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ARTICLE

High-throughput assessment of catalyst stability during autothermal reforming of model biogas

Cite this: DOI: 10.1039/x0xx00000x

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Received
Accepted

DOI:

www.rsc.org/

The long-term stability of Ni-based catalysts for autothermal reforming of model biogas has been assessed in a six parallel-flow reactor implemented to test simultaneously six different catalysts at 700°C under a feed consisting of 42% H₂O, 14% CH₄, 9% CO₂, 7% O₂ in argon. The reproducibility of catalyst performances measured in the 6 parallel reactors was ascertained using a commercial Ni-based catalyst. A screening of 12 catalyst formulations identified 5-0.05 wt.% Ni-Rh/MgAl₂O₄ as a robust catalyst for autothermal reforming of model biogas over 200 h time-on-stream.

Introduction

Biogas is a complex gas mixture produced from the anaerobic digestion of biomass, which contains methane and carbon dioxide as main components [1]. Biogas can be combusted directly, though exhibiting a lower heating value than natural gas. Biogas can also be reformed into hydrogen, which is a base feedstock for the chemical industry and can also be used as a fuel in fuel-cells to produce electricity [2].

Since biogas contains essentially methane and carbon dioxide, the dry reforming (DR) of methane (Eq. 1) is an obvious pathway to produce syngas:



Yet, this reaction is strongly endothermic and must be conducted at high temperatures (800-900°C), whereas the CH₄/CO₂ ratio in biogas (generally closer to 1.5 than to 1) is not suitable for complete methane conversion. Methane can also be converted into syngas by steam reforming (SR, Eq. 2):



SR is also an endothermic reaction but yields more hydrogen than DR. SR limits carbon deposition and steam is generally introduced in excess in order to shift the water-gas shift equilibrium (Eq. 3) towards more H₂ and less CO production at the reactor outlet.

Water-gas shift (WGS):



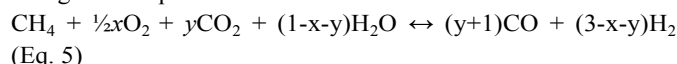
Partial oxidation is a slightly exothermic reaction, actually the result of two consecutive reactions: first the highly exothermic combustion of methane at the beginning of the catalyst bed, followed by steam and CO₂ reforming of the remaining methane and the WGS reaction.

Catalytic Partial Oxidation (CPO):



Autothermal reforming (ATR) is seen as a practical option to minimize energy supply to the reactor. ATR consist of adding oxygen (or air), which results in combustion of a part of the methane into carbon dioxide and water followed by reforming and WGS reactions.

The general equation for ATR is:



in which the O₂/CH₄ ratio has to be adjusted to reach the thermal balance between exothermic and endothermic reactions. According to thermodynamic calculations (HSC chemistry software) formation of CO and H₂ by steam and dry reforming is favored at temperature above ca. 630°C.

Catalytic reforming of methane has been widely studied and carried out using different catalysts. Few studies have focused on biogas. The most commonly used catalysts are nickel- and noble metal-based catalysts (Ru, Rh, Pd, Ir, Pt) [3][4]. Nickel-based catalysts are often used because those combine low cost and acceptable catalytic activity. The main issues with nickel are the deactivation caused by deposition of carbon and/or

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sintering of metal particles [5][6]. Noble metals, notably Pt and Ir, are more active than Ni [7]. Noble metals present better performances since they are less prone to oxidation, coking and sintering [8], but are more expensive and hence not the preferred option. Furthermore, the nature of the catalyst supports and metal-support interaction may play a significant role in the catalytic activity. Alumina is widely used as a support. However, the nickel spinel phase (NiAl_2O_4) can be formed at high temperature during the reforming reaction. NiAl_2O_4 is inactive and its formation leads to a faster deactivation [9][10]. Therefore, supports have been designed in order to prevent coking and oxidation. Incorporation of basic alkali-earth metals such as Mg and Ca into Al_2O_3 -based catalysts has been carried out in order to improve both stability and activity [11][12][13]. Other supports exhibiting oxygen mobility properties were studied in order to promote the gasification of deposited carbon [14–16].

Biogas composition varies depending on the origin of the biomass. Although mainly composed of methane and carbon dioxide, biogas typically contains also sulphur compounds [17]. H_2S presence is a major problem due to its irreversible poisoning effect on metals [18]. Biogas can also contain volatile organic compounds such as chlorinated compounds. Methyl chloride was shown to impact on the H_2/CO ratio by increasing the surface acidity of the alumina support [19]. Model biogas composed of clean methane and carbon dioxide (60:40 vol:vol) was used in our study.

Many catalysts have been tested for methane or biogas reforming with different combinations of active metals on various supports [20]. However, these tests were performed under different conditions of temperature and pressure with different feed ratios, flow rates and reactor designs, making a fair comparison difficult.

High-throughput catalyst testing has become a widely accepted tool in catalyst development. However, it is mainly used in the screening and discovery of new catalysts formulations [21], [22], less commonly to characterize specific catalyst properties [23] or long-term performances. On the other hand, this technology is hardly reported for the study of long-term catalyst stability. This is rather surprising as an obvious gain in time can be obtained for these kind of tests, compared to testing each sample separately.

In the present study, long-term catalyst stability was assessed using a six parallel-flow reactor, specially implemented to test simultaneously six catalysts under essentially identical flow rate, temperature and feed composition. Four types of supports were investigated: spinels, mixed oxides, perovskites and hydrothermal-type precursors. The supports were impregnated with the same nickel amount and tested under similar conditions.

Experimental

Catalyst preparation

Magnesium spinel (MgAl_2O_4) was prepared by co-precipitation. An aqueous solution containing Mg and Al

nitrate (Sigma-Aldrich and Fluka) with a Al:Mg molar ratio of 2:1 (concentrations of 0.66 and 0.33 mol L^{-1} respectively) was added drop by drop into an aqueous solution of ammonium carbonate (Sigma-Aldrich) under vigorous stirring. The ammonium carbonate solution was prepared in order to contain large excess of carbonates, ensuring precipitation of all the metallic cations. The precipitate was aged for 3 h at room temperature. After centrifugation and washing with de-ionized water, the powder was dried overnight at 120°C. The dry deposit was then calcined at 800°C for 5 h in air.

The same procedure was applied to synthesize ZnAl_2O_4 spinel, using nitrates of Al and Zn (Sigma-Aldrich) with a Al:Zn molar ratio of 2:1.

LaAlO_3 was prepared by a modified sol-gel method (Pechini). Ethylenediaminetetraacetic acid (EDTA, Sigma-Aldrich) was added to an aqueous solution containing the metal nitrates (concentration of 0.5 mol L^{-1} , Sigma-Aldrich) with a La:Al molar ratio of 1:1. EDTA is used as a chelating agent. A few milliliters of ammonia solution were added to obtain a clear solution. Finally, a solution of citric acid (2.5 mol L^{-1} , $n(\text{citric acid}) = n(\text{Al}) + n(\text{La})$) was added to the solution containing the chelated metals. The temperature of the solution was slowly heated to 100°C. Stirring was continued until evaporation of water lead to a transparent gel. The gel was then dried and calcined following four different steps (120°C – 3h ; 300°C – 3h ; 400°C – 3h ; 800°C – 5h).

The same procedure was applied to prepare LaNiO_3 with nitrates of lanthanum and nickel with a La:Ni molar ratio of 1:1.

$\text{CeO}_2\text{-Al}_2\text{O}_3$ was prepared by co-precipitation. An aqueous solution containing Ce and Al nitrates (Fluka) with a Ce:Al molar ratio of 1:2 (concentrations of 0.17 and 0.34 mol L^{-1}) was gradually added to an aqueous solution of ammonium carbonate under fast stirring. The carbonate solution was prepared in order to contain large excess of carbonates, assuring precipitation of all metallic cations. The precipitate was aged for 3 h. After centrifugation and several washing cycles with de-ionized water, the precipitated powder was dried overnight at 120°C, then calcined at 800°C for 5 h.

The same method was used to prepare $\text{ZrO}_2\text{-Al}_2\text{O}_3$ with nitrates of zirconium and aluminium (Aldrich and Fluka) with a Zr:Al molar ratio of 1:2.

Ni was deposited on the different supports (spinel, perovskites, mixed oxides) by deposition-precipitation using nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka) and urea (Sigma-Aldrich). Stirring was continued for 4 h while the temperature was increased to 100°C in order to remove excess urea. After centrifugation and several washing with de-ionized water, the samples were dried at 120°C over night and calcined at 550°C for 4 h in air.

5 wt.% Ni-0.05 wt.% Rh/ MgAl_2O_4 and 5 wt.% Ni -0.05 wt.% Rh/ LaAlO_3 were also prepared by wet impregnation of MgAl_2O_4 or LaAlO_3 with a solution containing nickel nitrates $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka), rhodium nitrates $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ (Alfa Aesar). Stirring was continued for 6 h. After evaporation of

water, the slurry was dried at 120°C overnight and calcined at 550°C for 4 h in air.

Hydrotalcite-type precursors were prepared by co-precipitation. An aqueous solution containing nitrates of Ni, Mg and Al (Fluka and Sigma-Aldrich) was added dropwise to a saturated solution containing NaHCO₃ and NaOH. The precipitate was aged for 1 h. After centrifugation and washing with de-ionized water, the deposit was dried over night at 120°C. The dry deposit was then calcined at 800°C for 5 h in air.

A commercial Ni-based catalyst (HiFUEL R110, Alfa Aesar, Ref. 45465) was used as reference catalyst.

Catalyst characterization

Powder X-ray diffraction patterns (XRD) were recorded using a Bruker D5005 diffractometer with a CuK radiation at $\lambda = 1.5418 \text{ \AA}$.

Elementary analysis of the fresh catalysts was performed by ICP-AES using a Jobin Yvon Activa Spectrometer D ICP-OES to determine the Ni loading.

Specific surface areas (SSA) were measured by nitrogen adsorption on catalysts at -196°C on a BELSORP-Mini (Bel-Japan).

Thermal analyses (DTA-TGA) were performed in air with a SETARAM analyser equipped with a mass spectrometer for online gas analysis. The samples were placed in a Pt crucible and heated at 10°C/min under a flow of synthetic air (50 mL/min).

Catalytic activity and stability measurements

A proprietary automated six-parallel reactor technology was implemented (Figure 1) to perform high-throughput long-term testing of the catalysts. The liquid water flow rate was controlled by a HPLC pump (Shimadzu LC 20-AD) and vaporized in a custom-made evaporator at 200°C, before mixing with the gaseous reactants whose flow rate was controlled by mass-flow controllers. All gas lines and valves were heated at 160°C to prevent steam condensation. Six tubular quartz reactors (length 180 mm, 4 mm ID) were placed in a six-position tubular furnace. The temperature in each reactor was measured under inert gas flow and at 700°C differences of $\pm 8^\circ\text{C}$ between the 6 reactors was found. Taking an activation energy of 110 kJ/mol for the steam reforming of methane [24], this will lead to a $\pm 10\%$ variation in the reaction rate at 700°C. After mixing the reactants, the main gas stream was split into six flows, each being directed into a reactor. Special attention was given to distribute the flows equally, since six different catalyst beds create each different pressure drops and can cause unequal flow distribution. To solve this issue, six identical stainless steel capillaries with small internal diameters (1/16" OD, 0.01" ID, 200 mm length) were placed upstream to the reactors. The pressure drop created by the capillaries was much more important than that created by the catalyst bed. Measurement of the individual flows through the reactor showed deviations of

$\pm 4 \text{ mL/min}$ for a flow of 80 mL/min per reactor. A 6-port automatic selection valve placed at the reactor exit allowed selecting the effluent of one specific reactor to be sent to a mass spectrometer for gaseous product analysis. The selection valve was automatically switched every five minutes in order to measure sequentially the performances of each reactor using an online mass spectrometer. Pressure transducers placed upstream and downstream the reactors also measured the pressure drop in each reactor being analysed, to check for a possible increase in the pressure due to extensive coke deposition.

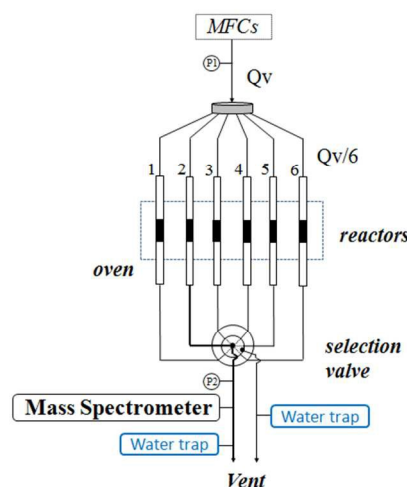


Figure 1: Setup for reactors inlet and outlet

Catalytic tests

Tests were performed at 700°C and at a pressure of 1.6 bar. Prior to testing, the catalyst samples were pelletized, crushed and sieved to obtain a particle size fraction between 100-200 microns. Catalyst beds were composed of 20 mg of catalyst and diluted with quartz powder (100-200 microns), to obtain a similar bed length of 8 mm whatever the catalyst density. The catalysts were reduced in situ with a H₂ argon mixture (4:1, vol:vol) for 3 hours, at 700°C. The reaction mixture consisted of 42% steam, 14% CH₄, 9% CO₂, 7% O₂ in a balance of argon. This composition represents a model bio-gas containing 60 % CH₄ and 40 % CO₂, which is reacted with a mixture of O₂ and H₂O under the conditions O₂/CH₄ = 0.5 and H₂O/CH₄ = 3. If oxygen were supplied as air, the balance gas would be nitrogen. Argon was substituted for nitrogen because N₂ would forbid analyzing CO by mass spectrometry (same molecular ion), and Ar was also used as internal standard for products quantification. The total flow rate of the reactant gases was 380 mL.min⁻¹ resulting in a Gas Hourly Space Velocity (GHSV) in each reactor of 38,000 m³m⁻³h⁻¹ and a Weight Hourly Space Velocity (WHSV) of 190 L(h g_{cat})⁻¹. Online analysis of the reactors exit stream was performed with a mass spectrometer (MS) monitoring m/z fragments 2 (H₂), 4 (He), 15 (CH₄), this fragment was chosen rather than the molecular ion because it is nearly as intense (90%) as mass 16 in the methane

fragmentation spectrum, whereas O₂ significantly contributes to mass 16, and also CO, CO₂ and H₂O to a lesser extent), 18 (H₂O), 28 (CO, corrected for the contribution of CO₂ to this fragment), 32 (O₂), 40 (Ar), 44 (CO₂). Quantitative analysis was performed by calibrating the MS response using different partial pressures of all relevant compounds diluted in argon. The Ar signal was used as internal standard and the other ion current intensities were converted to molar flows knowing the molar flow rate of Ar and the sensitivity coefficient of each m/z fragment relative to Ar, which is constant. Accurate water quantification with a MS is difficult, but the liquid water flow rate was precisely controlled by a calibrated HPLC pump, therefore the molar flow rate of steam at the reactor inlet was known accurately.

Results and Discussion

Catalyst characterization

The nickel loading and surface areas of the tested catalysts are reported in Table 1. A similar amount of Ni, around 5 wt.%, was generally deposited on the catalysts, with the exception of sample NRL, which exhibited a lower loading (3.9 wt.%), and sample LN (LaNiO₃ perovskite) for which the bulk nickel concentration was 26 wt.%. Four catalysts (NC, NS, NA, CC) with higher Ni loadings (10-20%) and two catalysts doped with a small amount of Rh (NRL and NRM) were also included in the screening. The catalysts exhibited substantial variations in specific surface areas. It was generally high for spinel and hydrotalcite-type catalysts, with NM presenting the highest value (158 m² g⁻¹). The perovskites had lower surface areas, ranging from 2.7 to 15 m² g⁻¹. Specific surface areas of mixed oxides catalysts were 57 and 119 m² g⁻¹ for NCA and NZA respectively.

Table 1: Ni loading and specific surface area of prepared catalysts

catalysts	Code	Ni loading (%)	BET Surface Area (m ² g ⁻¹)
5 wt.% Ni/MgAl ₂ O ₄	NM	5.1	158
5-0.05wt.%NiRh/MgAl ₂ O ₄	NRM	5.1	118
5 wt.% Ni/ZnAl ₂ O ₄	NZ	4.5	99
5 wt.% Ni/LaAlO ₃	NL	4.5	15
5-0.05 wt.% NiRh/LaAlO ₃	NRL	3.9	7.8
LaNiO ₃	LN	26	2.7
5 wt.% Ni/CeO ₂ -Al ₂ O ₃	NCA	5	57
5 wt.% Ni/ZrO ₂ -Al ₂ O ₃	NZA	5	119
Hydrotalcite-type precursor	HT	4.3	116
NiO/CaAl ₁₂ O ₁₉	NC	14	10
20 wt.% Ni/SiO ₂	NS	20	40
20 wt.% Ni/Al ₂ O ₃	NA	20	123
Commercial catalyst	CC	10	16

The selection of catalysts and support for the screening was based on general trends found in the literature related to steam and dry reforming of methane over Ni-based catalysts: basic supports are preferred to acidic supports, which are prone to

coking due to cracking reactions taking place on the acid sites. The basic character enhances steam activation as hydroxyl groups, which react with the coke and improve its gasification. Ceria combines a basic character with oxygen mobility properties and has also been shown to improve the gasification of coke in dry reforming reactions.

The Mg-Al-Ni hydrotalcite-type catalyst (HT) has also a basic character and a high surface area. Ni ions are initially incorporated in a mixed hydroxy-carbonate structure, then extracted upon reduction as metallic Ni, which should lead to the formation of well dispersed Ni particles. The LaNiO₃ perovskite catalyst (LN) was intended to behave similarly (synthesis of a mixed oxide and surface reduction leading to well dispersed metallic Ni particles on LaNi_{1-x}O₃), but its very low SSA might forbid a good dispersion of Ni.

Since Ni²⁺ tends to react with alumina at high temperature to form the inactive spinel NiAl₂O₄ (and any possible sub-stoichiometric Ni_{1-x}Al₂O_{4-x} composition), MgAl₂O₄ and ZnAl₂O₄ spinels were used as supports because they combine a high surface area, a basic character in the case of MgAl₂O₄, whereas Mg²⁺ and Zn²⁺ ions occupy the crystallographic positions where Ni²⁺ ions migrate in the alumina structure. Therefore, these supports should prevent, or at least limit, the migration of nickel in the support.

Six-parallel reactor set-up validation with a commercial catalyst

In order to obtain reliable information about the catalyst performances and to assess the repeatability of the results, the set-up was validated by testing the same mass of commercial Ni-based catalyst in the 6 reactors (Fig. 2).

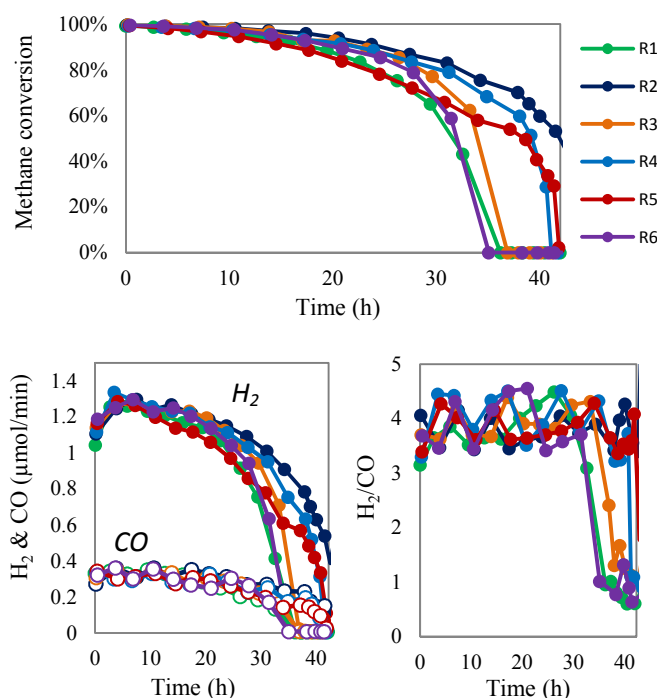


Figure 2: Autothermal reforming of model biogas (60%-40% ; CH₄-CO₂) at T=700°C with S/C =3, O/C=0.5 a) Methane conversion (%) b) H₂ and CO production c) H₂/CO ratio over time

Methane was fully converted at t=0 in all reactors, but declined steadily. The production of hydrogen and of carbon monoxide were similar in each reactor at full conversion and decreased with decreasing methane conversion. At t=0, the production of H₂ was of about 1 μmol/min and that of CO about 0.3 μmol/min. The H₂/CO ratio remained around four until the sharp drop in the methane conversion. The deactivation profiles were similar: a slow deactivation was observed followed by an abrupt loss of the activity though scattered over a range of about 5 h. As the methane conversion fell to zero, the hydrogen and monoxide productions were simultaneously suppressed.

Figure 3 shows the composition (on dry basis, i.e. not taking the steam into account) of reactor #6 exit stream. With a S/C ratio of 3, the steam is in large excess and is only partly consumed during the reaction. H₂ and CO molar fractions reach about 40% and 10% respectively at full methane conversion. Complete conversion of methane and oxygen is observed during the first hours. After 15 hours, the methane molar fraction increases while the oxygen molar fraction remains zero. When the methane molar fraction reaches 10% (corresponding to 60% conversion), the oxygen conversion is no longer complete. Methane and oxygen conversions suddenly drop to zero and hydrogen and carbon monoxide productions drop similarly. The catalyst is fully deactivated. Similar behavior was observed on all reactors.

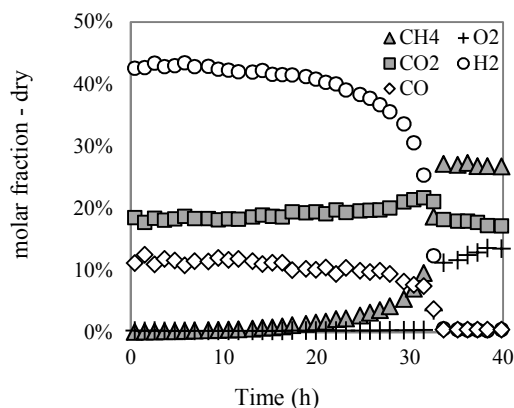


Figure 3: Dry outlet gas concentrations during autothermal reforming of model biogas (60%-40% ; CH₄-CO₂) at T=700°C with S/C =3, O/C=0.5

The catalyst stability in the six reactors varied between 40 +/- 5 hours. This corresponds rather well to the variation of the methane steam reforming rate of +/- 10% which can be attributed to slight differences in the reactor temperatures, catalyst loadings and reactant flow rates. The six deactivation profiles, however, were sufficiently similar to allow discriminating unambiguously between fast-deactivating and stable catalysts.

The role of oxygen in the catalyst deactivation is evidenced by the experiments shown in Figure 4. After 43 hours, oxygen was removed from the feed gas, and the catalyst in reactors 2 and 5

started to convert methane again. Before oxygen removal, the O₂/CH₄ ratio in the feed stream is 0.5, which means that 25% of the methane is immediately burnt into CO₂ at the reactor inlet (the stoichiometry for methane combustion is O₂/CH₄=2). Oxygen is totally converted and Ni is likely to be oxidized in the CH₄ combustion zone, but the metallic Ni still present downstream in the reactor ensures the reaction of the remaining methane with steam, and possibly with CO₂. As soon as the catalyst is sufficiently deactivated that some of the oxygen is unconverted (this should theoretically happen when the methane conversion falls below ≈25%, but it might also happen before since NiO is not a very good catalyst for methane combustion [25], the gaseous oxygen will rapidly oxidize the metallic Ni and deactivate the catalyst. These catalysts will not be reactivated when O₂ is removed from the feed because Ni is fully oxidized and unable to catalyse the steam reforming reaction. In reactors 2 and 5 the catalyst was not completely deactivated and still produced small amounts of H₂ + CO, which suggests that some metallic Ni was still present, and upon oxygen removal the hydrogen produced by methane steam reforming was able to reduce again the oxidized Ni. After ca. 47 hours, hydrogen was added to the feed. Methane conversions ranging from ca. 65 to 70% was observed in all six reactors. Oxidation of Ni appears to play an important part in the deactivation process.

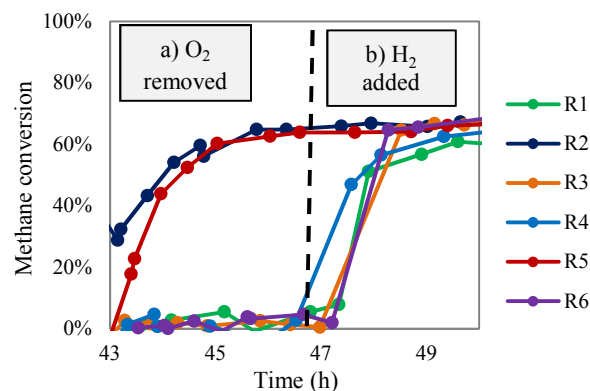


Figure 4: Methane conversion (%) during autothermal reforming of model biogas a) (60%-40% ; CH₄-CO₂) at T=700°C with S/C =3 and absence of oxygen b) (60%-40% ; CH₄-CO₂) at T=700°C with S/C =3 and addition of hydrogen

Catalyst screening for ATR of model biogas

The results of catalyst screening in terms of methane conversion are shown in Figure 5.

The catalyst performances at 700°C versus time-on-stream depended strongly on catalyst composition.

Comparing the behaviour of the ≈5 wt.% Ni catalysts loaded on different supports, our screening shows that the support properties that were shown to be beneficial in methane steam reforming do not appear as relevant when autothermal reforming of methane is involved: NM, NZ and NCA exhibited full initial conversion but deactivated within 2 hours, while NZA deactivated almost instantly. HT was found fully inactive, but the catalyst reduction temperature was probably too low to

reduce and extract Ni from the mixed-oxide structure, since the Ni reduction in Ni-Mg-Al hydrotalcite catalysts has been shown to take place between 750 and 900°C [26]. NL catalyst (5% Ni/LaAlO₃) deactivated more gradually and was fully deactivated after 16 h. Therefore LaAlO₃ appears an interesting support, despite its low SSA.

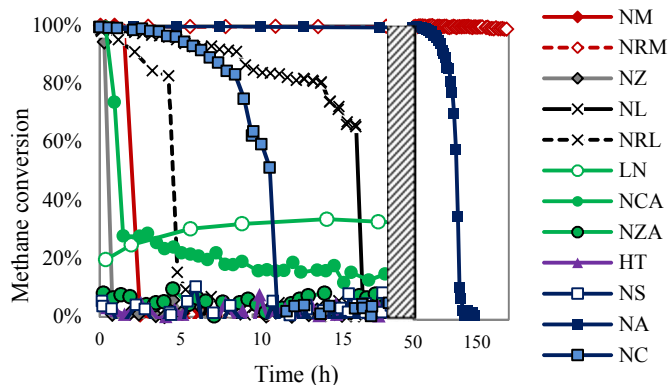


Figure 5: Methane conversion (%) during autothermal reforming of model biogas (60%-40% ; CH₄-CO₂) at T=700°C with S/C=3, O/C=0.5

Increasing the Ni loading was expected to delay the catalyst deactivation, since more Ni is available in the reactor, provided that it is dispersed enough and that the support exhibits the appropriate acid-base properties. This was generally verified since all 5 wt. Ni catalysts except NL deactivated before CC (10% Ni) and NC (14% Ni) catalysts, which in turn deactivated before NA (20% Ni). A noticeable exception was NS (20% Ni/SiO₂), which deactivated so rapidly that no methane conversion was observed, evidencing that SiO₂ is not a good support in this reaction. LN catalyst (26 wt.% Ni) revealed peculiar performances, with a moderate but constant methane conversion ($\approx 30\%$), which gradually dropped to zero after 20 h (not shown), probably due to the negative combination of high Ni loading and very low surface area.

Rh doping had a very strong influence on the stability of NM since NRM still fully converted methane after 200 h of reaction. In contrast, NRL deactivated before NL, which might be attributed to the very low surface area of the catalyst after its second impregnation by Rh. Ni-Rh bimetallic catalysts have been shown to exhibit enhanced stability for methane tri-reforming [27] and dry-reforming reactions [28], similarly to Ni-Pd [29–31] Ni-Pt [32] and Ni-Co formulations [33][34]. With the exception of LN, the deactivation profiles of all tested catalysts were rather similar to that of the commercial catalyst: the methane conversion decreased slowly for a certain time, then rapidly fell to zero. Hydrogen production versus time is shown in Figure 6. The order of deactivation time NS-HT-NZA < NZ < NCA < NM < NRL < NC < NL < NA < NRM was respected.

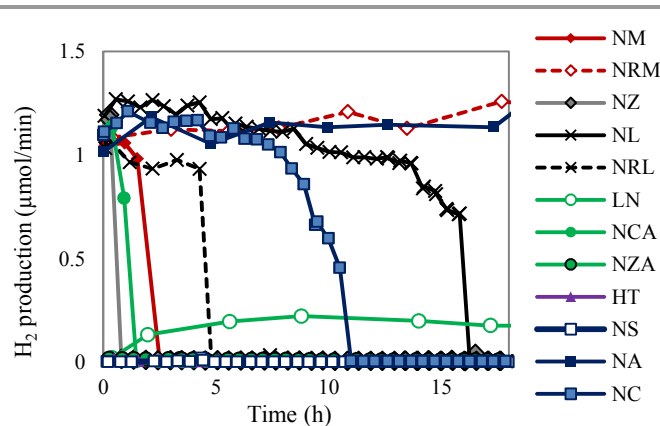


Figure 6: Hydrogen production ($\mu\text{mol/min}$) during autothermal reforming of model biogas (60%-40% ; CH₄-CO₂) at T=700°C with S/C=3, O/C=0.5

The hydrogen production profiles matched well the conversion profiles of methane shown in Figure 5. In agreement with the low methane conversion, the reaction on LN produced much less hydrogen than the other catalysts.

The abrupt changes in the slopes of the deactivation profiles exhibited by most catalysts suggested different deactivation mechanisms for each stage. For the slow initial deactivation: nickel and/or support sintering eventually combined with coke deposition may progressively deactivate the catalysts. Our reaction conditions imply working with an excess of steam ($\text{H}_2\text{O}/\text{CH}_4=3$) that can promote the sintering of oxides and metals, known to be a rather slow process. However, whatever be its origin, such a slow initial deactivation cannot account for the subsequent sharp collapse in the catalytic activity. The latter might be related to the presence of oxygen in the feed stream, leading to nickel oxidation. As mentioned previously, ATR of methane combines the combustion of methane (to provide heat) with steam/dry reforming of the remaining methane. Since methane combustion is much faster than reforming reactions and strongly exothermic ($\Delta H=-801 \text{ kJ/mol}$), it takes place at the catalyst bed inlet and leads to the formation of hotspots and temperature gradients along the bed [23, 24]. As shown in the case of methane partial oxidation [36], the combination of high temperature and presence of oxygen in the feed stream is likely to oxidize the nickel particles, which no longer participate in the reforming reactions. The high temperature front will diffuse further down the bed, leaving less metallic Ni available for the reforming reactions. Once the combustion zone reaches the end of the catalyst bed the methane conversion will drop to zero.

Post-reaction characterization of catalysts showed that XRD patterns were not significantly modified compared to fresh catalysts. Figure 7 presents the diffractograms of NM catalyst before and after ATR reaction. Both diffractograms exhibited the characteristic lines of the spinel phase MgAl_2O_4 , whereas no Ni or NiO lines were evidenced.

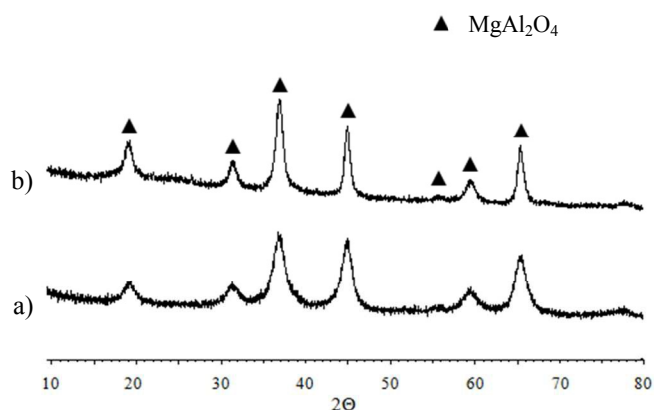


Figure 7: X-ray diffractogram of NM catalyst a) after reduction at 700°C b) after deactivation

However, the small amount of catalyst in each reactor (20 mg, mixed with quartz powder) provided only a low-resolution diffractogram, which did not allow a thorough comparison of fresh and used catalyst diffraction patterns. TGA-DTA-TPO analysis of the commercial catalyst after reaction revealed two small mass losses with maxima at ca. 350°C (-0.12%, exothermic) and 690°C (-0.11%, endothermic), associated with CO₂ production in sub-ppm amounts. The CO₂ production at low temperature might be attributed to the combustion of very reactive carbon, in direct contact with Ni. The high temperature CO₂ production is endothermic and thereby suggests the decomposition of carbonates formed on the basic support. Limited carbon deposition is consistent with the reaction conditions in which the H₂O/CH₄ ratio of 3 and the high CO₂ partial pressure should prevent extensive coking (carbon can be gasified by steam and by CO₂ through the reverse Boudouard reaction [37]). TEM examination of the deactivated commercial catalyst samples also revealed the presence of a carbon film on some Ni particles, although not on all of them (Figure 8), which probably corresponds to the carbon burning at low temperature in TGA-TPO experiments. Such carbon films are likely to participate in the slow initial deactivation, by progressively encapsulating the metal particles. There was no evidence of carbon whisker formation, also known as a potential long-term deactivation process. High resolution and electron diffraction also revealed the presence of oxidized nickel, which is clearly an issue for long-term stability in ATR.

Depending on its level of deactivation, the initially black-coloured catalyst bed exhibited after reaction a ring of light blue-green colour at its inlet, or was found fully blue-green for deactivated catalysts, which suggests the formation of inactive NiO or NiAl₂O₄. In this sense, the addition of small amounts of Rh to Ni appears to effectively promote nickel reduction and prevent bulk oxidation. Rh addition is also effective to inhibit carbon deposition [38]. Therefore, a 0.05 wt.% Rh addition has a positive effect on the catalyst resistance to deactivation under ATR conditions.

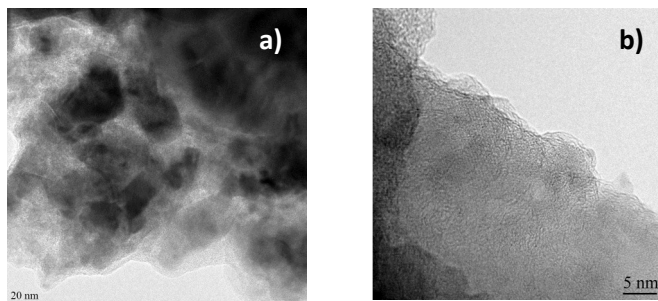


Figure 8: TEM images of deactivated commercial catalyst after ATR reaction showing the presence of a) oxidized nickel b) carbon deposits.

Conclusions

Assessing the stability of catalysts in ATR of bio-gas requires long-term experiments, since catalysts might deactivate rapidly after exhibiting apparently stable performances for several hours. A six-parallel flow reactor is a powerful tool to assess the long-term stability of six catalysts simultaneously in ATR of biogas. A screening of catalysts was performed in a short time demonstrating an order of deactivation time NS-HT-NZA < NZ < NCA < NM < NRL < NC < NL < NA < NRM. A slow initial deactivation process could be related to some carbon deposition, but the main fast final deactivation process is likely associated to nickel oxidation. Rh promotes Ni stability and thus 5-0.05 wt.% Ni-Rh/MgAl₂O₄ was identified as a robust catalyst for autothermal reforming of model biogas.

Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme ([FP7/2007-2013] under grant agreement n° 325383 (BioRobur). The authors thank Bernadette Jouguet for performing timely TGA-DTA analyses.

References

- 1 A. Demirbas, *Energ. Convers. Manage.*, 2008, **49**, 2106–2116.
- 2 J. Xuan, M. K. H. Leung, D. Y. C. Leung and M. Ni, *Renew. Sust. Energ. Rev.*, 2009, **13**, 1301–1313.
- 3 J. R. Rostrup-Nielsen and J.-H. Bak Hansen, *J. Catal.*, 1993, **144**, 38–49.
- 4 P. Ferreira-Aparicio, A. Guerrero-Ruiz and I. Rodriguez-Ramos, *Appl. Catal. A-Gen.*, 1998, **170**, 177–187.
- 5 J. Sehested, *Catal. Today*, 2006, **111**, 103–110.
- 6 S. Helveg, J. Sehested and J. R. Rostrup-Nielsen, *Catal. Today*, 2011, **178**, 42–46.
- 7 J. Wei, E. Iglesia, *J. Catal.*, 2004, **224**, 370–383.
- 8 P. O. Sharma, M. A. Abraham and S. Chattopadhyay, *Ind. Eng. Chem. Res.*, 2007, **46**, 9053–9060.
- 9 A. M. Gadalla and B. Bower, *Chem. Eng. J.*, 1988, **43**, 3049–3062.

- 10 K.-H. Lin, H.-F. Chang and A. C.-C. Chang, *Int. J. Hydrogen Energ.*, 2012, **37**, 15696–15703.
- 11 G. Xu, K. Shi, Y. Gao, H. Xu and Y. Wei, *J. Mol. Catal. A-Chem.*, 1999, **147**, 47–54.
- 12 A. A. Lemonidou and I. A. Vasalos, *Appl. Catal. A-Gen.*, 2002, **228**, 227–235.
- 13 C. Papadopoulou, H. Matralis and X. Verykios, "Utilization of Biogas as a Renewable Carbon Source: Dry Reforming of Methane" in *Catalysis for Alternative Energy Generation*, L. Guzzi and A. Erdöhelyi, Eds. Springer New York, 2012, 57–127. ISBN: 978-1-4614-0343-2.
- 14 Y. J. O. Asencios, J. D. A. Bellido and E. M. Assaf, *Appl. Catal. A-Gen.*, 2011, **397**, 138–144.
- 15 Y. J. O. Asencios, C. B. Rodella and E. M. Assaf, *Appl. Catal. B-Environ.*, 2013, **132–133**, 1–12.
- 16 O. A. Bereketidou and M. A. Goula, *Catal. Today*, 2012, **195**, 93–100.
- 17 S. Rasi, A. Veijanen and J. Rintala, *Energy*, 2007, **32**, 1375–1380.
- 18 S. Appari, V. M. Janardhanan, R. Bauri, S. Jayanti and O. Deutschmann, *Appl. Catal. A-Gen.*, 2014, **471**, 118–125.
- 19 M. P. Kohn, M. J. Castaldi and R. J. Farrauto, *Appl. Catal. B-Environ.*, 2014, **144**, 353–361.
- 20 H. J. Alves, C. Bley Junior, R. R. Niklevicz, E. P. Frigo, M. S. Frigo and C. H. Coimbra-Araújo, *Int. J. Hydrogen Energ.*, 2013, **38**, 5215–5225.
- 21 J. Pérez-ramírez, R. J. Berger, G. Mul, F. Kapteijn and J. A. Moulijn, *Catal. Today*, 2000, **60**, 93–109.
- 22 J. K. van der Waal, G. Klaus, M. Smit and C. M. Lok, *Catal. Today*, 2011, **171**, 07–210.
- 23 P. Laveille, G. Biaisque, H. Zhu, J.-M. Basset, V. Caps, *Catal. Today*, 2013, **203**, 3–9.
- 24 J. R. Rostrup-Nielsen, "Catalytic Steam Reforming" in *Catalysis*, J. R. Anderson and M. Bouchard, Eds. Springer-Verlag Berlin, 1984, **5**, 1–117. ISBN: 978-3-642-93249-6.
- 25 O. Dewaele, G. F. Froment, *J. Catal.*, 1999, **184**, 499–513.
- 26 K. Takehira, T. Shishido, P. Wang, T. Kosaka, K. Takaki, *J. Catal.*, 2004, **221**, 43–54.
- 27 U. Izquierdo, V.L. Barrio, J. Requies, J.F. Cambra, M.B. Guñmez, P.L. Arias, *Int. J. Hydrogen Energy*, 2013, **38**, 7623–7631.
- 28 M. Nowosielska, W. K. Jozwiak, J. Rynkowski, *Catal. Lett.*, 2009, **128**, 83–93.
- 29 J. Zhang, Y. Wang, R. Ma, D. Wu, *Appl. Catal. A*, 2003, **243**, 251–259.
- 30 K. Yoshida, K. Okumura, T. Miyao, S. Naito, S. Ito, K. Kunimori and K. Tomishige, *Appl. Catal. A-Gen.*, 2008, **351**, 217–225..
- 31 I.Z. Ismagilov, E.V. Matus, V.V. Kuznetsov, M.A. Kerzhentsev, S.A. Yashnik, I.P. Prosvirin, N. Mota, R.M. Navarro, J.L.G. Fierro, Z.R. Ismagilov, *Int. J. Hydrogen Energy*, 2014, **39**, 20992–21006.
- 32 L. Li, L. Zhou, S. Ould-Chikh, D. H. Anjum, M. B. Kanoun, J. Scaranto, M. N. Hedhili, S. Khalid, P. V. Laveille, L. D'Souza, A. Clo, J.-M. Basset, *ChemcatChem*, 2015, **7**, 819–829.
- 33 K. Takanabe, K. Nagaoka, K. Nariai, K. Aika, *J. Catal.*, 2005, **232**, 268–275.
- 34 X. You, X. Wang, Y. Ma, J. Liu, W. Liu, X. Xu, H. Peng, C. Li, W. Zhou, P. Yuan, X. Chen, *ChemCatChem*, 2014, **6**, 3377–3386.
- 35 J. A. C. Dias and J. M. Assaf, *Appl. Catal. A-Gen.*, 2008, **334**, 243–250.
- 36 D. Dissanayake, M. P. Rosynek, K. C. C. Kharas and J. H. Lunsford, *J. Catal.*, 1991, **132**, 117–127.
- 37 H. Döder, K. Kähler, B. Krause, K. Mette, S. Kühl, M. Behrens, V. Scherer, M. Muhler, *Catal. Sci. Technol.*, 2014, **4**, 3317–3328.
- 38 M. Nurunnabi, K. Fujimoto, K. Suzuki, B. Li, S. Kado, K. Kunimori and K. Tomishige, *Catal. Commun.*, 2006, **7**, 73–78.