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Rh–Ni synergy in the catalytic partial oxidation of methane: surface phenomena and catalyst stability

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Abstract

Ni, Rh and Rh/Ni containing catalysts obtained from hydrotalcite type precursors have been studied in the partial oxidation of methane. The catalysts have been characterised by HRTEM to evaluate the effectiveness of the preparation method in the dispersion of the metal. The tests carried out in the partial oxidation of methane at a residence time of 12 ms did not allow to enlighten significant differences of activity among the catalysts due to the proximity of the results with those obtained at the thermodynamic equilibrium. New tests at very low residence times have allowed the catalyst evaluation in conditions far from the thermodynamic equilibrium and in which oxygen is still present. The catalytic bed length and the amount of catalyst have been chosen after the analysis of the thermal profile with the IR thermography. The IR thermography was used with the different catalysts to measure the maximum surface temperature trend as a function of the residence time. The tests carried out at very short residence times allow to compare the catalysts in conditions where O_2 is not totally converted and enlighten the high activity of the Rh/Ni catalysts in which the Ni is maintained in the reduced state by the Rh. The comparison of the catalysts have also been carried out studying the endothermic dry reforming at low residence times. The study of the dry reforming of methane have also been related to the evaluation of the activity of the consecutive reaction of the catalytic partial oxidation process, without the effect of a large heat production. Finally, the dry reforming was also used to measure the coke formation on the most active catalysts.

Keywords: Catalytic partial oxidation; Methane; Catalyst

1. Introduction

The catalytic partial oxidation (CPO) of methane at low residence time has been claimed as an interesting industrial route for the syngas production [1–3]. The process based on this technology has not been exploited yet to an industrial scale since many aspects need to be clarified to allow the scale up with minimised risk. Only recently Haldor Topsoe has revealed a demonstrative unit operating at short residence time. Nevertheless the potential application in different conditions is related to the comprehension of many factors which may improve the control of the reaction [1,4–8], in particular, heat distribution, catalyst composition and catalyst stability with time on stream are strongly related and of fundamental importance [9–11]. In a recent paper it has been pointed out that the catalytic activity can be strongly affected by the thermal profile that depends on the catalyst composition [12,13]. Therefore, the relative effect on the heat distribution due to the gas composition and the catalyst composition and stability requires more detailed studies to understand limits and control possibilities [11,14]. Furthermore, the catalysts have been usually tested at complete oxygen conversion in conditions not

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far from the equilibrium which may be misleading for the evaluation of their activity [12]. This work tries to overcome these problems carrying out the study on the CPO at short and very short residence time to enlighten the activity in oxygen reach conditions and compare the intrinsic activity of the catalysts. The same materials have been utilised in the dry reforming reaction at low residence time in order to evaluate the catalyst activity in reforming reaction in the absence of oxygen and hot spot phenomena. For the present studies very active catalysts in the partial oxidation of methane have been used [15–17]. The catalysts have been prepared from hydrotalcite type (HT) precursors containing Mg and Al as inert elements and Rh, Ni or bimetallic Rh/Ni, Ir/Ni and Ru/Ni as active elements. The catalyst stability have been evaluated in terms of thermal stability in severe reaction conditions and coke formation. The advantages and the opportunity of the bimetallic catalysts will be discussed in terms of activity and stability in CPO and CO_2 reforming of methane.

2. Experimental

The catalysts (M/Mg/Al, where M is Rh, Ni, Rh/Ni, Ir/Ni or Ru/Ni) were prepared through the co-precipitation of an HT precursor and their compositions are reported in Table 1 [15–17]. The HT precursors of general formula $[M_x{}^{3+}M_{1-x}{}^{2+}(OH)_2]$ $(CO_3)_{x/2}{}^{2-}\cdot mH_2O$ were prepared by co-precipitation at constant pH, adding a solution containing the nitrate salts of the metal ions in a solution containing a slight excess of carbonates. The pH was maintained constant by NaOH addition. The precipitates were kept in suspension under stirring at 60 °C for 40 min, then filtered and washed with distilled water till a Na_2O content lower than 0.02 wt.% was obtained. The precipitate were dried overnight at 90 °C, calcined at 900 °C and reduced in situ at 750 °C in equimolar H_2/N_2 feed of 7 l/h.

Table 1
Composition and surface area of the prepared samples

Sample	Composition	Atomic ratio	Surface area calcined at 900 °C (m^2/g)
Ni10	Mg/Al/Ni	61/29/10	53
Ru/Ni	Mg/Al/Ru/Ni	59/35/0.1/6	88
Ir/Ni	Mg/Al/Ir/Ni	59/35/0.1/6	102
Rh/Ni	Mg/Al/Rh/Ni	59/35/0.1/6	88
Rh1	Mg/Al/Rh	71/28/1	97
Rh5	Mg/Al/Rh	71/24/5	91

XRD powder analyses were carried out using a Philips PW1050/81 diffractometer equipped with a graphite monochromator and controlled by a PW1710 unit ($\lambda = 0.15418$ nm). A 2Θ range from 10° to 80° was investigated at a scanning speed of 70°/h. The surface areas were determined by N_2 adsorption using a Carlo Erba Sorpty model 1700. The metal particle distributions of the Rh, Ni and Rh/Ni containing catalysts were measured analysing the images collected with a TOPCON EM002K HRTEM operating at 200 kV and measuring more than 200 Rh particles, the sample was prepared suspending a small amount of catalyst in a methyl alcohol solution and depositing it on a carbon greed.

2.1. Catalytic tests

The catalytic tests were carried out in a quartz reactor using an oven heated at 750 and 500 °C, feeding a gas mixture $CH_4/O_2/He = 2/1/4$ (v/v) or operating in autothermal conditions, without an external insulation, after the ignition of the reaction by means of a thermal gun. The quartz reactor with an internal diameter of 6 mm was filled with 0.2 g of catalyst (bed length: 8–9 mm) for the tests carried out at a residence time of 12 ms or with 0.05 g of catalyst (bed length: 3 mm) for the tests carried out varying the residence time between 9 and 1 ms. The reaction products were analysed on-line after water condensation by using two gas chromatographs equipped with HWD and carbosieve SII columns, with He as the carrier gas for the analysis of CH_4, O_2, CO and CO_2 and N_2 as carrier gas for the H_2 analysis.

The light off temperature have been measured monitoring the temperature of the catalytic bed in the tests carried out at 12 ms during a temperature programmed ramp of 5°/min starting from 200 °C.

2.2. Surface temperature measurement

The surface temperature was measured with IR thermography equipment (AGEMA) collecting emitted radiation with λ in the 2–5 μm range. The IR camera was equipped with two zooms to improve the spatial resolution on the catalyst surface and a filter for high temperature applications (higher than 500 °C) which allows the utilisation of a narrow λ range. The vertical thermal profile has been obtained plotting the maximum temperatures of horizontal lines drawn on the thermographic images.

3. Results and discussion

The preparation flexibility of the HT precursor was used to prepare a number of catalysts changing active metal type and content (Table 1). In all the prepared samples the HT phase was the only crystalline phase detected by XRD. The use of HT precursors allows, after calcination, the preparation of reproducible materials formed by mixed oxides with high thermal stability, as evidenced by the high surface area of the calcined materials (Table 1). The calcined samples contain MgO and spinel-type phases. Previous studies have shown that Rh is soluted in the MgO and spinel phases, Ni is soluted in the MgO phase, while the position of Ru and Ir present in small quantity is difficult to be identified [18]. The reduction of the calcined samples leads to the final catalysts characterised by the presence of the metal dispersed inside an inert matrix. The HRTEM carried out on the reduced Rh5 sample clearly evidences the high dispersion of such a catalyst, the image of the sample shows that the Rh is homogeneously distributed on a Mg/Al oxide matrix. The grains of the matrix are constituted by oxide nano-domains but the differentiation between the MgO type and spinel-type phase is not possible. The analysis of more than 100 metal nanoparticles shows that the metal is present as nanoparticles below 3 nm and well bonded to the inert matrix (Fig. 1). The same analysis carried out on the Ni10 and Ni/Rh catalyst and confirmed by the XRD analysis shows a Ni particle size in the range of 4–6 nm. The EDS analysis carried out with the smallest spot on the Rh/Ni catalyst was not able to identify any separated Rh particle which therefore may be present as a bimetallic phase.

Table 2
Methane conversion and CO and H_2 selectivities in the partial oxidation of methane (CO_2 and H_2O are the other products) carried out at a residence time of 12 ms, $CH_4/O_2/He = 2/1/4$ (v/v), 0.2 g of catalyst, oven temperature 750 °C

Sample	Conv. CH_4 (%)	Conv. O_2 (%)	Sel. CO (%)	Sel. H_2 (%)
Ni10	93.7	100	93.6	95.9
Ru/Ni	93.2	100	95.8	94.9
Ir/Ni	93.4	100	95.6	95.4
Rh/Ni	93	100	97.4	94.8
Rh1	92.8	100	97.5	94.9
Rh5	93.2	100	96.5	95.1

The catalytic activity of the samples in the partial oxidation of methane feeding the $CH_4/O_2/He = 2/1/4$ (v/v) mixture at 750 °C (oven temperature) in the range 12–5 ms of residence time is very high with methane conversion and CO and H_2 selectivity higher than 90% and very close to the thermodynamic equilibrium values (Table 2). In Fig. 2, the methane conversion of the different samples as a function of the external heat supplied, represented by the oven temperature, is reported. With an oven temperature of 750 °C the catalysts do not show any significant differences (Fig. 2), due to the high temperature which smooth the differences and moves the reaction towards the equilibrium. Setting the oven temperature at 500 °C, in the same conditions, the catalysts evidence slightly different performances being Ni10 the most active. The catalytic tests carried out in autothermal conditions without external heat supply show much more evident differences and, in particular, the Ni10 catalyst has the highest methane conversion, M/Ni bimetallic catalysts show intermediate results while Rh1 and Rh5 catalysts show the lowest methane conversions. These results seem to indicate that Ni10 has the highest activity, on the other hand, if we consider the light off temperature obtained during a temperature ramp tests, the behaviour is the opposite and the Rh catalysts are the most active while the Ni is the less active (being, respectively, $T_{\text{light off}}$ (Rh1 and Rh5) ≈ 240 °C, $T_{\text{light off}}$ (Ni10) ≈ 430 °C). The tests carried out in autothermal conditions allow the surface temperature measurement and the evaluation of the heat distribution along the catalytic bed. The thermography of the catalyst Rh1 and the axial thermal profile as a function of the active phase Rh1, Ni10 and Rh/Ni are shown in Figs. 3 and 4, respectively. The surface temperature profile strongly depends on the type of the active phase. By means of the analyses of the temperature profiles the following scale of catalyst temperature at the beginning of the catalytic bed is: Rh > Rh/Ni > Ru/Ni, Ir/Ni > Ni, while the scale of temperature at

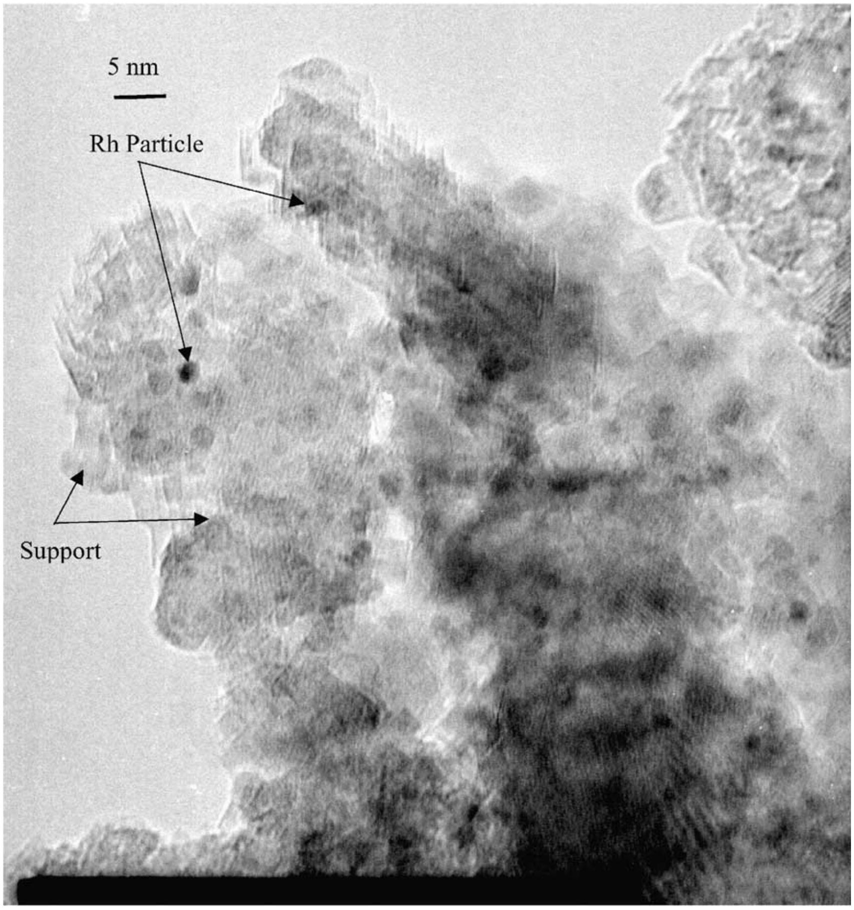

Fig. 1. HRTEM image (2 000 000×) of the Rh-5 sample after calcination at 900 °C and reduction at 750 °C.

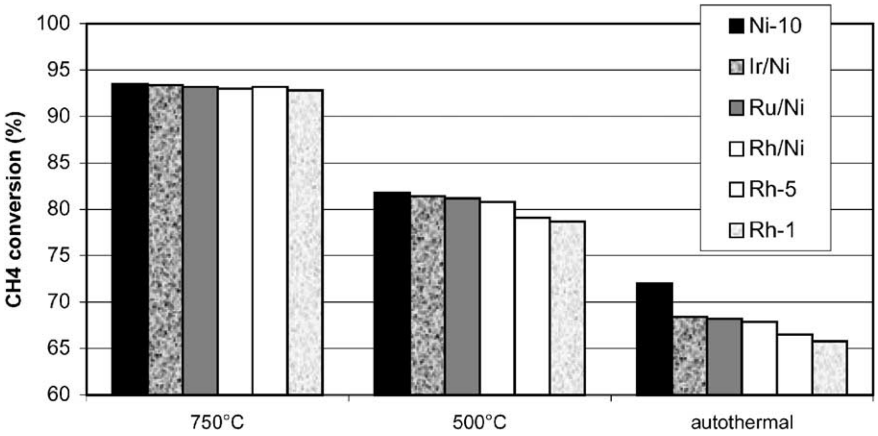

Fig. 2. Methane conversion in the partial oxidation of methane carried out at a residence time of 12 ms, $CH_4/O_2/He = 2/1/4$ (v/v), 0.2 g of catalyst, with different amounts of heat supplied (oven temperature 750 °C, 500 °C or autothermal condition).

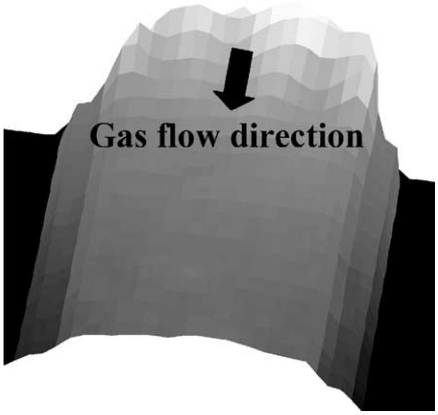

Fig. 3. Heat distribution and surface temperature 3D profile view of the Rh1 catalyst during partial oxidation of methane carried out at a residence time of 12 ms, $CH_4/O_2/He = 2/1/4$ (v/v), 0.2 g of catalyst in autothermal conditions.

the exit of the catalyst bed is inverse (Fig. 4). The highest surface temperature is reached in the first part of the catalytic bed for Rh1 while the temperature of Ni10 increases along the bed together with the amount of Ni^0. This is due to the fact that Ni is the less active element in oxygen reach conditions since part of the Ni is oxidised [19], while Rh is the most active one in the oxidation conditions, i.e. when unconverted oxygen is present. The methane conversion and the syngas selectivity of each catalyst are equal to those obtained at the thermodynamic equilibrium calculated on the bases of the exit temperature. Therefore, the apparent activity estimated by the methane conversion obtained in this conditions is related to the heat distribution and the exit temperature, and it is misleading to evaluate the intrinsic activity of the catalyst. On these bases, to enlighten the activity of the catalysts in oxygen reach conditions and compare the relative activity of each catalyst it is important to set up reaction conditions at which the results are far from the thermodynamic equilibrium, i.e. using a short bed and a much lower residence time. The thermal profile helps to the choice of the bed length and as a consequence of the optimum amount of catalyst that are, respectively, equal to 3 mm and 0.05 g. In this way it is possible to have completed or uncompleted oxygen conversion by modifying the residence time through the flow rate [12]. The short bed has been used to compare the activity of Rh1, Ni10, Rh/Ni and Rh5, in autothermal conditions, analysing the effect of the catalyst composition in terms of metal type and loading.

The Ni10 catalyst is not active in these conditions also using an ignition temperature of the thermal gun up to 650 °C (temperature of the catalytic bed: 610 °C). The XRD analysis of the catalyst shows only traces of Ni^0 since most likely it was re-oxidised by the oxygen present in the gas mixture [19]. On the other hand the Rh1 catalyst shows a very high activity and selectivity also at very low residence time (between 9 and 1 ms). At residence time below 3.0 ms the oxygen conversion is lower than 100% and decreases with decreasing residence time, therefore these conditions are far from the thermodynamic equilibrium and the methane conversion shows a maximum close to 3 ms (Fig. 5). Nevertheless, it is worth noting that the CO and H_2 selectivities are still high

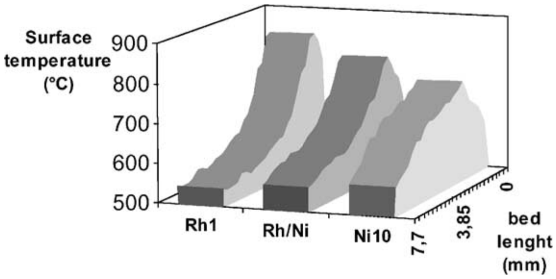

Fig. 4. Surface temperature profiles of the Rh1, Ni10, Rh/Ni catalysts during partial oxidation of methane carried out at a residence time of 12 ms, $CH_4/O_2/He = 2/1/4$ (v/v), 0.2 g of catalyst in autothermal conditions.

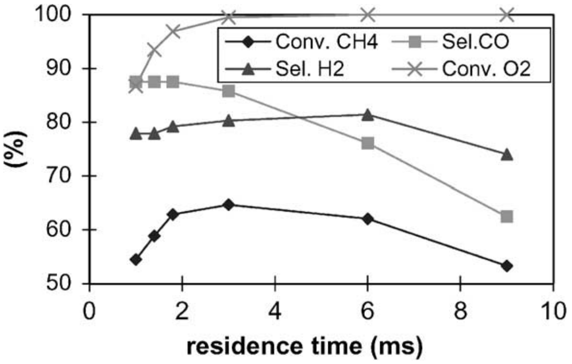

Fig. 5. Catalytic results of the Rh1 catalyst in the partial oxidation of methane carried out in autothermal conditions varying as a function of the residence time, $CH_4/O_2/He = 2/1/4$ (v/v), 0.05 g of catalyst.

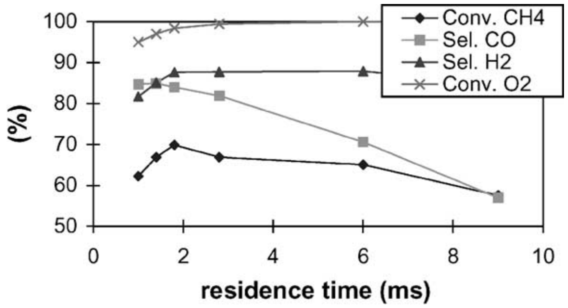

Fig. 6. Catalytic results of the Rh/Ni catalyst in the partial oxidation of methane carried out in autothermal conditions as a function of the residence time, $CH_4/O_2/He = 2/1/4$ (v/v), 0.05 g of catalyst.

(respectively, about 90 and 80%) when the oxygen conversion is clearly not complete. Also at an oxygen conversion below 90% (residence time of about 1 ms) the selectivity as a function of residence time is still almost constant. This behaviour, confirmed by that of the Rh/Ni catalyst allows to state that CO is a primary product while the trend of the H_2 selectivity is not easy to understand. The methane and oxygen conversions of Rh/Ni catalyst show a similar trend to those of the Rh catalyst: total oxygen conversion above 3 ms, maximum methane conversion at almost the same residence time (Fig. 6). However, some differences are also clear in the catalyst behaviours; the methane conversion of the Rh/Ni catalyst is higher than that of Rh1 and shows a discontinuity below 3 ms, and the oxygen conversion decreases much slower than that of the Rh1 catalyst. The results can be explained on the basis of the IR thermography and in particular analysing the maximum surface temperature on the top of the catalytic bed (radial maximum) and the maximum surface temperature along the catalytic bed (axial maximum). As a function of residence time, the two catalysts evidence two different behaviours (Fig. 7): (i) the Rh1 catalyst shows a constant increase of the temperature with decreasing residence time; (ii) the surface temperature of the Rh/Ni increases less at residence time higher than 3 ms. However, below this limit and at very low residence times it increases much more rapidly with decreasing residence time. The different behaviour, affected by the catalyst composition, confirms that the temperature of the catalysts is controlled by surface phenomena such as the number of active sites and their specific activity. Furthermore the discontinuity point in the methane conversion trend of the Rh/Ni catalyst (Fig. 6) is coincident with the change in the slope of the axial and radial maximum temperature curves (Fig. 7). The slope change is related to reduction phenomena occurring at the Rh/Ni surface and in particular attributable to the Ni, due to the increase of the reduction potential of the reaction mixture with the increase of the temperature. That means that the reduction of Ni changes with changing the residence time. The XRD analysis of the Rh/Ni catalyst, used at very low residence times, has shown a Ni^0 reflection corresponding to an almost complete Ni reduction. It has to be pointed out, that in conditions far from the thermodynamic equilibrium, the Rh/Ni catalyst is the most active catalyst. The synergetic effect of Rh and Ni is enhanced by the increase of the gas flow since the Rh is able to convert methane and oxygen increasing the surface temperature at the beginning of the bed and, therefore, increasing the amount of reduced Ni. On the other hand when only Ni is present in the catalyst the oxygen flow oxidises the Ni and decreases its activity. Therefore the presence of Rh and Ni in the same materials is important to enhance the activity in oxygen reach conditions, since Ni will be otherwise oxidised, and it is also important to decrease the Rh loading and catalyst costs.

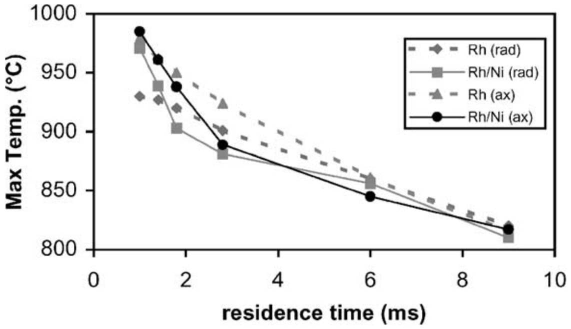

Fig. 7. Axial and radial maximum surface temperatures of the Rh1 and Rh/Ni catalysts during partial oxidation of methane carried out in autothermal conditions varying the residence time between 9 and 1 ms, $CH_4/O_2/He = 2/1/4$ (v/v), 0.05 g of catalyst.

The activity of the Rh5 catalyst has been compared in the same conditions to enlighten the effect of the amount of Rh. The oxygen conversion is always complete in all the reaction conditions also at a residence time of 1 ms. The methane conversion increases with the decrease of the residence time such as the CO and H_2 selectivity. The higher activity is due to the higher number of reaction site, indicating that the kinetic is controlled by the surface reaction rate also in these conditions.

The Rh1, Ni10 and Rh/Ni catalysts have also been compared in the dry reforming reaction ($CH_4/O_2/He = 2/1/1$, v/v) at very low residence time (12 ms) using the oven heated at 750 °C. The CO_2 reforming reaction is one of the consecutive reactions in the CPO process and it is strongly endothermic, therefore a higher activity has an opposite effect on the thermal distribution and profile with respect to the partial oxidation reaction. It is interesting to compare the activity of the catalysts in these conditions in order to analyse their relative activity without the presence of a strong exothermic effect. During the reaction all the catalysts have shown a decrease of the temperature measured by the thermocouple inserted in the catalytic bed below 700 °C. The Rh/Ni catalyst shows the highest reduction of reaction temperature (80 °C) and the best methane and CO_2 conversions (Fig. 8). The analysis of the catalytic results of Rh1 and Ni10 mono metallic catalysts evidences a different activity in the CH_4 and CO_2 conversions. The Rh1 catalyst is more active in the methane conversion while the Ni10 catalyst is more active in the CO_2 conversion [20]. Therefore the high activity of the Rh/Ni catalyst can be explained by a synergetic effect of Rh and Ni which increases the conversions even if the amount of Rh and Ni is much less than that of the mono metallic catalysts. The three catalysts have been tested in the dry reforming using a higher residence time (500 ms) in the range of temperature between 750 and 600 °C during a relative long test run, as reported in Fig. 9 for the Rh1 catalyst. The catalytic results do not show any difference among the catalysts in terms of activity, nevertheless the analysis of the carbon content after more than 60 h of time on stream has shown that the Rh and Rh/Ni catalysts do not evidence any coke formation differently from Ni10 (Table 3). Also in this case the presence of small amount of Rh, in the Rh/Ni catalysts, is an advantage since it inhibits

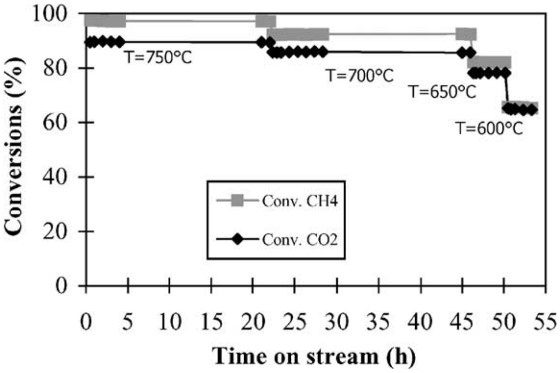

Fig. 9. CH_4, CO_2 conversions of Rh1 catalyst in the dry reforming of methane carried out at a residence time of 500 ms, $CH_4/CO_2/He = 1/1/2$ (v/v), 0.5 g of catalyst.

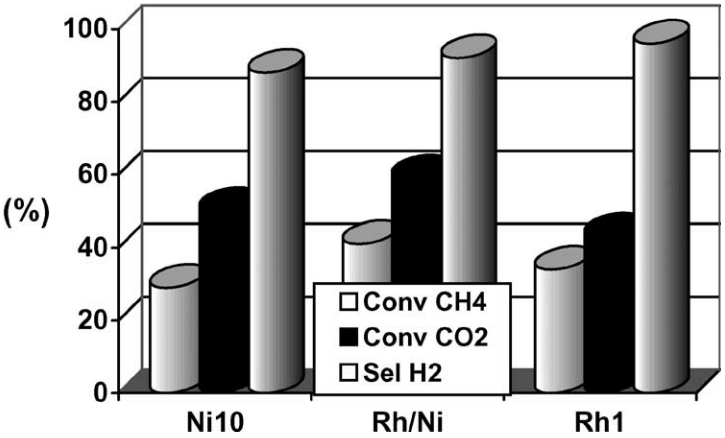

Fig. 8. CH_4, CO_2 conversions and H_2 selectivity of Rh1, Ni10 and Rh/Ni in the dry reforming of methane at a residence time of 12 ms, $CH_4/CO_2/He = 1/1/2$ (v/v), 0.2 g of catalyst, oven temperature 750 °C.

Table 3
Carbon content before and after 60 h of time on stream in dry reforming of methane

	Sample		
	Rh1	Rh/Ni	Ni10
Calcined (% deposited C)	0.73	0.64	0.62
Used (% deposited C)	0.71	0.67	3.05

the formation of coke. Therefore the presence of Rh and Ni in the same catalyst, gives rise to the best results in terms of activity in the CPO and consecutive dry reforming reaction and the use also in conditions in which the coke formation is favoured, ensuring a higher stability than that of the Ni catalyst.

4. Conclusions

The use of HT precursor is a general method to produce very active catalysts in the partial oxidation of methane at short residence time. The dispersion of the active metal inside the inert matrix depends on the type of the metal and is maximum for the Rh containing catalysts, in fact the HRTEM analysis carried out on the reduced Rh catalyst shows a metal particle size below 3 nm also at high metal loading.

In CPO the comparison of the results of Ni and/or Rh containing catalysts at a residence time of 12 ms obtained in tests with a large external heat supplies and without external heat supply (autothermal conditions) enlightens an increase of the differences among the catalyst behaviours with the Ni containing catalyst having the best activity. The IR thermography was utilised to measure the surface temperature of the catalysts and demonstrates that the results are not due to a higher activity of the Ni. The high performances of Ni have to be related to the lower activity of Ni in the oxidation conditions which shifts the temperature maximum towards the end of the catalytic bed where the thermodynamic equilibrium is reached. The activity was analysed in oxygen reach conditions by reducing the bed length and the residence time and moving far from the thermodynamic equilibrium. The Ni10 sample is inactive in these conditions, while Rh/Ni catalyst is much more active than the Rh1 catalyst in terms of methane and oxygen conversion. This result indicates the positive effect of Rh which allows to maintain a higher amount of Ni in the reduced state at low residence time, as confirmed by the maximum temperature trend measured by IR thermography.

The study of the activity in the dry reforming of methane leads to analogous conclusions and evidences a synergetic effect between Rh and Ni, with Ni being more active in the CO_2 conversion and Rh more active in the CH_4 conversion. A long duration test of more than 60 h also shows the interesting effect of Rh in the inhibition of coke formation absent in the Rh/Ni catalyst.

Finally the presence of Rh and Ni in the same catalyst allows an increase of CPO activity in oxygen reach conditions, a high stability towards the coke formation in the dry reforming reaction notwithstanding the low amount of Rh and a related reduction of the catalyst costs.

References

[1] G.A. Foulds, J.A. Lapszewicz, Catalysis, vol. 11, The Royal Society of Chemistry, Cambridge, UK, 1994, Chapter 10.
[2] D.A. Hickman, L.D. Schmidt, J. Catal. 138 (1992) 267.
[3] V.R. Choudhary, A.S. Mamman, S.D. Sansare, Angew. Chem. Int. Ed. Engl. 31 (1992) 1189.
[4] D.A. Hickman, E.A. Haupfear, L.D. Schmidt, Catal. Lett. 17 (1993) 223.
[5] V.R. Choudhary, A.M. Rajput, V.H. Rane, Catal. Lett. 16 (1992) 269.
[6] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Gray, A.J. Murrel, P.D.F. Vernon, Nature 344 (1990) 319.
[7] D. Dissanayake, M.P. Rosynek, K.C.C. Kharas, K.J. Lunsford, J. Catal. 132 (1991) 117.
[8] K. Walter, O.V. Buyeskaya, D. Wolf, M. Baerns, Catal. Lett. 29 (1994) 261.
[9] J.H. Mallens, B.J. Hoebink, G.B. Marin, J. Catal. 167 (1997) 43.
[10] Y. Chang, H. Heineman, Catal. Lett. 21 (1993) 215.
[11] L. Basini, K. Aasberg-Petersen, A. Guarinoni, M. Østberg, Catal. Today 64 (2001) 9.
[12] F. Basile, G. Fornasari, F. Trifirò, A. Vaccari, Catal. Today 64 (2001) 21.
[13] F. Basile, G. Fornasari, F. Trifirò, A. Vaccari, Studies in surface science and catalysis, in: A. Corma, F.V. Melo, S. Mendioroz, J.L.G. Fierro (Eds.), Proceedings of the 12th International Congress on Catalysis, vol. 130, Elsevier, Amsterdam, 2000, p. 449.
[14] L.D. Schmidt, O. Deutschmann, C.T. Goralsky, Studies in surface science and catalysis, in: A. Parmaliana, D. Sanfilippo, F. Frusteri, A. Vaccari, F. Arena (Eds.), Natural Gas Conversion V, vol. 119, Elsevier, Amsterdam, 1998, p. 685.

[15] L. Basini, G. Fornasari, F. Trifirò, A. Vaccari, Eur. Pat. Appl. 101 (1996) 059.
[16] F. Basile, L. Basini, G. Fornasari, M. Gazzano, F. Trifirò, A. Vaccari, J. Chem. Soc., Chem. Commun. (1996) 2435.
[17] F. Basile, L. Basini, G. Fornasari, M. Gazzano, E. Poluzzi, F. Trifirò, A. Vaccari, Studies in surface science and catalysis, in: B. Delmon, et al. (Eds.), Preparation of Catalyst VII, vol. 118, Elsevier, Amsterdam, 1998, p. 31.
[18] F. Basile, G. Fornasari, M. Gazzano, A. Vaccari, Appl. Cl. Sci. 16 (2000) 185–200.
[19] F. Basile, L. Basini, M. D'Amore, G. Fornasari, A. Guarinoni, D. Matteuzzi, G. Del Piero, F. Trifirò, A. Vaccari, J. Catal. 173 (1998) 247.
[20] Y. Chen, K. Tomishige, K. Yokoyama, K. Fujimoto, Appl. Catal. A 165 (1997) 335.