ELSEVIER

Catalysis Today 63 (2000) 427–437

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Development of Ni catalysts for gas production from biomass gasification. Reactivity in steam- and dry-reforming

C. Courson*, E. Makaga, C. Petit, A. Kiennemann

Laboratoire d'Etudes de la Réactivité Catalytique, des Surfaces et Interfaces,
ECPM-UMR 7515, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France

---

Abstract

Biomass gasification can be optimised in a fluidised bed by the use of metallic nickel as active phase grafted on olivine. Natural olivine ($(\text{Mg, Fe})_2\text{SiO}_4$) has been chosen as catalyst support because of its activity in biomass steam gasification and tar cracking, its high attrition resistance.

After impregnation of nickel oxide on olivine and calcination at 900, 1100 or 1400°C, different interactions between the precursor and the support have been revealed by X-ray diffraction, scanning electron microscopy and transmission electron microscopy coupled to energy dispersive X-ray spectroscopy. Temperature programmed reduction has completed this study and permitted to control the reducibility of the catalysts. The most promising catalyst determined after these different characterisation studies contained 2.8 wt.% of Ni and was calcined at 1100°C. It exhibited strong nickel–olivine interaction but the grafted nickel oxide particles stayed reducible under catalytic test conditions.

Already at 750°C, this catalyst presented a high activity in dry-reforming (95% methane conversion) and steam-reforming (88% methane conversion) and yield in syngas (80% and 75% CO yield, respectively). An excess of water content in steam-reforming inhibited the catalytic activation which could be retrieved by addition of a reducer like H_2.

No sintering of nickel particles and very little carbon deposition has been observed on this catalytic system by characterisation studies after catalytic tests. This can explain its very good ageing behaviour (at least 260 h at 800°C) and justifies its use in a fluidised bed pilot plant. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Biomass gasification; Dry-reforming; Steam-reforming; Nickel–olivine interaction

---

1. Introduction

Among the available sources of renewable energy, biomass appears promising for industrial exploitation, especially in small to medium size plants located close to the sites where feedstocks are available [1]. Such units are designed to convert biomass to electricity by fuel-cell processes. The valorisation of the biomass as a source of energy is obtained through a complex thermo-chemical process [2]. The biomass is transformed through combustion–gasification with water into permanent gases such as hydrogen, carbon monoxide, carbon dioxide and methane, organic vapours which condense in tar under ambient conditions and solid residues consisting of char and ash.

Fluidised bed steam gasification can maximise the gaseous product yield [3] as a result of high involved heating rate, advantageous residence time characteristics and efficient tar reduction. Since the specific objective is to produce a maximum of hydrogen to be used in a fuel cell, further improvement may be

---

* Corresponding author. Fax: +33-388136975.
E-mail address: kiennemann@chimie.u-strasbg.fr (A. Kiennemann).

PII: S0920-5861(00)00488-0

achieved by the catalytic reforming of methane and tar.

Natural basic minerals containing iron, as dolomite ($Ca(Mg, Fe)(CO_3)_2$) [4–6] or olivine ($(Mg, Fe)_2SiO_4$), are known to promote tar cracking and reforming [7,8]. For example, at 770°C the average tar content (in $g\,Nm^{-3}$ of dry gas) is decreased from 43 with sand to 0.6 for dolomite and 2.4 for olivine. The dry gas yield (in $Nm^{-3}\,kg^{-1}$ dry-ash-free biomass) is increased from 1.1 to 1.9 and 1.7, respectively, [8]. The main problem with dolomite is its fragility to attrition phenomena especially at high temperature. Olivine presents a higher resistance than dolomite and its density is comparable to that of biomass incorporated in the fluidised bed steam gasification process.

Addition of a reforming catalyst enhances the gas yields to syngas characterised by a high H_2/CO molar ratio. Among metals like Co, Pt, Rh, ... Ni appears as the most suitable choice for both technical and economic reasons [9,10] and the active part is reported to be the reduced metal [11]. It has been demonstrated that if a strong nickel–support interaction exists initially in the catalyst, nickel sintering as well as carbon deposition can be avoided [12–14]. Thus, on the one hand, nickel has to be inserted in a definite chemical structure rather than just dispersed onto it. On the other hand, the catalyst has to be reducible under gasification conditions and must also be resistant to the mechanical stresses and to the continuous oxidation and reduction cycles to be used in a fluidised bed steam gasification.

An attractive solution will be to associate nickel and olivine because of the definite structure of the latter and its mechanical strength. Moreover, olivine contains iron which can be of help in the stabilisation of nickel in the structure [12,14].

The aim of this work is firstly to demonstrate the possibility of integrating nickel in small amount into natural olivine by a convenient preparation, secondly to control the nickel oxide reducibility and finally to study the efficiency and stability of this catalyst in dry- and steam-reforming of methane. At the same time, the main objective of this work remains in the prevention of carbon deposition on the catalyst during the test.

Table 1
Elementary analysis of natural olivine

Element (wt.%)						
Mg	Si	Fe	Ni	Ca	Al	Cr
30.5	19.6	7.1	0.19	0.20	0.07	0.08

2. Experimental procedure

2.1. Preparation of Ni/olivine catalysts

Natural olivine comes from an Austrian mine and its mean elementary analysis, obtained by atomic adsorption, is given in Table 1.

This natural olivine already contains small amounts of nickel and other elements like calcium, aluminium and chromium. The mean formula calculated from these data is close to $(Mg_{0.92}Fe_{0.08})_2SiO_4$ with an iron excess (0.7 wt.%) in the form of free iron oxide. The specific surface area of the olivine is very low ($<1\,m^2\,g^{-1}$).

The Ni/olivine catalysts have been prepared by impregnation of this natural olivine with an excess of an aqueous solution of nickel nitrate. For 10 g of support, a solution obtained with 1.95 g of $Ni(NO_3)_2{\cdot}6H_2O$ in 30 ml of solvent (water) was used. After water evaporation, the samples have been calcined under air for 4 h at different temperatures (900, 1100 or 1400°C). The impregnation of nickel nitrate on olivine has permitted to obtain catalysts containing 2.8 wt.% Ni detected by elementary analysis.

2.2. Techniques for characterisation of the nickel–olivine samples

The catalytic system characterisation passes through the olivine study. Ni/olivine samples have been compared with fresh olivine as well as olivine calcined under the same conditions as the catalysts.

All these samples have been characterised by elementary analysis performed in the CNRS Centre in Vernaison, by powder X-ray diffraction (XRD) on a Siemens D500TT diffractometer using Cu Kα radiation, by scanning electron microscopy (SEM) on a JEOL JSM 840 microscope, by transmission electron microscopy (TEM) on a Topcon EM 002B apparatus coupled to energy dispersive X-ray spectroscopy

(EDXS). For the TEM analysis, the samples have been grounded in a mortar then deposited on a Cu grid covered with a perforated carbon membrane. The statistical distribution of heavy elements (Si, Mg, Fe, Ni) has been obtained by microanalysis with a large window ($\phi = 200\,\text{nm}$). An analysis performed on different areas of the sample with a small window ($\phi = 14\,\text{nm}$) to observe its homogeneity [15].

The reducibility of the catalysts has permitted to understand their performances in methane reforming. It has been followed by temperature programmed reduction (TPR) performed on 200 mg of catalyst placed in a U-shaped quartz tube (6.6 mm ID). The reductive gas mixture ($H_2 = 0.12\,\text{Nl}\,\text{h}^{-1}$ and $\text{Ar} = 3\,\text{Nl}\,\text{h}^{-1}$) passed through the reactor heated from room temperature to 910°C with a slope of $15°\text{C}\,\text{min}^{-1}$ then kept up at 910°C until the baseline stabilisation. A thermal conductivity detector analysed the effluent gas after a water trap and permitted to quantify the hydrogen consumption.

2.3. *Catalytic tests of the nickel–olivine catalysts*

In order to determine the catalytic activity and stability of the various catalysts in the conditions of biomass gasification, the reactions of dry- and steam-reforming of methane have been studied.

The operating conditions were the following: fixed bed quartz reactor (6.6 mm ID); inlet temperature: 600–850°C; total feed flow rate: $3\,\text{Nl}\,\text{h}^{-1}$; weight of catalyst: 400 mg. The feed flow rates are given in Table 2.

The outlet gas was analysed by two gas chromatographs used simultaneously and manned with TCD. The first one gave the amount of remaining CH_4 and of produced CO, CO_2 separated on a carbosieve SII column (3 m; 80–100 mesh; He: $25\,\text{ml}\,\text{min}^{-1}$); the second one quantified CO and H_2 production separated on a molecular sieve (5 Å; 2 m; 80–100 mesh; Ar: $18\,\text{ml}\,\text{min}^{-1}$).

The temperature program was composed of three different steps without reducing treatment. During the initial step ($10°\text{C}\,\text{min}^{-1}$ from room temperature to 500°C), no syngas formation was observed for each catalytic test. During the second step (continuous increase of $3°\text{C}\,\text{min}^{-1}$ from 500 to 800–850°C), chromatographic analyses were performed for every 50°C. The last step was a stage at the higher temperature for an ageing study.

Given the following reaction schemes for the dry- and steam-reforming, respectively:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{1}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{2}$$

methane conversion and H_2 yield can be calculated.

$$\text{Conversion}\,(CH_4)\,(\%) = \frac{(CH_4)_{\text{in}} - (CH_4)_{\text{out}}}{(CH_4)_{\text{in}}} \times 100 \tag{3}$$

$$\text{Yield}\,(H_2)\,(\%) = \frac{(H_2)_{\text{out}} - (H_2)_{\text{in}}}{(CH_4)_{\text{in}}} \times \frac{100}{A} \tag{4}$$

for *dry-reforming*, $A = 2$, for *steam-reforming*

$$A = \frac{2S(\text{C}) + 3S(\text{CO}) + 4S(\text{CO}_2)}{100} \tag{5}$$

where

$$S(\text{C or CO or CO}_2) = \frac{(\text{C or CO or CO}_2)_{\text{out}}}{(CH_4)_{\text{in}} - (CH_4)_{\text{out}}} \times 100 \tag{6}$$

Table 2
Feed flow rates ($\text{Nl}\,\text{h}^{-1}\,\text{g catalyst}^{-1}$), here $R_1 = CO_2/CH_4$ or H_2O/CH_4 and $R_2 = H_2/CH_4$

		CH_4	CO_2	H_2O	H_2	Ar
Dry-reforming	$R_1 = 1$	0.75	0.75	–	–	6
Steam-reforming	$R_1 = 1;\ R_2 = 0$	0.75	–	0.75	–	6
	$R_1 = 3;\ R_2 = 0$	0.75	–	2.25	–	4.5
	$R_1 = 3;\ R_2 = 2$	0.75	–	2.25	1.5	3

3. Results and discussion

3.1. *Characterisation of the nickel–olivine initial interaction*

The XRD diagrams of olivine and catalyst calcined at 1100°C are presented in Fig. 1. All the lines for olivine calcined at 1100°C (curve a) are close to those of the Mg_2SiO_4 forsterite (JCPDS 34-0189) and no parasite crystalline phase can be observed except for a

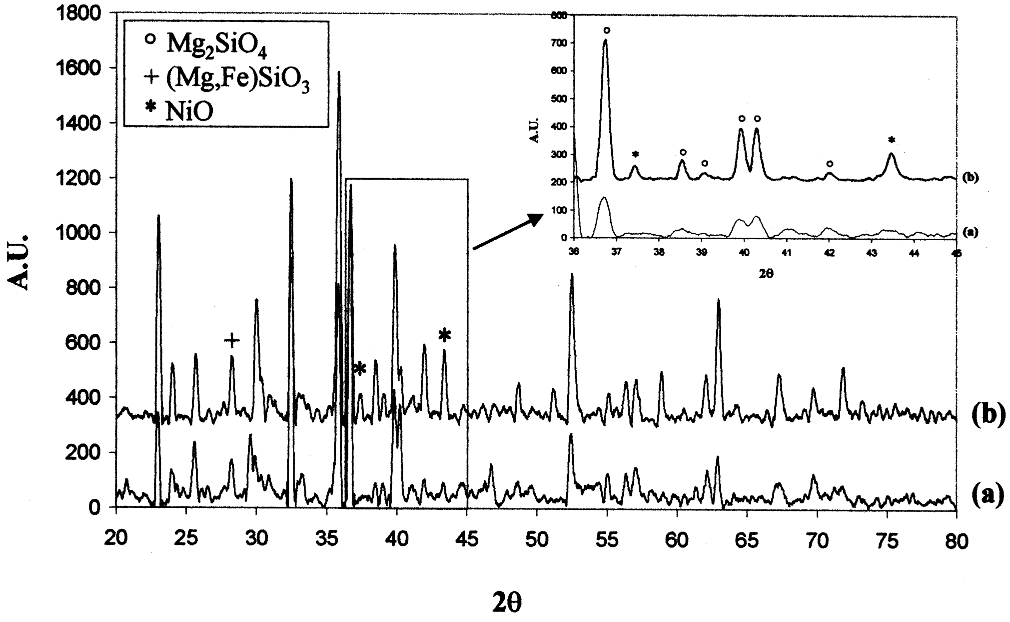

Fig. 1. X-ray diffractograms of (a) olivine calcined at 1100°C and (b) Ni/olivine calcined at 1100°C. References Mg_2SiO_4 (34-0189 JCPDS file), (Mg, Fe)SiO_3 (19-0606 JCPDS file) and NiO (1-1239 JCPDS file).

little contribution of the (Mg, Fe)SiO_3 phase visualised by its 100 intensity line at 28.2° (2θ).

XRD of the catalyst calcined at 1100°C (Fig. 1, curve b) shows that the olivine phase is maintained as the only crystalline phase with a slight shift compared to the JCPDS file of the Mg_2SiO_4 reference. The most particular area (zoom on Fig. 1) is situated at 2θ between 37.5° and 43.5° characteristic of the cubic NiO phase (JCPDS 1-1239). These two lines indicate the presence of large sized aggregates and are also observed for the catalyst calcined at 900°C. They disappear after calcination of the sample at 1400°C and its XRD diffractogram becomes similar to that of the initial olivine. This indicates a decrease in size of the nickel containing particles or more probably their insertion into the olivine structure.

The SEM of the fresh olivine shows porosity of this support (holes of diameters ranging from 1 to 5 μm). After calcination at 1100°C, the porosity observed on fresh olivine disappears, more compact grains are formed and the local crystallinity is increased and can be observed by the appearance of oriented crystals showing a series of parallel plans. The scanning electron micrographs of olivine calcined at 1100°C is given in Fig. 2a.

On the scanning electron micrographs of the Ni/olivine catalyst calcined at 900°C, a deposit of almost spherical uniform grains (probably NiO) with size between 0.1 and 0.2 μm can be observed and hides completely the surface of the support.

Increasing the calcination temperature to 1100°C leads to less homogeneous definition of the sample (Fig. 2b). Some areas are similar to what is obtained after calcination at 900°C with deposited particles of same size but more linked to the support. Other areas show a less dense coverage by nickel oxide with bigger deposited grains (1 μm). Finally, in some areas the smooth support is observed and the formation of plans begins like on the olivine calcined at 1100°C.

Calcination at 1400°C leads to the formation of a very smooth surface of the support, similar to that obtained with olivine calcined at the same temperature without observable deposit. This confirms the insertion of the nickel crystallites into the olivine structure.

The distribution of the elements (Mg, Fe, Si) obtained on olivine calcined at 1100°C by EDXS shows a heterogeneous local contribution as well as the

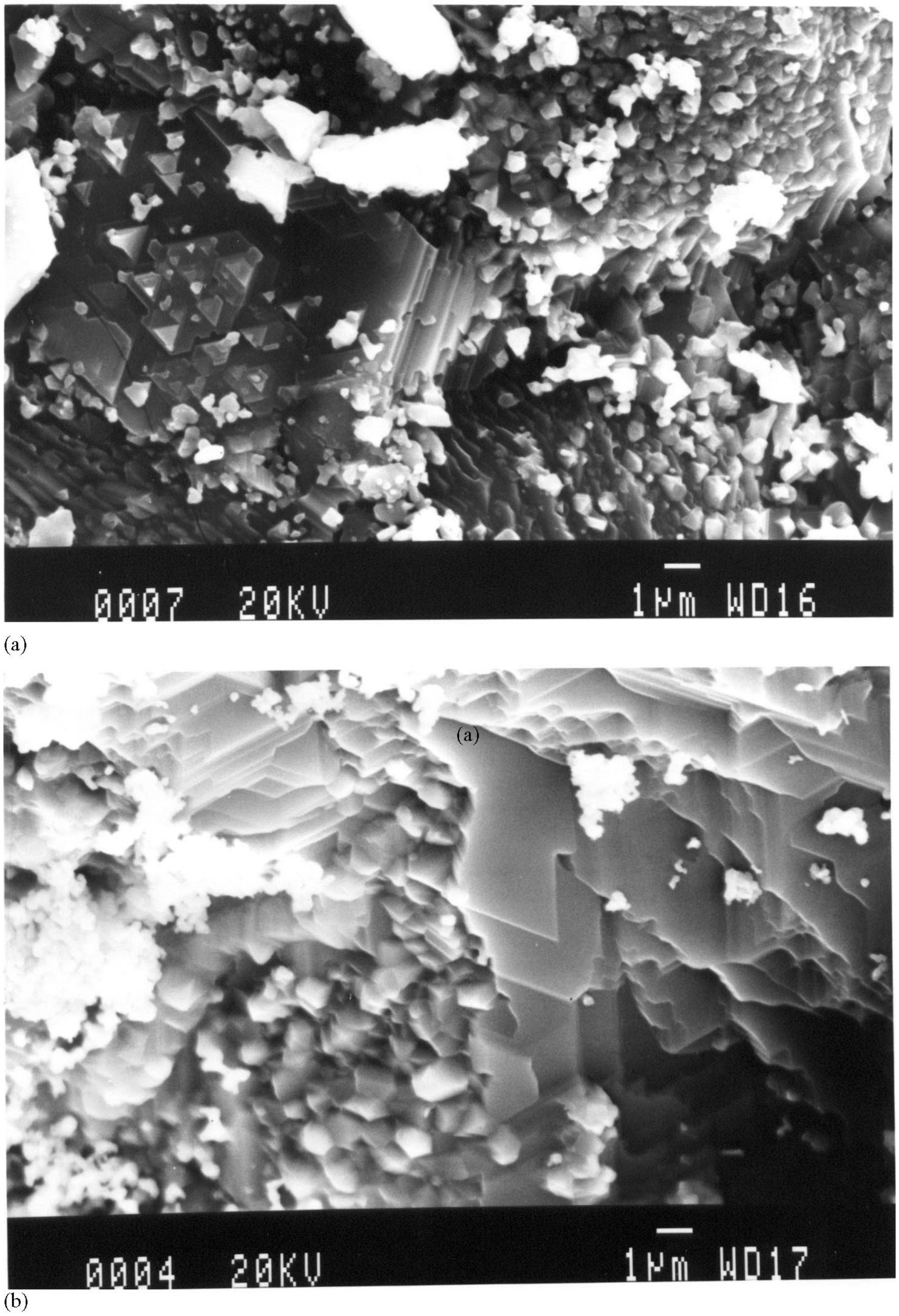

Fig. 2. Scanning electron micrographs of (a) olivine calcined at 1100°C and (b) Ni/olivine calcined at 1100°C.

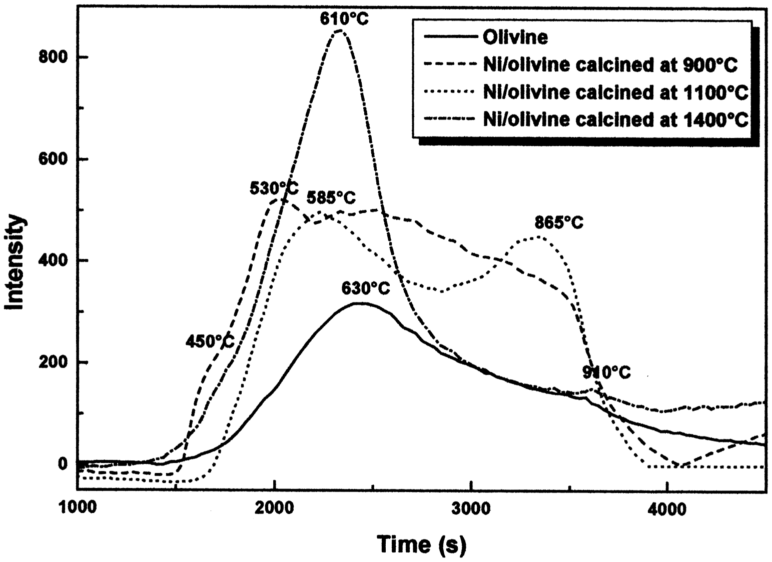

Fig. 3. TPR of fresh olivine; Ni/olivine catalysts calcined at 900, 1100 and 1400°C.

presence of iron containing particles without interaction with the olivine structure.

After impregnation and calcination at 900 or 1100°C, crystallites with a 0.1 μm size can also be observed by TEM and can be identified as nickel oxide aggregates without noticeable change in support composition. After calcination at 1400°C, the nickel oxide aggregates are no more observed and the EDXS analysis confirms that nickel is integrated into the olivine structure. The TPR profiles for olivine and Ni/olivine samples calcined at different temperatures are given in Fig. 3.

For the olivine, a reduction peak is observed around 630°C. This peak is attributed to the reduction of the free iron oxide associated to the olivine structure and detected in the TEM/EDXS analysis. Earlier works in our laboratory [14] have shown that iron inserted in a well-defined structure as oxide cannot be reduced in these conditions. Therefore it is likely that the framework iron of the olivine can only be reduced at temperatures higher than 900°C. This peak around 600°C can also be seen for the Ni/olivine catalysts and its surface increases with the calcination temperature. A drift at 910°C can also be observed and be attributed to the reduction of the nickel oxide present in low amount in the framework of the olivine.

For the catalyst calcined at 900°C, the reduction peak of free iron occurs with a maximum at 530°C. A shoulder at 450°C is present and can be ascribed to the presence of NiO aggregates without interaction with the olivine support. The presence of this nickel, reducible at low temperature, induces a synergy phenomenon in the reduction of the free iron oxide. The latter is reduced 100°C lower than for the fresh olivine in our conditions. TPR indicates a third broad massive corresponding to particles less feature reducible than free NiO like nickel containing particles grafted to the olivine surface.

After calcination at 1100°C, the low temperature reduction peak attributed to free NiO disappears. Only the two features ascribed to the reduction of free iron and grafted nickel oxides are observed. The grafted nickel oxide particles are reduced around 865°C in our conditions.

Calcination at 1400°C modifies strongly the TPR profile. The peak corresponding to the free iron oxide is increased and nickel is no more reduced below 910°C. This indicates that nickel is substituted for the iron of the olivine structure at 1400°C and the integrated nickel becomes difficult to reduce.

TPR study could be used to choose the most appropriated catalyst for the methane reforming particularly

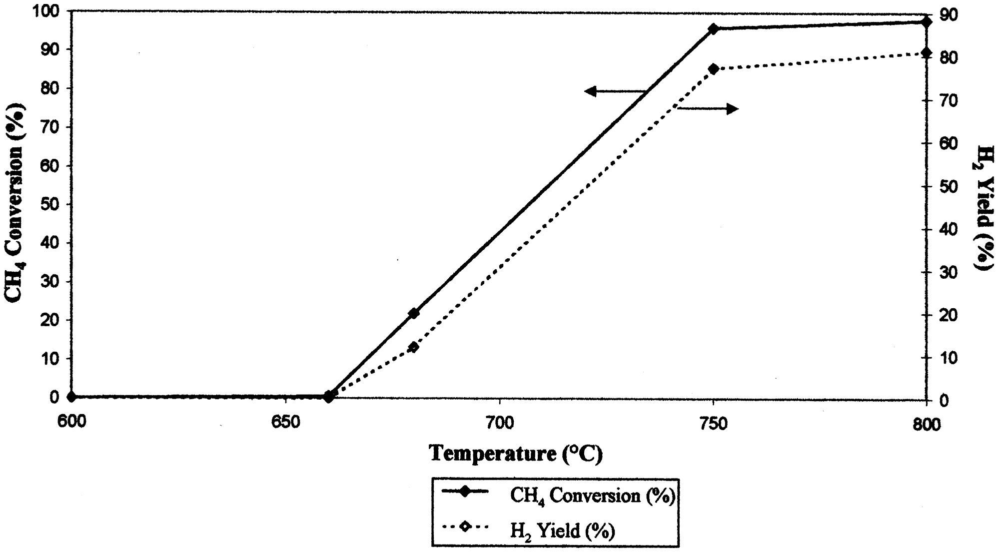

Fig. 4. Methane conversion and hydrogen yield versus reaction temperature in dry-reforming of methane with $CO_2/CH_4 = 1$ for 2.8 wt.% Ni/olivine calcined at 1100°C.

the disappearance of the low temperature reduction peak (around 450°C) and the presence of the reduction peak associated with grafted nickel oxide particles (around 865°C). The best-adapted calcination temperature for the Ni/olivine catalyst seems to be 1100°C.

3.2. Activity of the nickel–olivine catalysts

In order to determine the catalytic activity of the various catalysts and the olivine support, the reaction of dry-reforming with CO_2/CH_4 ratio (noted R_1) equal to 1 was studied.

Olivine alone presents no activity at 800°C, methane conversion is at the most 1% and the hydrogen yield close to zero.

An important difference in catalytic activity is observed depending on the calcination temperature of the impregnated samples. Methane conversion and hydrogen yield are given (Fig. 4) versus reaction temperature (from 600 to 800°C) for the most promising catalyst calcined at 1100°C.

The samples calcined at 900 and 1100°C present similar high activities. Methane conversion is higher than 95%, hydrogen yield is near to 80% at 750 and 800°C and the H_2/CO ratio varies between 0.8 and 0.9. These results confirm the presence of accessible and reducible nickel particles on olivine support.

The sample calcined at 1400°C has a very low activity even at 850°C (methane conversion of 3% and hydrogen yield of 1%) or 900°C (methane conversion of 6% and hydrogen yield of 2%). These last results can be linked to the TPR curve of this catalyst which shows no reduction peak for nickel, indicating that the latter is completely integrated into the olivine structure.

A study was performed on the olivine support and on the most promising Ni/olivine catalyst in steam-reforming with $R_1 = H_2O/CH_4 = 1$. In order to better simulate the outlet gas mixture of gasification (30% H_2O, 31.5% H_2, 17.5% CO, 14% CO_2 and 6.3% CH_4), the steam-reforming of methane with $R_1 = H_2O/CH_4 = 3$ and $R_2 = H_2/CH_4 = 2$ has also been studied.

Olivine alone presents no activity at 850°C, methane conversion is at the most 2.2% and the hydrogen yield close to 0.25%.

Methane conversion and hydrogen yield were followed during steam-reforming (Fig. 5) from 650 to 850°C with the optimised catalyst.

The best results were obtained with $R_1 = 1$. Even at 750°C, methane conversion is higher than 88% and hydrogen yield higher than 75% and they increase with increasing temperature. With $R_1 = 3$ and without hydrogen, the catalyst is not active between 600 and

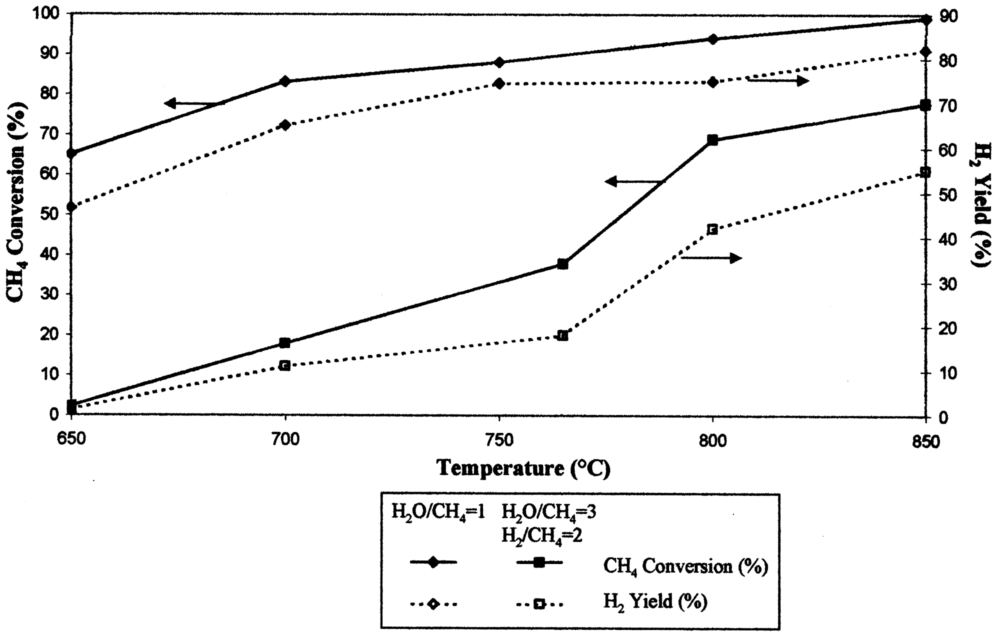

Fig. 5. Methane conversion and hydrogen yield versus reaction temperature in steam-reforming with $H_2O/CH_4 = 1$ or $H_2O/CH_4 = 3$ and $H_2/CH_4 = 2$ for 2.8 wt.% Ni/olivine calcined at 1100°C.

800°C but it has a very high activity (98% of methane conversion and 66% of hydrogen yield) at 850°C. Its activation seems to be difficult because of the high water content. With the same amount of water and $R_2 = 2$, methane conversion and hydrogen yield also increase with increasing temperature. It has to reach 850°C to obtain a 70% CH_4 conversion and a 55% H_2 yield but hydrogen permits the catalyst activation at lower temperatures.

The same catalyst, calcined at 1100°C, was tested in isothermal conditions to study its stability versus time on stream at 750°C for dry-reforming and at 800°C for steam-reforming under the three different gas mixtures. Methane conversion is given in Fig. 6.

For the dry-reforming ($R_1 = 1$), methane conversion slightly decreases versus time on stream but stays higher than 85% for at least 250 h. For steam-reforming with $R_1 = 1$ and $R_2 = 0$, methane conversion becomes rapidly stable between 80 and 85% for at least 200 h.

With $R_1 = 3$ and $R_2 = 0$, methane conversion decreases rapidly with time on stream and is about 60% after 10 h and about 38% after 50 h. The high water amount has a negative influence on the activity and the stability of this catalyst. Water is probably adsorbed on the catalyst and covers active nickel species.

With $R_1 = 3$ and $R_2 = 2$, methane conversion is firstly low but increases with time on stream, reaches about 70–75% after 30 h and remains stable for at least 40 h. In this case, hydrogen addition permits to obtain a more reducing gas mixture and to reach sufficiently active species of nickel to keep a good activity.

3.3. Characterisation of the nickel–olivine samples after catalytic tests

The analysis by XRD shows that the olivine structure (Fig. 7, curve a) is retained during the different catalytic tests.

After dry-reforming (Fig. 7, curve b), NiO phase (JCPDS 1-1239) and Ni–Fe alloy with a high Fe/Ni ratio (JCPDS 37-0474) can be observed. The presence of NiO particles implies that Ni particles formed during catalytic test were sufficiently small (about 10 nm) to be deoxidised under ambient conditions. But NiO particles can also result of the Ni^0 reoxidation by the oxygen contained in the catalyst support.

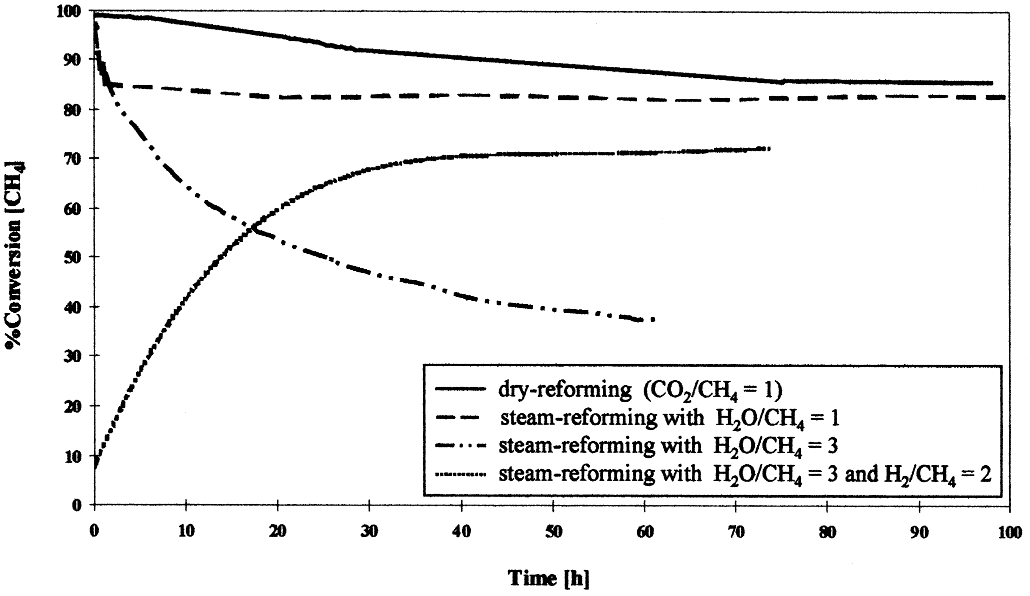

Fig. 6. Methane conversion versus time on stream in dry-reforming ($CO_2/CH_4 = 1$) and steam-reforming with $H_2O/CH_4 = 1$ or $H_2O/CH_4 = 3$ and $H_2/CH_4 = 0$ or $H_2/CH_4 = 2$ for 2.8 wt.% Ni/olivine calcined at 1100°C.

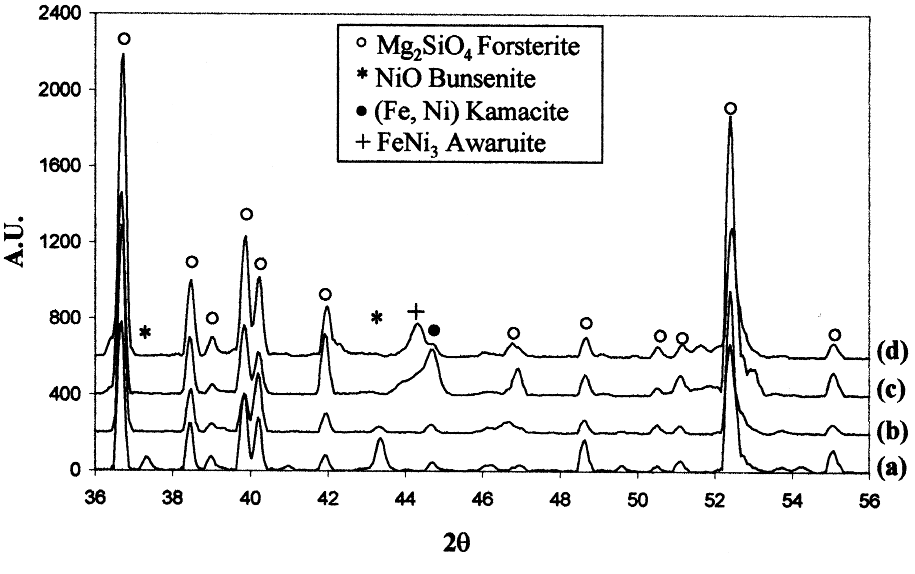

Fig. 7. X-ray diffractograms of Ni/olivine calcined at 1100°C: (a) before, (b) after dry-reforming, (c) after steam-reforming with $H_2O/CH_4 = 1$ and (d) after steam-reforming with $H_2O/CH_4 = 3$ and $H_2/CH_4 = 2$ for 2.8 wt.% Ni/olivine calcined at 1100°C. References Mg_2SiO_4 (34-0189 JCPDS file), NiO (1-1239 0189 JCPDS file), (Fe, Ni) (37-0474 JCPDS file) and $FeNi_3$ (38-0419 JCPDS file).

Table 3
Elementary analysis of carbon (wt.%) after catalytic tests on the sample calcined at 1100°C, here $R_1 = CO_2/CH_4$ or H_2O/CH_4 and $R_2 = H_2/CH_4$

Dry-reforming	$R_1 = 1$	0.13
Steam-reforming	$R_1 = 1;\ R_2 = 0$	0.34
	$R_1 = 3;\ R_2 = 0$	0.76
	$R_1 = 3;\ R_2 = 2$	0.69

After steam-reforming with $R_1 = 1$ and $R_2 = 0$, Ni–Fe alloy (JCPDS 37-0474) with a high Fe/Ni ratio is detected with the olivine structure (Fig. 7, curve c). On the contrary, with $R_1 = 3$ and $R_2 = 2$ (Fig. 7, curve d), the Ni–Fe alloy detected (JCPDS 38-0419) contains a lower Fe/Ni ratio (0.33).

So, the catalytic test conditions seem to lead to iron oxide reduction and migration of Fe to the Ni particles to form Ni–Fe alloys with a high Fe/Ni ratio. A more reducing gas mixture (addition of H_2) favours the nickel oxide reduction and the migration of Ni^0 to the Ni–Fe alloys. In this case, Ni–Fe alloys with a low Fe/Ni ratio are formed.

The scanning electron micrographs of the sample calcined at 1100°C are compared before and after dry- and steam-reforming for $R_1 = 1$. In these samples, the size of nickel containing particles remained constant during catalytic tests. In fact, these particles are better linked and grafted to the olivine surface which seems to be smoother. So, no nickel containing particle migration is observed.

Elementary analysis of carbon in the “after test” samples are given in Table 3. The samples contain very low carbon contents (always lower than 1 wt.%). Less coke is formed in dry-reforming and after steam-reforming, the carbon content tend to increase versus water concentration in the inlet gas mixture.

The state of Ni on the surface and the low carbon formation explain the good ageing behaviour of these catalysts.

4. Conclusion

This work has shown the interest to use complementary studies like XRD, SEM and TEM coupled to EDXS for the characterisation of catalytic samples prepared by NiO on olivine impregnation then calcination at different temperatures (900, 1100 or 1400°C).

The TPR has permitted to study the different types of Ni–olivine interactions, to know the reducibility of the samples during catalytic tests and to determine the choice of the most appropriate Ni/olivine system. The latter contained 2.8 wt.% of Ni and was calcined at 1100°C for 4 h.

This catalyst has met the requirements of activity and yield in syngas and of stability with time of stream (>260 h). In dry-reforming with $CO_2/CH_4 = 1$, methane conversion reached 95% and hydrogen yields were 80% at 750°C. In steam-reforming with $H_2O/CH_4 = 1$, methane conversion and hydrogen yield were, respectively, higher than 88% and 75% at 750°C. In steam-reforming with $H_2O/CH_4 = 3$ and $H_2/CH_4 = 2$ ratios, methane conversion was close to 70% and hydrogen yield close to 55% at 850°C.

Now, the Ni/olivine catalytic system appears ready to be used in catalytic biomass gasification in a fluidised bed.

Acknowledgements

Authors are highly indebted to the E.U. for the financial support (contract JOR3-CT97-0196).

References

[1] H.H. Landsberg in Energy the Next Twenty Years, Ballinger, Cambridge, MA, 1979, p. 77.
[2] M.J. Antal, in: K.W. Boer, J.A. Duffie (Eds.), Advances in Solar Energy, Part II, American Solar Energy Society, New York, 1985.
[3] J. Corella, M.P. Aznar, J. Delgado, E. Aldea, Ind. Eng. Chem. Res. 30 (1991) 2252.
[4] C. Ekstrom, N. Lindman, R. Pettersson, in: R.P. Overend, A.T. Milne, K.L. Mudge (Eds.), Fundamentals of Thermochemical Biomass Conversion, Elsevier, London, 1985, p. 601.
[5] D.C. Elliot, E.G. Baker, Biomass 9 (1986) 195.
[6] A. Olivares, M.P. Aznar, M.A. Caballero, J. Gil, E. Frances, J. Corella, Ind. Eng. Chem. Res. 36 (1997) 5220.
[7] T. Gruidl, Diploma Thesis, Technical University of Vienna, Austria, 1996.
[8] S. Rapagna, N. Jand, C. Courson, C. Petit, A. Kiennemann, P.U. Foscolo, in: Proceedings of the First World Conference

and Exhibition on Biomass for Energy and Industry, Sevilla, June 5–9, 2000.
[9] S.C. Tsang, J.B. Claridge, M.L.H. Green, Catal. Today 23 (1995) 3.
[10] J. De Deken, P.G. Menon, G.F. Froment, G. Haemers, J. Catal. 70 (1981) 225.
[11] V.R. Choudhary, V.H. Rane, A.M. Rajput, Catal. Lett. 22 (1993) 289.
[12] C. Petit, A. Kiennemann, P. Chaumette, O. Clause, US Patent No. 5,447,705 (1995).
[13] T. Hayakawa, H. Harihara, A.G. Andersen, K. Suzuki, H. Yasuda, T. Tsunoda, S. Hamakawa, A.P.E. York, Y.S. Yoon, M. Shimizu, K. Takehira, Appl. Catal. A 149 (1997) 391.
[14] H. Provendier, C. Petit, C. Estournès, S. Libs, A. Kiennemann, Appl. Catal. A 180 (1999) 163.
[15] M. Houalla, F. Delannay, I. Matsuura, B. Delmon, J. Chem. Soc., Faraday Trans. 76 (1980) 2128.