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Autothermal reforming of methane over Ni/γ-Al_2O_3 catalysts: the enhancement effect of small quantities of noble metals

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Abstract

The effect of introducing small amounts of Pt, Pd and Ir ($<0.3\%$ by weight) into Ni/γAl_2O_3 catalysts (15% Ni w/w) for the autothermal reforming of methane (ATR) was investigated. While the unpromoted catalyst took the partial oxidation of methane to equilibrium, the promoted ones increased the methane conversion in ATR. No electronic modifications of nickel sites were observed with the addition of noble metals, but they did cause an increase in metal surface area. The effect of noble metals on this reaction, under these conditions, was assigned to this expansion of the metal surface.

Keywords: Autothermal reforming; Noble metals; Catalysts

1. Introduction

In recent years, there has been much interest in the production of hydrogen for high efficiency generation of electricity in fuel cells. Among all the sources of hydrogen available, the natural gas, composed mainly of methane, has been used most widely because this gas is very abundant, clean and can easily be converted to hydrogen [1]. To effect this conversion, some processes are frequently listed, such as steam reforming [1–12], partial oxidation [1,3–6,8–10,13,14] and, more recently, autothermal reforming (ATR) of methane [2,4,15,16].

Steam reforming of methane is the reaction outlined in Eq. (1). It generates a high H_2/CO ratio, recommending it for hydrogen production. However, it has the disadvantage of being endothermic, which makes the process less viable for production of hydrogen as a fuel.

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H_{298\,K} = +206\,kJ/mol \tag{1}$$

On the other hand, partial oxidation, shown in Eq. (2), does not have the disadvantage of being endothermic, but it generates a lower H_2/CO ratio than steam reforming.

$$CH_4 + 0.5\,O_2 \rightarrow CO + 2H_2, \quad \Delta H_{298\,K} = -36\,kJ/mol \tag{2}$$

An alternative process to generate syngas, known as autothermal reforming, or autothermal conversion, of methane, consists in combining partial oxidation and steam reforming of methane adiabatically, so as to produce a suitable H_2/CO ratio without external energy consumption. These features make this process specially indicated for hydrogen fuel production [4].

As ATR is a combination of the two process above, the active catalysts used are the same as those for these two processes, namely the VIII-B group metals, specially Ni, Pt, Pd, Rh, Ru and Ir [14,17,18].

It has been demonstrated that the activity of nickel catalyst can be increased with the addition of low contents of noble metals, although the real mechanism for this increase in activity is not clear. These findings have stimulated study of diverse bimetallic nickel catalysts.

Nickel–platinum bimetallic catalysts showed higher activity during autothermal reforming than separate nickel and platinum catalyst blended in the same bed. It was hypothesized that nickel catalyzes steam reforming, while platinum catalyzes partial oxidation and, when they are added to the same support, the heat transfer between the two sites is enhanced [16].

It was found that the addition of small amounts of platinum, palladium and rhodium to $Ni_{0.03}Mg_{0.97}O$ catalysts used in reforming of methane with carbon dioxide promoted a significant increase in activity, which was attributed to the segregation and exposure of noble metal on the surface of the catalyst [19].

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In a study of CO_2-reforming of CH_4 with nickel–ruthenium and nickel–palladium bimetallic catalysts supported on silica, it was shown that the first catalyst had notably higher activity than nickel monometallic catalyst, which was attributed to an enrichment of the Ni catalyst surface in nickel due to the formation of nickel–ruthenium clusters whose the surface was mostly covered in nickel, while nickel–palladium had only a slightly enhanced reaction rate [20].

Small additions of Pt (0.09% w/w) to Ni/Al_2O_3 catalyst (0.9% w/w) increased considerably the activity of this catalyst in methane reforming with O_2 and CO_2. This effect was suggested to be a consequence of the increase in the reducibility of Ni due to the formation of an alloy or hydrogen spillover [21].

In this context, the objective of this work is the study of nickel catalysts promoted with platinum, palladium and iridium in low contents and their activity in the catalysis of autothermal reforming of methane, to gain a better understanding of the promoter action of these noble metals in the catalyst.

2. Experimental

The catalysts were prepared by successive wet impregnations, as follows. γ-Alumina (Degussa.) crushed to 115–150 mesh was impregnated with aqueous solutions of $Ni(NO_3)_2{\cdot}6H_2O$ (Aldrich Chem. Co.), followed by either aqueous $H_2PtCl_6{\cdot}2H_2O$ (Aldrich Chem. Co.), HCl solution of $PdCl_2$ (Aldrich Chem. Co.) or aqueous solution of $IrCl_4{\cdot}x\mathrm{HCl}$ (Aldrich Chem. Co.), being calcined between the two successive impregnations at 823 K in air and, after the second impregnation, at 873 K in air. The loads of Ni in the catalysts were around 13% (w/w). Pt loads were 0.05 and 0.27% (w/w), in samples named I-PtNiAl and II-PtNiAl, Pd loads 0.10 and 0.24% (w/w), in I-PdNiAl and II-PdNiAl respectively, and Ir load 0.3%, in I-IrNiAl. In addition, a sample was made without noble metals, named NiAl. Before reactions and analysis, catalysts were reduced at 873 K for 3 h in 5% H_2/N_2, flowing at 80 ml/min.

Catalysts were submitted to TPD-H_2 experiments (Temperature programmed hydrogen desorption) to determine the metal surface area, and DRIFTS analysis (diffuse reflectance infra-red with Fourier-transformed spectroscopy) of CO adsorption, in order to verify the electronic influence of noble metals on nickel sites, or the presence of these metals on the surface.

Partial oxidation of methane was carried out over unpromoted catalysts to test if this sample was active for this reaction. These experiments took place in a quartz fixed-bed micro-reactor, with internal diameter of 0.9 cm, using 0.1000 g of catalyst, with flow rates of 40 ml/min methane and 107.5 ml/min air, with 18.6 mol% of oxygen ($W/F = 16.6$ g min/mol), the molar CH_4:O_2 ratio being stoichiometric (2:1).

The ATR experiments were done in the same reactor, with 0.1000 g of catalyst, at 20 ml/min of methane, 53.4 ml/min of air and 3.6 g/h of water, corresponding to the molar CH_4:H_2O:O_2 ratio 1:4:0.5 ($W/F = 15.8$ g min/mol). Both these experiments and those of partial oxidation were performed at a temperature varying from 873 to 623 K, in steps of 50 K.

For all catalytic experiments, enough sample was used to give a bed-depth of about 1 mm, and the reaction temperature was measured by a thermocouple inserted in a quartz well, which was immersed in the catalytic bed. A furnace was used to heat and to keep the temperature of the bed, because the reactor was not adiabatic.

In all catalytic experiments, the products were analyzed by online gas-chromatography. The chromatograph was equipped with two channels with one thermal conductivity detector each. One channel was composed of serial Porapak®-N and 13X molecular-sieve packed columns, and used helium as carrier gas, for the analysis of nitrogen, oxygen, methane, carbon monoxide and carbon dioxide. The other channel was composed of another 13X molecular-sieve packed column, using nitrogen as carrier gas, for the analysis of hydrogen and methane.

The heat balance was made by subtracting the rate of heat into the reactor from the rate of heat out of the reactor, and dividing this value by the mole flow rate of methane on the feed stream. The rates of heat into and out of the reactor were calculated by multiplying the mole fraction of each component of the stream by its heat of formation at the process temperature.

3. Results and discussion

Fig. 1 shows the conversion of methane and the mole fractions of H_2 and CO in the product stream, for the Pd-promoted catalysts, in comparison with unpromoted catalyst, in ATR. It is clear that Pd promotes the conversion of methane, leading to greater quantities of H_2 and CO in the products than the unpromoted catalyst, but interestingly the conversion of methane is highest, among these samples, with the I-PdNiAl sample, whose Pd content is only 0.1% w/w.

It was also found that Pt strongly promoted conversion of methane in the ATR by the Ni catalyst, as shown in Fig. 2. It can be seen that the concentrations of H_2 and CO in the product stream are much higher in the promoted catalysts than in the unpromoted. Moreover, the promotion effect of Pt is higher than that of Pd, and the maximum conversion, among these samples, was achieved with I-PtNiAl.

Ir also promoted the conversion of methane in the ATR by the Ni catalyst, as it is shown in Fig. 3.

This promotion effect can be caused by a number of potential factors, such as the possible formation of a metal alloy, causing electronic changes in nickel; the exposure of noble metal, supposing that this metal has a higher turnover

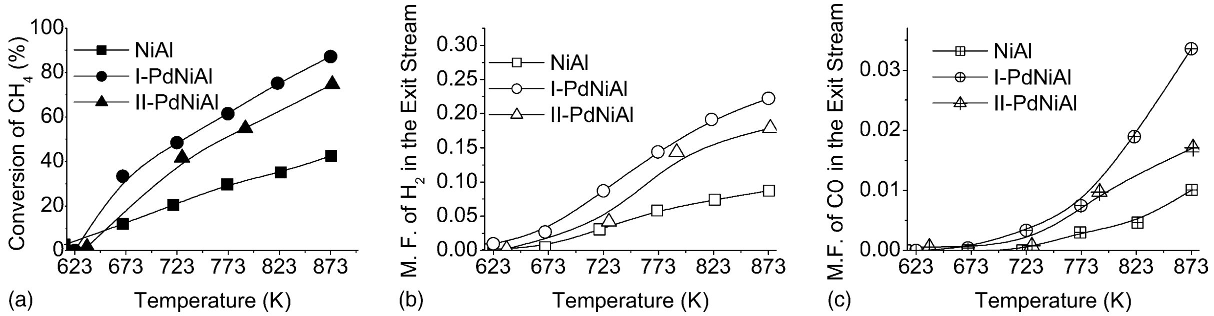

Fig. 1. Autothermal reforming of methane over Pd-Ni/Al_2O_3 samples. (a) Conversion; (b) mole fraction (M.F.) of H_2 in the exit stream; (c) mole fraction (M.F.) of CO in the exit stream.

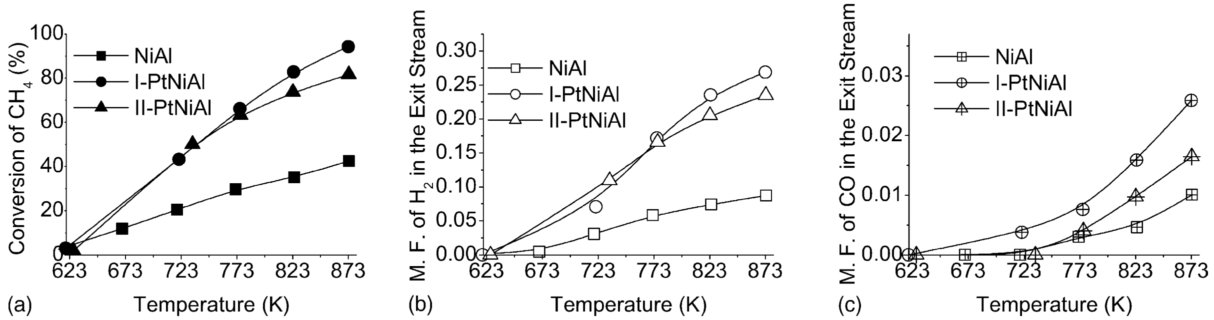

Fig. 2. Autothermal reforming of methane over Pt-Ni/Al_2O_3 samples. (a) Conversion; (b) mole fraction (M.F.) of H_2 in the exit stream; (c) mole fraction (M.F.) of CO in the exit stream.

frequency (TOF), by migration of this metal to the nickel surface; multi-functionality of the catalyst, the noble metal catalyzing partial oxidation, and nickel catalyzing steam reforming, as has been suggested [16]; or simply the higher amount of nickel exposed to the reaction, resulting from promotion of its reduction by noble metals, an effect already known [19–23].

DRIFTS spectra of the samples NiAl, II-PtNiAl, II-PdNiAl and I-IrNiAl during CO chemisorption, illustrated in Fig. 4, show that all peaks produced by the NiAl sample are also seen with samples II-PtNiAl, II-PdNiAl and I-IrNiAl, around the same wave numbers. This means that Pt, Pd and Ir, in these loads, do not alter significantly the CO adsorption onto nickel, indicating that these metals, in low contents, do not modify significantly the electronic properties of nickel. Furthermore, the absence of any extra peak, corresponding to these noble metals may indicate that they are not covering the nickel surface. These results lend support to the argument that the effect of Pd, Pt and Ir can only be explained by bifunctionality of catalyst or by the larger area of nickel exposed. These peaks are attributed to multiple carbon monoxide, at 2069 cm^{-1}, linear carbon monoxide, at 2034 cm^{-1}, bridge carbon monoxide on (1 1 1) planes, at 1947 cm^{-1}, and bridge carbon monoxide in (1 0 0) planes, at 1907 cm^{-1}, although some hypotheses claim that this last peak corresponds to multicentered carbon monoxide [24,25]. Given that the ratio between high frequency and low frequency peaks is relatively constant for all samples, it is supposed that there is no significant change in metal particle size on adding the noble metals.

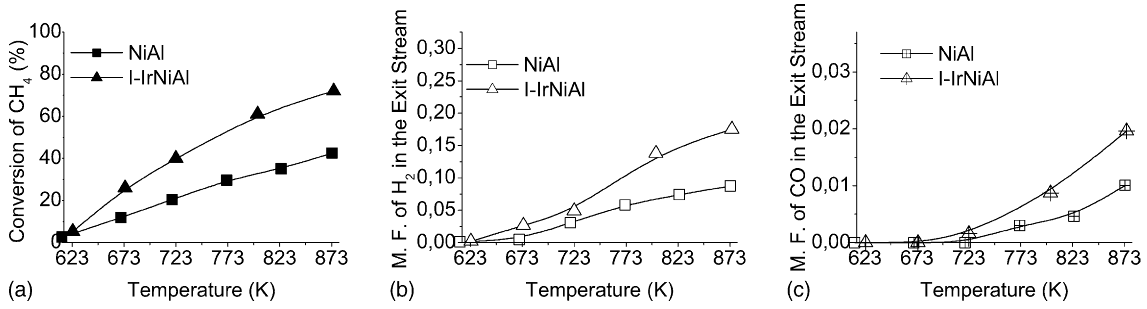

Fig. 3. Autothermal reforming of methane over Ir-Ni/Al_2O_3 samples. (a) Conversion; (b) mole fraction (M.F.) of H_2 in the exit stream; (c) mole fraction (M.F.) of CO in the exit stream.

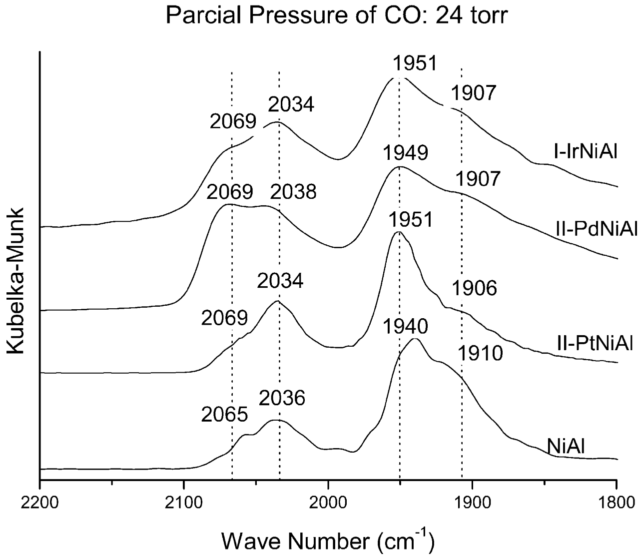

Fig. 4. DRIFTS spectra of CO adsorbed at 24 Torr on NiAl, II-PtNiAl, II-PdNiAl and I-IrNiAl samples.

The Pd-promoted sample exhibited a higher intensity in the 2069 cm^{-1} peak, corresponding to multiple carbon monoxide. This peak is related to surface defects, since these defects are more energetic sites, and favour the adsorption of more than one carbon monoxide molecule per site [24]. This means that the Pd-promoted samples had a higher density of surface defects.

According to the hypothesis of catalyst bifunctionality, in which nickel catalyzes steam reforming and the noble metal catalyzes partial oxidation of methane [7], the unpromoted sample (without any noble metal) should offer low or no conversion of methane during partial oxidation, and the noble metal would be responsible for the most of the conversion of this reaction in ATR. However, the partial oxidation test over unpromoted catalyst, in similar conditions of temperature and W/F to the ATR tests, gave conversions near to equilibrium (Fig. 5). This indicates that during the ATR, the partial oxidation should be in equilibrium over any of these catalysts, even the unpromoted one. Thus, if the hypothesis were valid, the conversion of methane in ATR would not be expected to rise with addition of promotor, which evidently is not true. This indicates that the effect of noble metal here is not exactly the promotion of partial oxidation.

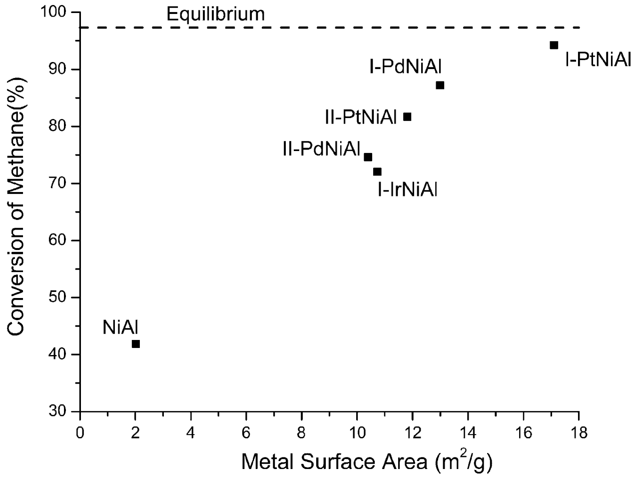

Fig. 6. Conversion of methane at 873 K in autothermal reforming vs. metal surface area.

Finally, it is known that the addition of noble metals to nickel catalysts favours the reduction of this metal [19–23]. And such an increase in reduction would probably cause an expansion of the metal surface area of the catalyst, which was actually observed. With the increase in the surface area of the active phase, an increase in catalyzed conversion of the reagents is expected. Furthermore, if the rate of the process is limited by the metal surface area, and if the increase of this area by noble metals gives a proportional increase in the number of exposed nickel sites, and if all sites are equally active for these reactions, it is expected that this increase in metal surface area causes a proportional increase in methane conversion in the ATR. It can be seen in Fig. 6 that there is indeed a proportional relation between exposed metal surface area of catalyst and methane conversion in ATR. This indicates that the effect of addition of the noble metals Pt, Pd and Ir to Ni/γ-Al_2O_3, at these low contents, is only to increase the metal surface area of nickel.

This increase of metal surface area is probably due to the fact that the noble metal is reduced at a lower temperature than nickel. Then, once in the reduced phase, these metals adsorb hydrogen dissociatively and, through hydrogen

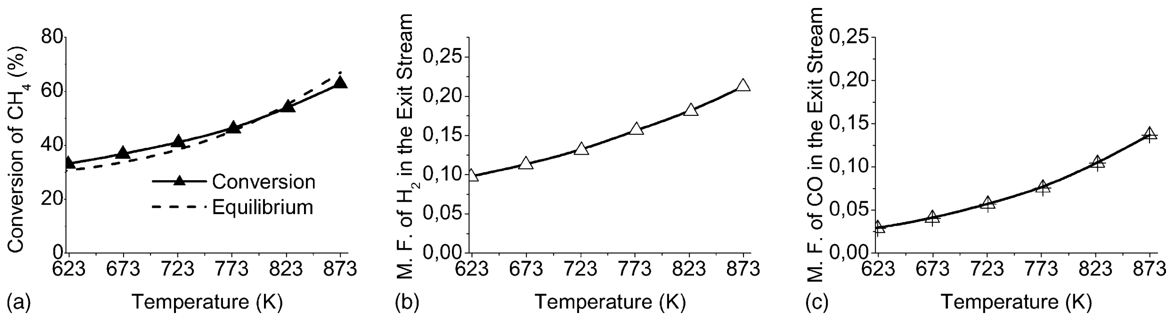

Fig. 5. Partial oxidation of methane over Ni/Al_2O_3. (a) Conversion; (b) mole fraction (M.F.) of H_2 in the exit stream; (c) mole fraction (M.F.) of CO in the exit stream.

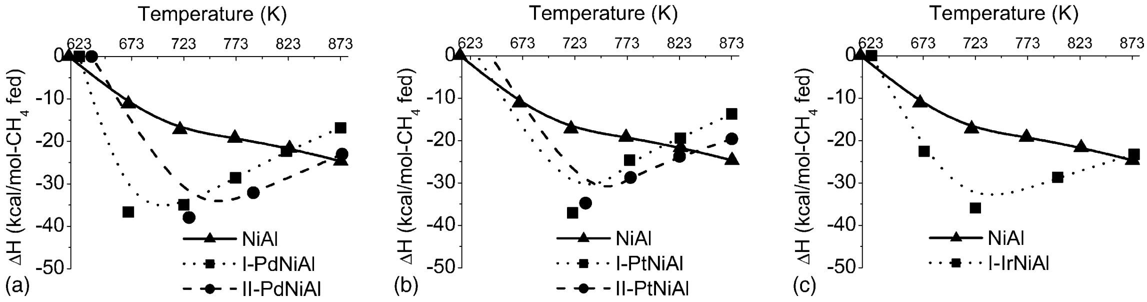

Fig. 7. Heat balance of the ATR process for each sample. ΔH is expressed in kcal/mol of CH_4 on feed stream.

spillover, catalyze nickel reduction [19–23]. The fact that Pt has a greater effect than Pd or Ir is not yet explained and is being studied further.

Fig. 7 shows the heat balance of the process for each sample. For all samples, the process is somewhat exothermic, due to the feed condition, what is advantageous for maintaining the temperature of the process in not perfectly isolated reactor.

4. Conclusion

It has been demonstrated, in the experimental results reported here, that platinum, iridium and palladium increase methane conversion during ATR.

As no electronic changes are apparent in the metal catalytic sites, and neither segregation nor significant exposure of noble metals on the catalyst surface occur, according to the DRIFTS analysis, and considering that the unpromoted $Ni/\gamma\text{-}Al_2O_3$ takes partial oxidation to equilibrium at the same W/F and temperature as in ATR, it is concluded that the effect of promotor is neither to catalyze partial oxidation, nor to alter the metal site.

However, methane conversion during ATR was found to rise proportionally with the metal surface area. Therefore, it is proposed here that the effect of these low contents of these noble metals in the catalyst is limited mainly to increasing the area of the exposed metal surface to reaction, irrespective of the noble metal added.

Hence, the only difference between the effects of platinum, palladium and iridium lies in the exact mechanism by which these noble metals affect the exposed metal surface, a question being studied in greater depth.

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