogen outlet molar fraction, thus proving to be stable and worth being further investigated to assess their activity and determine appropriate reaction rate expressions. On the other hand, the catalyst samples not containing CeO_2 showed an appreciable decay in their performance during the test. This result suggests that CeO_2 plays an important role in catalyst stability.

This work is part of the activities of the CoMETHy project, which is aimed at developing an innovative compact and modular steam reformer to convert reformable fuels (methane, biogas, ethanol, etc.) to pure hydrogen, by using several heat sources (solar, biomass, fossil, refuse derived fuels, etc.), depending on the locally available energy mix.

Table 1: List of catalysts tested

ID	Sample name	Active Specie/s - load wt%	Support
1	Ni(10)CeZrLa	Ni-10	78 % ZrO_2 17 % CeO_2 5 % La_2O_3
2	Rh(1)ZrCeLa	Rh-1	78 % ZrO_2 17 % CeO_2 5 % La_2O_3
3	Ni(10)ZrLa	Ni-10	90 % ZrO_2 10 % La_2O_3
4	Rh(1)ZrLa	Rh-1	90 % ZrO_2 10 % La_2O_3
5	10Ni/ CeO_2	Ni-10	CeO_2
6	3Pt10Ni/ CeO_2	Pt-3, Ni-10	CeO_2

Table 2: Summary of operating conditions used in the experimental tests

Parameter	Units	Values
Feed: simulated biogas	-	-
CO ₂ /CH ₄ molar ratio	-	1
H ₂ O/CH ₄ molar ratio	-	2.5 ; 3
GHSV	h ⁻¹	30,000
Pressure	atm	1 ; 7
Temperature	°C	500

2. Experimental

2.1 Catalysts

Table 1 lists the catalysts tested toward biogas SR. Catalysts from 1 to 4 were synthesized and supplied by Aristotle University of Thessaloniki (Greece), while catalysts 5 and 6 were synthesized and supplied by University of Salerno, Dept. of Industrial Engineering (Italy).

All the catalyst samples were received as fine powders. In order to uniform the particle-size, before being tested the powders were pelletized in thin slabs of about 1.5 cm diameter and 2 mm height. Subsequently, the slabs were crushed and sieved to recover the fraction with a particle-size in the range 255-350 μm, which was used in the stability tests.

2.2 Experimental apparatus and procedure

The catalysts samples were tested in a stainless steel fixed bed-tubular reactor with an inner diameter of 8 mm placed inside a ceramic oven. In each test, 400 mg of catalyst powder were loaded on a stainless steel microporous plate placed inside the reactor. Before starting the stability test, the catalyst was reduced with 10 % H₂/N₂ for about 1 h at the temperature of 550 °C. The reaction temperature was measured by means of a thermocouple placed at the reactor axis, on the upper surface of the catalyst bed; temperature control was obtained by regulating the power of the oven.

During the stability tests, the gaseous reactants were fed from the top of the reactor; the flow rate and the composition of the inlet feed stream was controlled and monitored through a mass flow controller for each component. Liquid water was vaporised and mixed with the gaseous CH₄/CO₂ stream before entering the reactor.

The reactor outlet stream was firstly sent to a condenser to remove water and then analysed with an Advance Optima 2000 (ABB, Zurich, Switzerland) continuous industrial process to measure and record H₂ molar fraction (dry basis).

The P&ID diagram of the experimental setup is reported in Figure 2.

Each stability test was carried out by keeping the catalyst sample on stream up to 50 h. For one of the tested catalyst Ni(10)/CeZrLa catalyst, that seemed to show the best performance in terms of activity, the stability tests were repeated also for 90 h.

A summary of the operating conditions used in the experimental tests is reported in Table 2. The conditions apply to all catalysts, except for the H₂O/CH₄ molar ratio 2.5, which has been used only for Ni(10)CeZrLa.

3. Results and discussion

The hydrogen molar fraction (dry basis) in the reactor outlet stream measured during a set of selected tests is reported in Figures 3 to 6.

Figure 3 and 4 report the results of tests performed at atmospheric pressure on catalyst 4 (Rh(1)ZrLa) and 3 (Ni(10)ZrLa). These catalysts showed a progressive decrease in their activity during the test, which is apparent from the reduction of hydrogen concentration in the reactor gas outlet. Indeed, for Ni(10)ZrLa (Figure 4), the test was stopped after only 35 h on stream since the hydrogen molar fraction had already decreased by about 30 %.

On the other hand, the remaining 4 catalysts proved fairly stable in atmospheric pressure tests (data not reported) and also when tested at a pressure of 7 bar (Figure 5).

In order to understand the cause of the lower stability of Rh(1)ZrLa and Ni(10)ZrLa compared to the other samples tested in this work, it is interesting to note that these two catalysts are the only ones not containing CeO₂ in their support. Compared to the other oxides used here as supports, CeO₂ has a

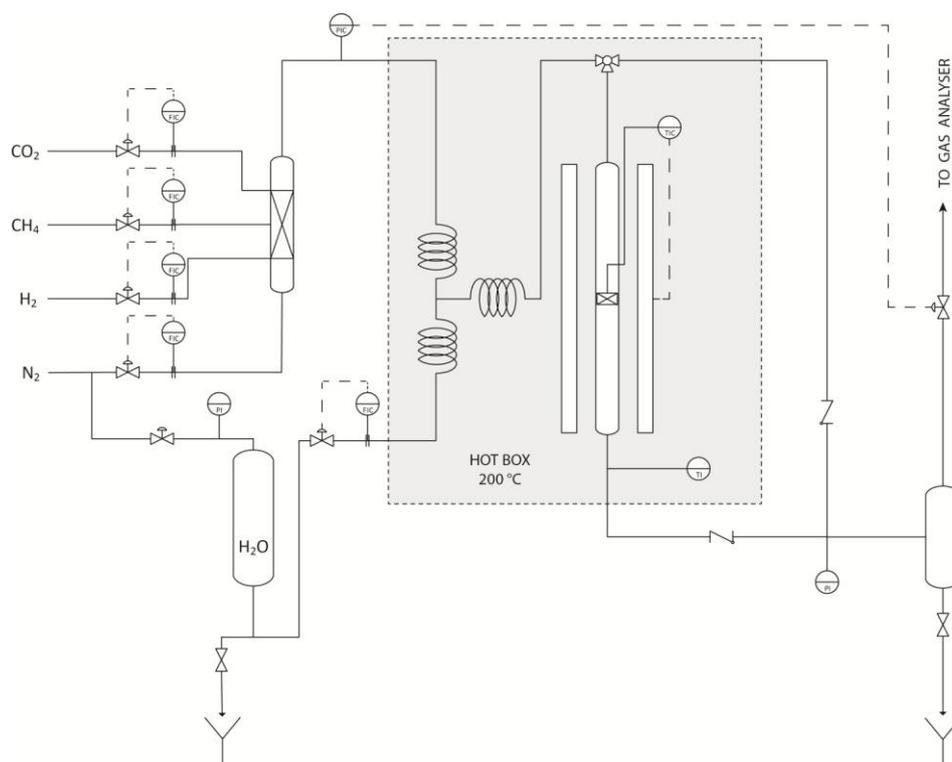


Figure 2: P&ID of the experimental setup.

particular oxygen storage and release (OSC) capacity, which allows to provide active oxygen for the gasification of carbonaceous deposits: this feature has previously been highlighted in catalysts for steam reforming of other feedstocks such as acetic acid (Vagia and Lemonidou, 2010) and ethanol (Ciambelli et al., 2010). Therefore, the deactivation of Rh(1)ZrLa and Ni(10)ZrLa could be ascribed to coke formation. Another experimental evidence that suggests the same conclusion is that Rh(1)ZrLa and Ni(10)ZrLa proved stable in tests carried out at the same pressure, temperature and S/C ratio, but with a CO₂-free, CH₄-H₂O feed, which is less prone to carbon formation.

Even if catalyst activity is beyond the scope of this paper, the experimental results shown here have identified Ni(10)CeZrLa as the catalyst with the best performance in terms of hydrogen production; additionally, the literature reports that lanthana into ceria-zirconia mixed oxides enhances the thermal stability of the catalyst (Bernal et Al, 1997). These considerations indicate Ni(10)CeZrLa as one of the most interesting among the catalysts tested here.

Therefore Ni(10)CeZrLa was selected to be tested under further, more challenging conditions:

- Lower steam-to-carbon ratio (2.5)
- Longer time-on-stream (90 h)

Figure 6 compares the results obtained with Ni(10)CeZrLa by using S/C=3 and S/C=2.5, all other operating conditions being equal. No effect on stability due to the reduction of the S/C ratio is observed, although, as shown by the curves of Figure 1, it is evident that at 500°C and S/C=2.5 the risk of carbon formation is higher. It is worth noting that industrial reformers are usually operated with S/C≥3, which is higher than requested by the reaction stoichiometry (S/C=2), both to promote methane conversion and prevent catalyst deactivation due to coke formation. However, if safe and efficient operation were possible with lower S/C, important energy savings could be obtained.

As for the 90 h stability test, the data are not reported here, but the hydrogen molar fraction in the reactor outlet stream kept fairly constant throughout the experimental run, thus confirming the stability of the catalyst even for a longer time-on-stream.

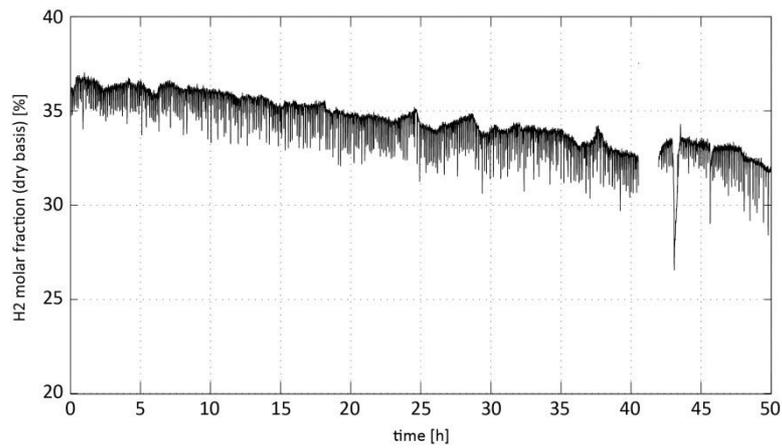


Figure 3: Stability test for Rh/LaZr, (simulated biogas feed, 1 bar, 500 °C, 30,000 h⁻¹, S/C = 3)

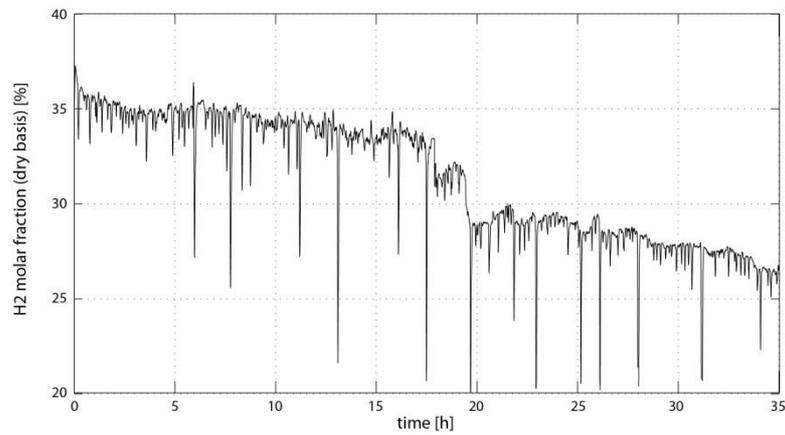


Figure 4: Stability test for Ni/LaZr, (simulated biogas feed, 1 bar, 500 °C, 30,000 h⁻¹, S/C = 3)

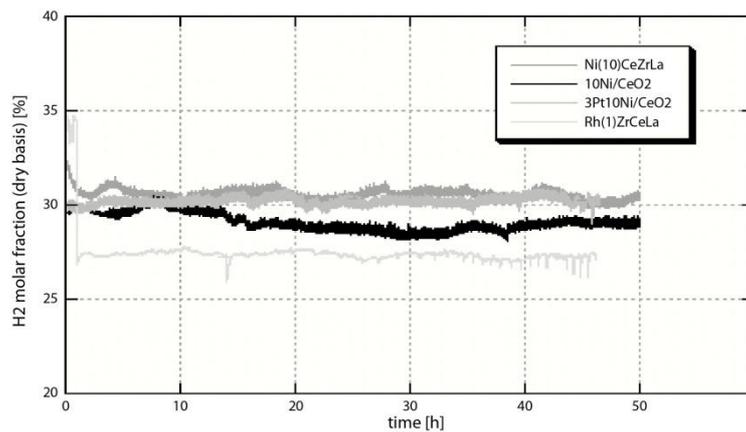


Figure 5: Stability test for Ni/CeLaZr, Rh/CeLaZr, Ni/CeO₂, PtNi/CeO₂ (simulated biogas feed, 7 bar, 500 °C, 30,000 h⁻¹, S/C = 3)

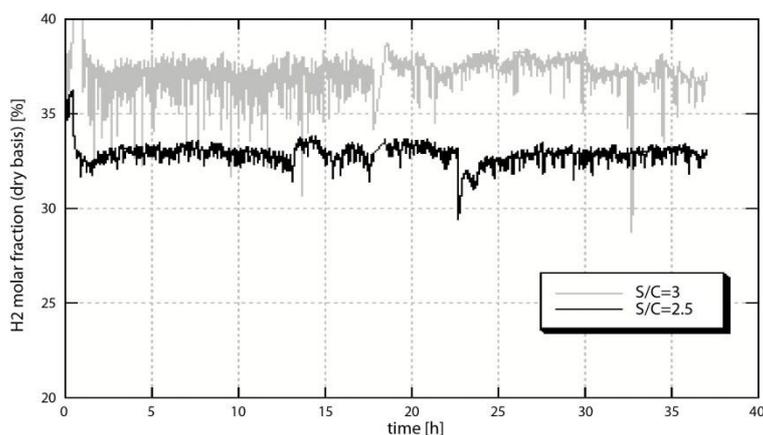


Figure 6: Stability test for Ni/CeLaZr, at different S/C=2.5 and S/C=3 (simulated biogas feed, 1 bar, 500 °C, 30,000 h⁻¹)

4. Conclusions

Four out of the six catalysts tested proved fairly stable up to 50 h on stream under biogas reforming conditions and are worth being further investigated to determine appropriate kinetic expressions.

Especially, the experimental results showed the eligibility of these catalyst to work in more challenging operating conditions compared to the conventional methane steam reforming processes: higher CO₂ concentration in the feed (more prone to carbon formation due to the higher carbon content), lower temperatures and S/C were used, thus increasing the risk of carbon formation.

As for the catalysts that underwent deactivation during the tests, the results obtained suggest that the cause for the lower stability is related to the lack of CeO₂ in the catalyst support, which provides a higher stability due to its greater ability to store and release oxygen for the gasification of carbonaceous deposits.

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