Short communication

# Autoreduction of promoted Ni/γ-Al₂O₃ during autothermal reforming of methane

Joelmir Augusto Costa Dias*, José Mansur Assaf

*Laboratório de Catálise, Departamento de Engenharia Química, Universidade Federal de São Carlos,
Via Washington Luiz, Km 235, CEP 13565-905, São Carlos, SP, Brazil*

## Abstract

The addition of the noble metals Pt, Pd and Ir to the Ni/γ-Al₂O₃ catalyst used in the autothermal reforming of methane was investigated, with the aim of making the reaction ignite without previous reduction of the catalyst with H₂. In TPR-CH₄, the catalysts promoted with Pt and Ir chloride suffered reduction at temperatures lower than 500 °C, while the unpromoted catalyst and those promoted by addition of PdCl₂ did not suffer reduction. Pd promoted the reduction only when added as the nitrate. The catalytic tests of intermittent start-up, alternating with air flow, showed results consistent with those from the TPR-CH₄. Pt- and Ir-promoted catalysts were active in all the start-ups, producing a great quantity of hydrogen, while the sample promoted via paladium chloride did not produce hydrogen in significant quantity, converting methane only to CO₂ and water. The samples promoted via palladium nitrate were very active in autothermal reforming without previous reduction, producing a great quantity of hydrogen.
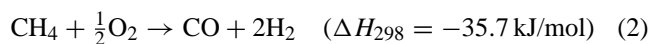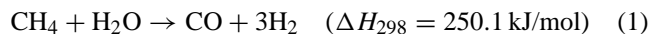© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Autothermal reforming of methane; Ni/γ-Al₂O₃; Autoreduction; Noble metals; TPR-CH₄

## 1. Introduction

Fuel cells, which have shown a notable progress in recent years, are being developed for stationary or portable energy generation. The technological advance of these devices is propelled by the recognition of their potential for high efficient energy generation coupled with low toxic-gas emission [1].

The preferred fuel for these devices is hydrogen, produced from sources that depend on the particular applications. In transport, methanol, gasoline and diesel are strong candidates. In stationary systems, natural gas (composed basically of methane) is the recommended source. However, as all of these sources are hydrocarbon or oxygenated, they need to be reformed in order to be transformed to hydrogen [1].

Among the processes used to transform natural gas to hydrogen, three stand out: steam reforming (Eq. (1)), partial oxidation (Eq. (2)) and autothermal reforming of methane, the last being a combination of steam reforming with partial oxidation [2]:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (\Delta H_{298} = 250.1 \, \text{kJ/mol}) \quad (1)$$

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \quad (\Delta H_{298} = -35.7 \, \text{kJ/mol}) \quad (2)$$

Steam reforming shows the higher efficiency in hydrogen production. However, the energy required for the process, due to its endothermicity, is considered its greatest disadvantage for fuel production. Partial oxidation, which is exothermic, requires external cooling. Thus, autothermal reforming seems to be the best option for the production of hydrogen as a fuel, combining the high efficiency of steam reforming with the lack of need for external energy of partial oxidation [3].

Autothermal reforming is a catalytic process, and the active catalysts for this process are the same as those for steam

---

reforming and partial oxidation, i.e. the transition metals of the VIII-B group, in the following activity order: Rh > Pd > Ni > Pt > Co [4]. Although it has an intermediate activity, nickel is a good candidate for this process, due to its low price and high availability, compared to the other cited metals.

Some research has been carried out on the promotion of nickel catalysts by adding noble metals, and they have proved to be excellent promoters of activity [5–8].

Besides the activity promotion, other important factors are the capacity of a catalyst to start the reaction rapidly without the necessity of previous reduction with hydrogen, and its capacity for intermittent operation, these being essential properties for the use of the catalyst in reformers for portable and small-scale stationary fuel cells. In this regard, given their ease of reduction at low temperature and their ability to dissociate methane with formation of atomic hydrogen, the noble metals are good candidates as promoters of the capacity for fast and intermittent ignition.

In previous work, it has been demonstrated that the addition of small amounts (up to 0.3%) of the noble metals Pt, Pd and Ir to Ni/$\gamma$-Al$_2$O$_3$ (15% (w/w) Ni) increased significantly the activity of the catalysts in the autothermal reforming of methane. No alterations were observed in the DRIFTS analysis of CO adsorption, due either to electronic influence of noble metals over nickel, or to segregation of noble metals in bimetallic particles, which indicates that the metallic surface of the catalyst consisted basically of nickel. Furthermore, the conversion of methane during the autothermal reforming increased in proportion to the metallic surface area, regardless of the noble metal added, showing that the only effect of these noble metals, at these low contents, was to increase the exposed area of nickel at the surface [8].

Therefore, in light of the strong increase in the activity of a nickel catalyst that can be achieved by adding less than 0.3% (w/w) of Pt, Pd and Ir, the objective of this work was to investigate the potential of these noble metals, also at contents below 0.3%, to promote fast and intermittent ignitions of autothermal reforming of methane in Ni/$\gamma$-Al$_2$O$_3$ (15% (w/w) Ni).

## 2. Experimental

Catalysts were prepared by successive impregnation of $\gamma$-alumina (Degussa) with solution of the metal salts. Ni(NO$_3$)$_2$·6H$_2$O (Aldrich Chem. Co.), H$_2$PtCl$_6$·2H$_2$O (Aldrich Chem. Co.), PdCl$_2$ (Aldrich Chem. Co.), Pd(NO$_3$)$_2$ (Aldrich Chem. Co.) and IrCl$_4$·$x$H$_2$O (Aldrich Chem. Co.) in water (except PdCl$_2$, which needed to be dissolved in dilute HCl), in concentration around 0.3 M. The Ni content in the catalysts was 15% (w/w). The contents of noble metals (w/w) were 0.05% and 0.27% Pt, in samples labeled I-PtNiAl and II-PtNiAl, 0.10 and 0.24% Pd, from chloride, in samples I-PdNiAl-Cl and II-PdNiAl-Cl, 0.10 and 0.30% Pd, from the nitrate, in samples I-PdNiAl-N and II-PdNiAl-N, and 0.30% Ir in the sample I-IrNiAl. The order of impregnation was first

nickel and second the noble metal. The catalyst was calcined at 550 °C for 5 h in flowing air between the two impregnations, and at 600 °C for 5 h in the air flow after the impregnations.

The samples were submitted to temperature-programmed reduction with methane (TPR-CH$_4$), with a feed of 2% CH$_4$/He (AGA), in order to test the possibility of activating the catalyst in the absence of hydrogen, given that methane would be the reducing agent responsible for the activation of nickel in the unreduced catalysts during the autothermal reforming of methane. In these tests, the temperature was increased at 5 °C min$^{-1}$ to 600 °C, where it was held until the end of methane consumption.

The catalytic tests were made with a feed of methane (AGA), air (AGA) and deionized water. The products were analyzed by in-line gas chromatography. In each run a sample of 0.1000 g of catalyst was used, forming a bed shorter than 1 mm, in order to minimize the axial thermal dispersion. A thermocouple was used in a well inserted in the bed. The autothermal reforming tests were made in all the catalysts, with a feed ratio of 1CH$_4$:4H$_2$O:0.25O$_2$, using a feed of 20 ml min$^{-1}$ (1 atm, 298 K) of CH$_4$, 49 ml min$^{-1}$ (1 atm, 298 K) of air (20.3% (v/v) O$_2$) and 3.7 g h$^{-1}$ of steam. The first ignition of each sample was made heating the catalyst to 550 °C in synthetic air, flowing at the catalytic test flow-rate. At this temperature, the methane flow was initiated and, after thermal stabilization, the flow of steam was added. Then the temperature was adjusted to 600 °C and the product analysis was started. For each sample, six ignition tests were run, alternated with airflow at 550 °C. All the start tests followed the same steps of methane and steam feed.

## 3. Results

Figs. 1–3 show the results of analysis of the catalyst samples by TPR-CH$_4$. In this analysis, the reagent was a mixture of 2% (v/v) CH$_4$/He, and the effluent was analyzed by a thermal conductivity detector in negative polarity (an increase in thermal conductivity leads to a negative signal).
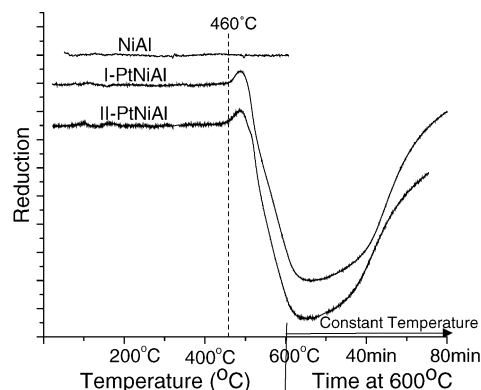


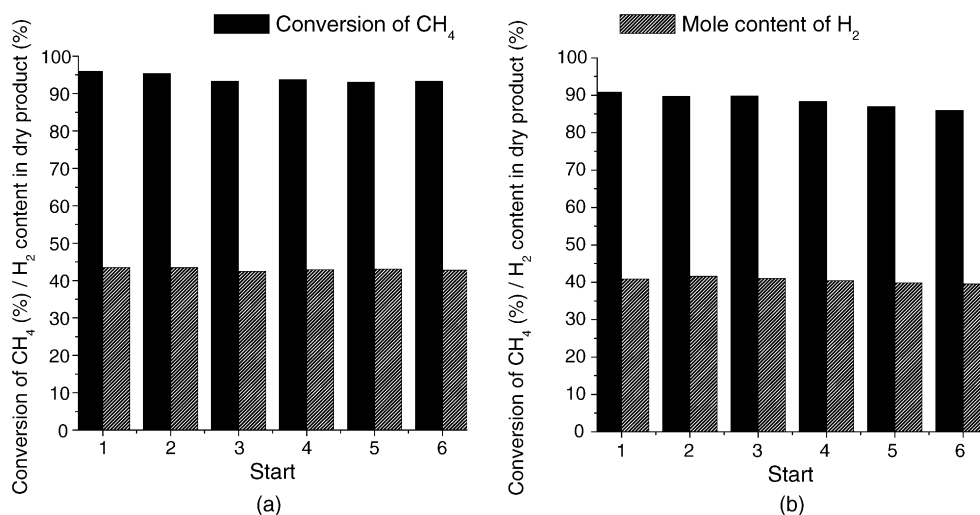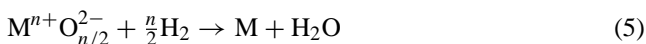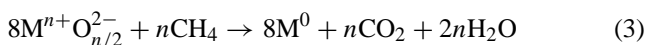Fig. 1. TPR-CH$_4$ of Pt-promoted catalysts.

Fig. 2. Conversion of methane and hydrogen content in the dry product formed in catalysts without previous reduction: (a) sample I-PtNiAl, (b) sample II-PtNiAl.

The reactions that possibly occur during the reduction are the following:

$$8M^{n+}O_{n/2}^{2-} + nCH_4 \rightarrow 8M^0 + nCO_2 + 2nH_2O \qquad (3)$$

$$CH_4 \xrightarrow{M^0} C + 2H_2 \qquad (4)$$

$$M^{n+}O_{n/2}^{2-} + \tfrac{n}{2}H_2 \rightarrow M + H_2O \qquad (5)$$

Reaction (3) is the reduction of metal ions by methane. Reaction (4) occurs in the presence of the $M^0$ formed in (3) and generates hydrogen, which reduces the unreduced metal ions, through the third reaction.

As the thermal conductivity detector was used in negative polarity, the carbon dioxide and water generated produce a positive signal, even though methane is consumed (all of these gases have lower thermal conductivity than He), due to the

fact that three molecules of water + carbon dioxide are made from each molecule of methane. The liberation of hydrogen, which has a similar thermal conductivity to He, associated with the consumption of methane, produces a negative signal.

Fig. 1 shows the results of TPR-CH$_4$ of the Pt-promoted catalysts.

This figure shows that the sample that only contains nickel does not suffer reduction until 600 °C. However, the platinum-containing samples exhibit reduction, which possibly starts through reaction (3), at 460 °C. Above this temperature, H$_2$ starts to be formed by reaction (4), and reduces Ni. The formation of Ni$^0$ causes an increase in the consumption of CH$_4$, producing further H$_2$, lowering the thermal conductivity signal, until it reaches a minimum, from which it begins to increase. This increase represents the deactivation of nickel particles by deposited carbon. It can be seen that, in
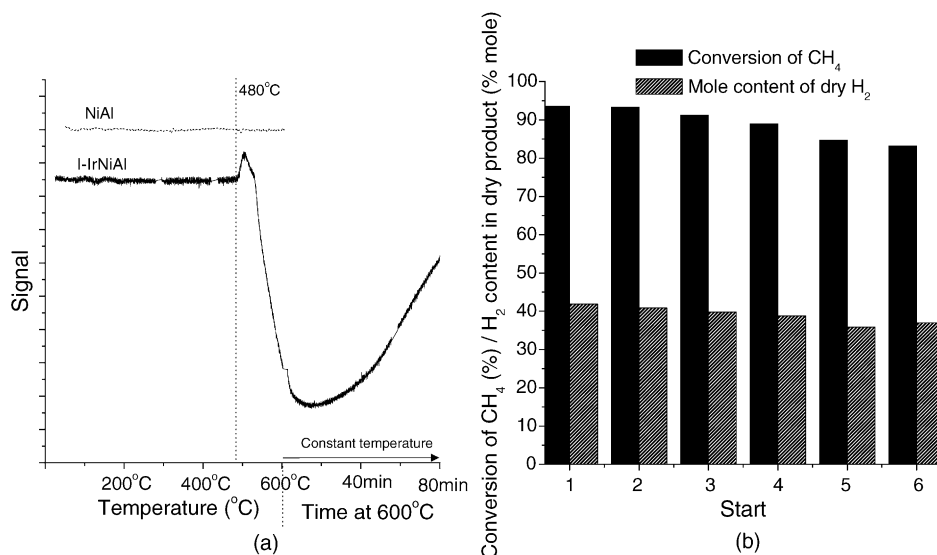


Fig. 3. (a) TPR-CH$_4$ of the Ir-promoted catalyst and (b) ignition test of the Ir-promoted catalyst.

the presence of methane, the catalyst can initiate its activity at temperatures above 460 °C. It is also important to see that the reduction start temperature is independent of the amount of platinum in the catalyst, indicating that the reduction of a small quantity of metal is enough to promote the nickel reduction until its stabilization.

As was expected after the TPR-CH$_4$ tests, the NiAl catalyst did not promote ignition in any of the start tests. By contrast, both PtNiAl samples successfully ignited the feed in every starts test in the series, without exception (Fig. 2).

It is observed that the platinum-promoted catalysts, when submitted to methane and air feed, suffered reduction and converted the same amount of methane as the same catalysts, when previously reduced with hydrogen, as made in previous work [8]. Furthermore, it can be seen that the hydrogen content of the dry product (after removing the water) did not suffer variation during the tests. These results indicate that these catalysts are very promising for application in the generation of hydrogen for portable and small-scale fuel cells.

Fig. 3 shows the results of the TPR-CH$_4$ and ignition tests for the catalyst I-IrNiAl.

It can be seen that iridium is also a good promoter for the ignition of the reaction on the nickel catalyst, without previous reduction with hydrogen. It is seen in the TPR-CH$_4$ that its reduction begins at 480 °C, around 20 °C above the platinum-promoted catalysts. However, for this sample a few ignitions are needed before the stabilization of the catalyst, as a significant decrease is observed in the activity at the beginning of the run. It can be concluded that iridium is also a good promoter for the Ni/γ-Al$_2$O$_3$ catalyst, for fast and intermittent ignitions for portable and small-scale fuel cells.

Although they are good promoters, the high price of platinum and iridium is a great obstacle to the use of these metals in industrial catalysis. Clearly, the development of cheaper materials with the same properties would be very valuable. Therefore, the study of palladium, which is much cheaper, as
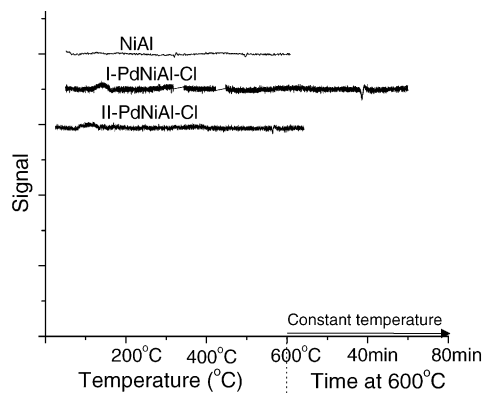


Fig. 4. TPR-CH$_4$ of catalysts promoted with palladium added to catalysts as chloride.

a substitute for platinum and iridium is the main aim of this work.

Fig. 4 shows the TPR-CH$_4$ results for the PdNiAl-Cl series.

It can be seen that palladium, when added as chloride, differently from platinum and iridium, does not favour the reduction of the catalyst with methane. This occurs possibly because the palladium is not reduced by methane, so that hydrogen is not produced by decomposition of methane, and there is no reduction of nickel. Fig. 5 shows the ignition tests for catalysts promoted with Pd (added as chloride).

Fig. 5 shows that, although the catalysts did not show reduction during TPR-CH$_4$, the PdNiAl-Cl samples showed activity, with conversion of methane around 30–40%, but producing low quantities of hydrogen. It is known that palladium, in oxidized form, is an excellent catalyst for total oxidation, or combustion, of methane, what is not true of metallic palladium [9]. As the H$_2$ content in the product was low with both samples, it can be concluded that the methane conversion afforded by these catalysts is basically due to the catalysis of
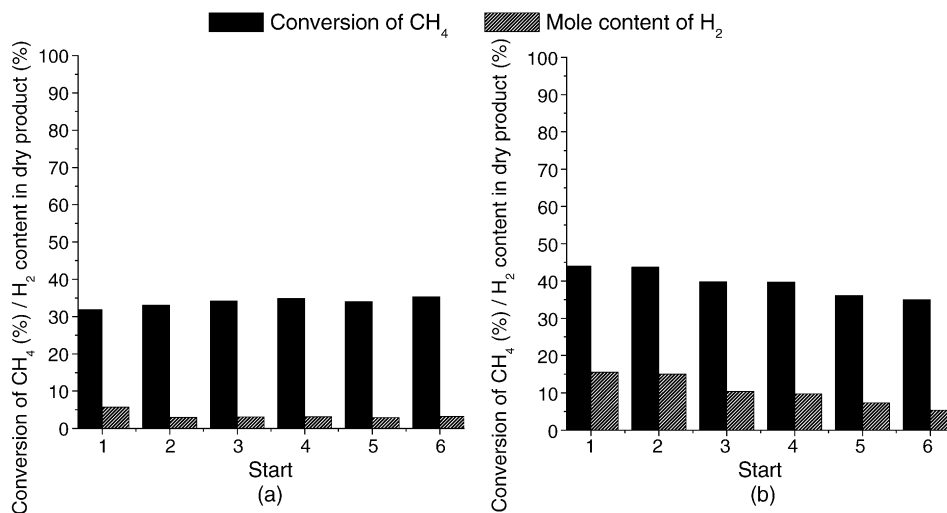


Fig. 5. Conversion of methane and hydrogen content in the dry product formed in catalysts without previous reduction: (a) sample I-PdNiAl-Cl, (b) sample II-PdNiAl-Cl.

the total oxidation by $Pd^{2+}$. This hypothesis is verified in the analysis of reaction enthalpy. The small quantity of hydrogen formed is probably due to the fact that combustion is very exothermic, forming small hotspots, which reduce a few palladium sites, and possibly nickel, creating some reforming sites that will produce some hydrogen. This would also be responsible for the fact that the conversion of methane is a bit higher than the 25% expected for the feed ratio $CH_4:O_2$ 2:1, according to the total oxidation stoichiometry.

It is known that the interaction of metal with support strongly depends on the preparation. When palladium is added in the form of chloride, the chlorine is not removed during calcination, and forms species with the palladium such as $Pd_xO_yCl_z$. These species disperses the palladium considerably over the surface. However, owing to the stronger interaction of this metal with alumina, its reduction is difficult [10]. Therefore, possibly due to the formation of these species, palladium is not reduced by methane, does not catalyze the nickel reduction, and is active predominantly for the total oxidation of methane. Hence, palladium, when added as chloride, is not a good candidate promoter of nickel for autothermal reforming of methane for fuel cells with intermittent operation.

However, it is known that palladium, when added to alumina as the nitrate, forms only oxide species after calcination. These oxide species are formed as clusters with low dispersion over the surface due to weak interaction with alumina. Also, due to this weak interaction with the support, palladium is reduced very easily in this form, sometimes even at room temperature in a hydrogen atmosphere [10]. In this light, and knowing that palladium is the cheapest noble metal among those used here, catalysts promoted with palladium based on nitrate were tested. Fig. 6 shows the results of TPR-CH4 of these samples.
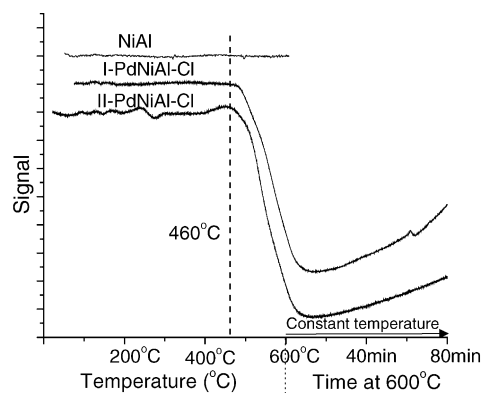


Fig. 6. TPR-$CH_4$ of catalysts promoted with palladium added to catalysts as nitrate.

In this figure, it is possible to see that the catalyst reduction really occurs and begins at around 460 °C, in these samples. This occurs because of the ease of reduction of palladium in these samples, in contrast to the samples of the PdNiAl-Cl series.

On the basis of Fig. 6, it can be predicted that these catalysts will be active in the start test of methane autothermal reforming. Fig. 7 shows the results of these tests.

The results in Fig. 7 verify that the promotion of the Ni/γ-$Al_2O_3$ catalyst with palladium becomes efficient when this noble metal is added in the form of nitrate, converting a great amount of methane and generating a great quantity of hydrogen. It is evident that the catalysts give ignition in all starts, with practically the same activity, making these catalysts more viable for use in fuel cells with fast and intermittent starts than those promoted with platinum and iridium, chiefly because palladium is cheaper than the other noble metals.
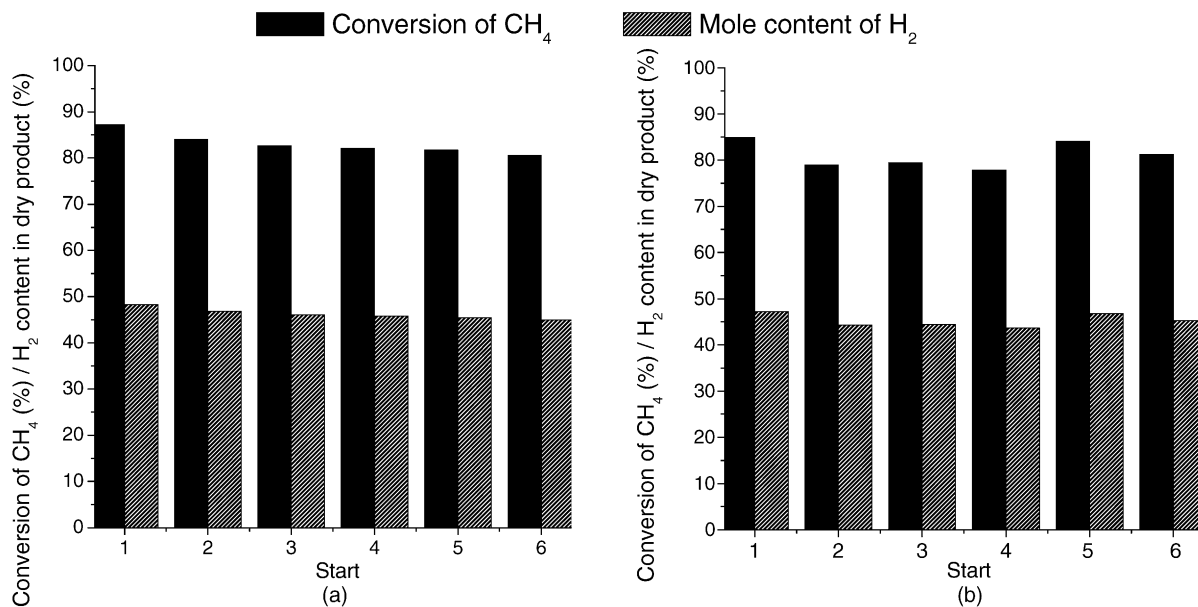


Fig. 7. Conversion of methane and hydrogen content in the dry product formed in catalysts without previous reduction: (a) sample I-PdNiAl-N, (b) sample II-PdNiAl-N.

## 4. Conclusions

It is concluded that platinum, palladium and iridium are good promoters of the reduction of the nickel catalyst with methane, an important property for application of the catalyst in the production of hydrogen for portable or small-scale fuel cells.

The platinum-promoted nickel catalysts are activated at 460 °C, irrespective of the platinum content, indicating that, once the first metal particles are reduced, the reduction of the catalyst will proceed to its end, possibly by the hydrogen liberated by the decomposition of methane on these metal particles.

The iridium-promoted catalyst is activated at 480 °C, but its surface does not reach stabilization. The changes that occur in these samples are possibly related to the growth of metal particles.

It was important to realize that palladium, when added as the chloride, did not promote nickel activation with methane, possibly due to the formation of compounds like $Pd_xO_yCl_z$ and, during the catalytic tests, since the palladium was in oxidized form, it catalyzed predominantly the total oxidation of methane.

On the other hand, when the palladium was added to the catalyst as nitrate, its reduction occurred at low temperatures, so it promoted the reduction of nickel with methane at around 460 °C, also regardless of the amount of palladium. This reduction allowed the self-activation of nickel and the ignition of autothermal reforming, when carried out over this catalyst.

From the point of view of cost, Pd is the most promising of these metals for use in small fuel cells.

## References

[1] S. Ahmed, M. Krumpelt, Int. J. Hydrogen Energy 26 (2001) 291.
[2] S. Cavallaro, S. Freni, J. Power Sources 76 (1998) 190.
[3] A. Ersoz, H. Olgun, S. Ozdogan, C. Gungor, F. Akgun, M. Tiris, J. Power Sources 118 (2003) 384.
[4] S. Ayabe, H. Omoto, T. Utaka, R. Kikuchi, K. Sasaki, Y. Teraoka, K. Eguchi, Appl. Catal. A: Gen. 241 (2003) 1.
[5] K. Tomishige, S. Kanazawa, M. Sato, K. Ikushima, K. Kunimori, Catal. Lett. 84 (2002) 69.
[6] J. Zhang, Y. Wang, R. Ma, D. Wu, Appl. Catal. A: Gen. 243 (2003) 251.
[7] L. Ma, D.L. Trimm, Appl. Catal. A: Gen. 138 (1996) 265.
[8] J.A.C. Dias, J.M. Assaf, J. Power Sources 130 (2004) 106.
[9] K. Persson, P.O. Thevenin, K. Jansson, J. Agrell, S.G. Järås, L.J. Pettersson, Appl. Catal. A: Gen. 249 (2003) 165.
[10] A.B. Gaspar, L.C. Dieguez, Appl. Catal. A: Gen. 201 (2000) 241.