CO_2 reforming of methane over Ni–Ru and Ni–Pd bimetallic catalysts

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This paper reports the effect of noble metal addition (Ru, Pd) to supported Ni catalysts towards the reaction of CO_2 reforming of methane. On the basis of FT-IR spectra of adsorbed CO, H_2 chemisorption and TPR measurements it has been proposed that the different behaviour of the Ni-based bimetallic catalysts can be related to different metal–metal interactions occurring on the catalysts. In particular, the strong improvement in the activity and stability observed in the case of ex-nitrate Ni–Ru catalysts has been attributed to an enrichment of the catalyst surface in nickel due to the formation of Ni–Ru clusters with the surface mainly covered by Ni. This leads to an increase in the metallic dispersion of Ni and favours the formation of more reactive intermediate carbonaceous species.

Keywords: dry reforming, bimetallic catalysts, Ni–Ru, Ni–Pd, FT-IR spectroscopy, TPR

1. Introduction

In recent years the reforming of methane by carbon dioxide to produce syngas (dry reforming: $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$) is receiving considerable attention because of the possibility to convert two of the cheapest carbon-containing materials into useful feedstock for further chemical processes [1–5]. This reaction is able, in fact, to generate a syngas with a low CO/H_2 ratio, suitable for the oxo and Fischer–Tropsch syntheses.

The conventional catalysts in methane dry reforming are based on Ni or noble metal supported systems [1–5]. The greatest obstacle to successful industrial application is the relevant formation of coke which deactivates the catalysts. Noble metals (Pt, Ru, etc.) have been reported to be less susceptible to coking than Ni [1–3]. However, due to the much lower cost of nickel, from the industrial standpoint it is still worthwhile to develop Ni-based catalysts that are resistant to carbon deposition. Up to now the addition of alkali or alkali earth dopants to nickel [6–8] or the use of supports with basic characteristics [9,10] have been reported to be the best methods to minimize carbon deposition.

It is well known that bimetallic catalysts may sometimes exhibit superior activity, selectivity and deactivation resistance as compared to the corresponding monometallic samples [11,12]. On this basis in this work we have studied the effect of noble metal addition (Ru or Pd) to supported Ni catalysts for the CO_2 reforming of methane, with the aim both to improve the performance of the catalyst and to clarify the factors involved in controlling the reactivity and stability of the system. Silica has been chosen as a support because of its being essentially a relatively inert support, thus enabling to obtain information mainly related to the active metal species.

2. Experimental

Ni-based bimetallic catalysts were prepared by incipient wet co-impregnation of the support (SiO_2 supplied by Grace with a BET surface area of 490 $m^2\,g^{-1}$) with aqueous solutions of the precursors. $Ni(NO_3)_2$ was always used as the Ni precursor. The nitrate or chloride salts were used as precursors of Ru and Pd (respectively, $Ru(NO)(NO_3)_3$ or $RuCl_3$ for Ru and $Pd(NO_3)_2$ or $PdCl_2$ for Pd). The sample code used has the following meaning: the numbers before the element symbol indicate the wt% of the metal in the sample, whereas the letter in brackets indicates the precursor of the second metal used (n = nitrate; cl = chloride).

Catalytic activity tests were carried out at 873 K in a flow microreactor directly connected with the analytical system (gas chromatograph and quadrupole mass spectrometer). A reaction mixture of CO_2 (15%) and CH_4 (15%) diluted with He has been always used, with a W/F ranging from 22.7 to 2.27 $g_{cat}\,h/mol_{CO_2}$. Before catalytic activity measurements, the catalysts were reduced *in situ* at 873 K in flowing H_2 for 1 h.

For IR spectra the powdered samples were pressed into self-supporting discs of about 25 $mg\,cm^{-2}$ and 0.1 mm thick. Before CO admission all samples were pretreated as follows: reduction in H_2 at 873 K for 1 h, outgassing at 873 K for 1 h, cooling at room temperature. The FT-IR spectra were collected on a Perkin–Elmer System 2000 spectrophotometer with a resolution of 2 cm^{-1}, equipped with a MCT detector.

H_2 chemisorption was measured in a static system operating at room temperature. Before the measurements the samples have been pretreated as for FT-IR experiments.

Temperature-programmed reduction (TPR) tests were carried out in a conventional flow apparatus with a TCD detector, at a heating rate of 5 K/min using a 5% H_2/Ar mixture.

Temperature-programmed surface reaction (TPSR) of carbon was carried out in a flow reactor at a heating rate of 10 K/min using a 20% H_2/He mixture. A quadrupole mass spectrometer was used to analyze the composition of the effluent stream. The surface carbon was previously produced in the decomposition of CH_4 at 673 K for 5 min.

3. Results and discussion

Catalytic activity results of the investigated catalysts towards the CO_2 reforming of methane are summarized in table 1. Among the monometallic samples (prepared starting from nitrate or chloride precursors) the order of stability observed is Ru $>$ Ni $\gg$ Pd. These results are in accordance to the literature data on the subject. It has been in fact reported that noble metals are more resistant to coking than Ni, probably because carbon is not dissolved in these metals [1–5]. Pd is the only noble metal that still forms carbon, probably because of the formation of an interstitial solid solution of carbon in palladium [3,13]. This could explain the very high deactivation rate observed on our silica-supported monometallic Pd samples. The data of table 1 suggest also that the carbon deposition is controlled by the dispersion of the metal active phase. In fact, the higher the dispersion of the metal, the lower the deactivation rate (compare the monometallic Ru samples prepared by nitrate and chloride). This behaviour is in agreement with the results of several authors, which report that on small highly dispersed Ni particles the formation of coke is restrained [3,14–16].

In the case of Ni-based bimetallic samples prepared starting from nitrate precursors table 1 shows that the presence of Ru strongly improved the catalytic performance of Ni-based catalysts both in terms of activity (ca. one order of magnitude higher) and stability during several hours of operations. The addition of Pd to supported Ni catalyst caused just a slight increase in the reaction rate, accompanied, however, by a higher deactivation rate than that observed on the monometallic Ni sample. On Ni-based bimetallic samples prepared starting from the chloride precursors of the second metal, the presence of the second metal (Ru or Pd) causes a moderate decrease in the catalytic activity of the monometallic Ni sample. It must be observed that also in this case the Ni–Pd samples present a very high deactivation rate.

H_2 chemisorption data of table 1 show that, when nitrate is used as the precursor, addition of Pd or Ru to Ni/SiO_2 causes an increase in the amount of hydrogen chemisorbed (compared to the Ni monometallic sample). In particular the very high value of H_2 uptake measured on the ex-nitrate Ni–Ru catalyst (2Ni0.6Ru(n) sample) suggests that Ni dispersion on this sample is quite high compared to the monometallic nickel (2Ni sample). In fact, even if we subtract the amount of H_2 chemisorbed on Ru (in the extreme hypothesis of 100% Ru dispersion), the H_2 uptake on Ni in the 2Ni0.6Ru(n) sample is always more than twice higher than that observed on the 2Ni sample. An opposite behaviour is observed when chloride is used as second metal precursor. In this case, in fact, the amount of H_2 uptake has been found (table 1) to strongly decrease on addition of the second metal (both Ru and Pd), indicating a significantly lower Ni dispersion on the ex-chloride bimetallic catalysts.

Figure 1 shows the TPR profiles of the mono- and bimetallic Ni–Ru catalysts. Considering the monometallic samples it is possible to observe that the reduction temperatures of the supported Ru samples (ex-nitrate or ex-chloride) are rather lower than that found on the monometallic Ni catalyst (maximum at ca. 570 K). Both Ni–Ru bimetallic samples present essentially a single reduction peak, with a maximum of temperature (ca. 500 K) which is intermediate between those of the corresponding monometallic samples. This suggests that ruthenium and nickel must be in close interaction each other. A similar result has been also reported by Rynkowski et al. [17,18] on alumina-supported Ni–Ru and Ni–Pt systems.

Figure 2 shows the TPR profiles of the mono- and bimetallic Ni–Pd samples. It can be noted that also in this case the monometallic Pd samples (ex-nitrate or ex-chloride) present a reduction peak with a maximum at a temperature lower than the 2Ni sample. Differently from that observed on Ni–Ru, the Ni–Pd samples show essen-

Table 1
Chemical composition, H_2 uptake and catalytic activity of mono- and bimetallic catalysts.

Code	Ni (wt%)	Ru or Pd (wt%)	H_2 uptake ($ml_{(STP)}\ g_{cat}^{-1}$)	Dispersion (%)	V^a ($mol_{CO_2}\ g_{cat}^{-1}\ h^{-1}$)	Average deactivation rate ($\%\ h^{-1}$)
2Ni	2.05	–	0.54	14	0.267	2.8
0.6Ru(n)	–	0.60	0.48	70	0.185	0.4
0.6Pd(n)	–	0.58	0.09	14	0.029	18.2
0.6Ru(cl)	–	0.62	0.17	25	0.216	1.8
0.6Pd(cl)	–	0.57	0.10	15	0.096	18.4
2Ni0.6Ru(n)	1.94	0.63	1.90	–	1.870	0.4
2Ni0.6Pd(n)	1.96	0.60	0.80	–	0.330	7.4
2Ni0.6Ru(cl)	2.02	0.55	0.16	–	0.195	2.7
2Ni0.6Pd(cl)	1.97	0.59	0.30	–	0.199	5.4

[a] Measured at 873 K.

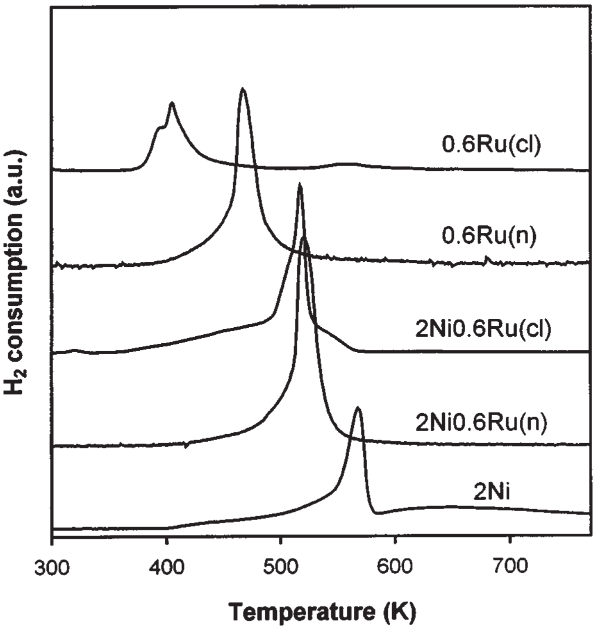

Figure 1. TPR profiles of mono- and bimetallic Ni–Ru catalysts.

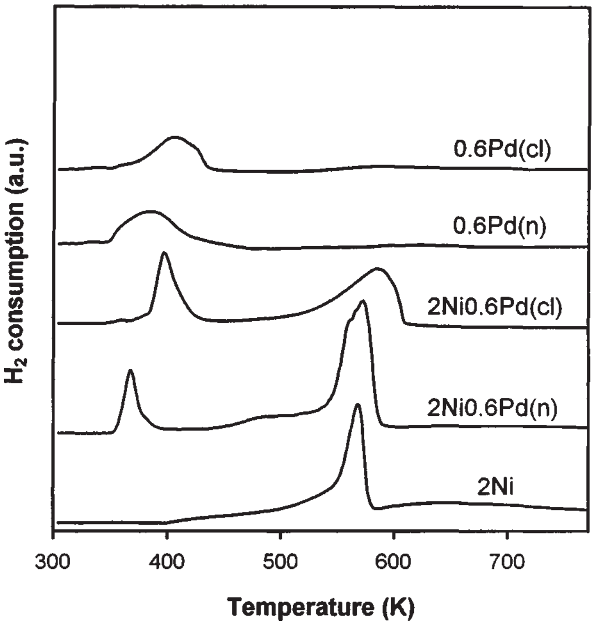

Figure 2. TPR profiles of mono- and bimetallic Ni–Pd catalysts.

tially two separate reduction peaks with maxima close to those observed for the reduction of the corresponding monometallics. This indicates that in the case of Ni–Pd/SiO_2 catalysts Ni and Pd do not relevantly interact each other but tend to form separate aggregates.

Figure 3 shows the FT-IR spectra recorded after admission of CO and following outgassing at room temperature on the ex-nitrate (figure 3(A)) and ex-chloride (figure 3(B)) mono- and bimetallic Ni–Ru samples. On the ex-nitrate Ru monometallic sample (0.6Ru(n)) three main bands are present at 2034, 2062 and 2138 cm^{-1}. According to the literature data these bands can be respectively attributed to CO linearly adsorbed on Ru^0 (2034 cm^{-1}), $Ru^{\delta+}$–CO species (2062 cm^{-1}) and $Ru^{\delta+}$–$(CO)_x$ species (2138 cm^{-1}) [19,20]. Also in the case of the ex-chloride monometallic sample (0.6Ru(cl)) the spectrum shows three main bands (at 2021, 2080 and 2146 cm^{-1}), which can be attributed to the same carbonyl species observed on the 0.6Ru(n) sample. However, on the 0.6Ru(cl) sample the bands of CO on $Ru^{\delta+}$ are slightly shifted to higher frequency compared to the 0.6Ru(n) sample, due to the withdrawal effect of chlorine [21]. It has been in fact reported that Ru catalysts derived from the reduction of $RuCl_3$ retain residual chlorine following the pretreatment in hydrogen [22]. It must be also noted that on 0.6Ru(cl) the Ru^0–CO band is sharper than that found on 0.6Ru(n). This difference can be related to the different Ru particle size (see dispersions of table 1). Smaller particles lead, in fact, to a larger amount of Ru particles on the surface and most likely to greater heterogeneity [19,23], thus broadening the IR band. Formation of larger metal particles on samples prepared by chloride precursors has been widely reported in the literature [19,24]. The monometallic Ni sample (2Ni) shows an intense band at 2049 cm^{-1}, attributed to CO linearly adsorbed on Ni^0

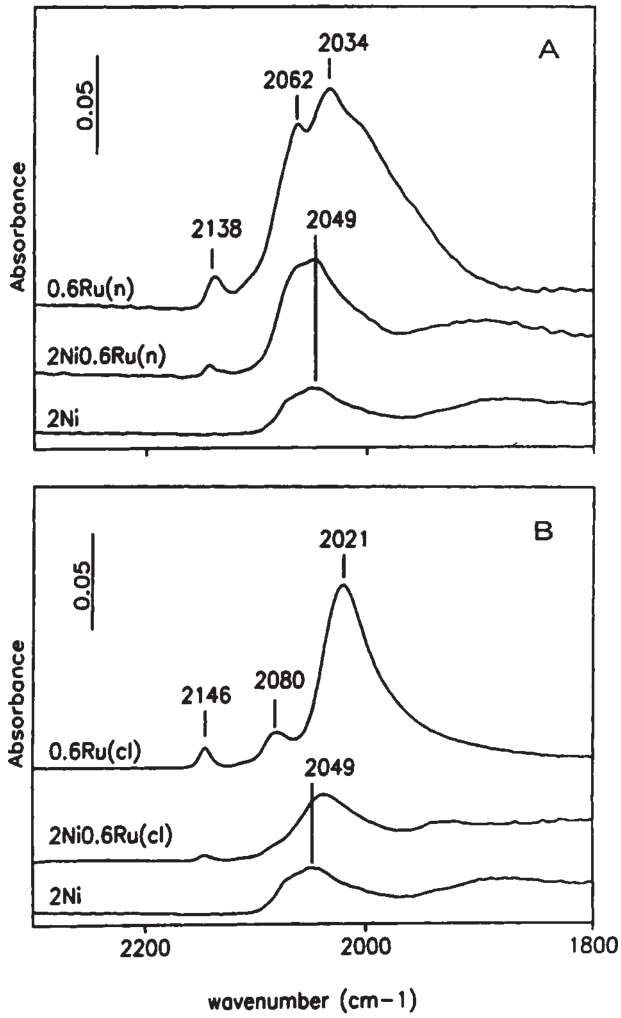

Figure 3. FT-IR spectra after admission of CO and following outgassing at room temperature on mono- and bimetallic Ni–Ru catalysts.

[25,26]. A broad band at lower frequency with a maximum at ca. 1900 cm^{-1} is also present, assigned to bridged CO on Ni^0 [25,26]. On the ex-nitrate Ni–Ru bimetallic sample (2Ni0.6Ru(n)) the intensity of all Ru bands is much lower than on the 0.6Ru(n) sample, whereas the Ni bands (especially the linear Ni–CO band at 2049 cm^{-1}) appear to be more intense. This suggests that a much lower amount of ruthenium is present on the surface of the Ni–Ru catalyst, compared to the monometallic Ru, whereas the amount of Ni on the surface should be enhanced (see also H_2 chemisorption data). This result points to the formation of Ni–Ru bimetallic particles having a surface mainly covered by nickel. An enrichment of the catalyst surface in nickel has been also reported by Rynkowski et al. [18] in the case of Ni–Pt bimetallic systems. Also taking into consideration the TPR and H_2 chemisorption results previously discussed it can be proposed that the effect of segregation of ruthenium by nickel is related to the lower reduction temperature of the ruthenium precursor with respect to the nickel precursor. Ru nucleation centres are formed first with formation of small Ru clusters and then Ni atoms are deposited on top of them when the reduction of nickel begins. This is also in accordance with the high nickel dispersion of the 2Ni0.6Ru(n) sample. A similar behaviour has been also reported by Crisafulli et al. [19] on silica-supported Ru–Cu catalysts.

Also on the bimetallic Ni–Ru sample prepared starting from chloride (2Ni0.6Ru(n) sample of figure 3(B)) the intensity of all IR bands of CO related to ruthenium is much lower than on the corresponding monometallic Ru sample, indicating that also on these samples a large part of ruthenium is encapsulated by nickel. In this case, however, the Ni–CO bands are of similar intensity compared to the Ni monometallic sample. In accordance to H_2 chemisorption results, this indicates that the amount of Ni on the surface is lower than that observed on the ex-nitrate Ni–Ru sample. Probably the formation of larger clusters of Ru on the ex-chloride samples limits the dispersion of nickel, despite the fact that Ni is always located on top of Ru.

The FT-IR spectra recorded after admission of CO and following outgassing at room temperature on mono- and bimetallic Ni–Pd samples are reported in figure 4. The monometallic Pd samples present a rather symmetric band (at 2077 cm^{-1} for the 0.6Pd(n) sample and 2086 cm^{-1} for 0.6Pd(cl)) assigned to CO linearly adsorbed on metallic Pd [27], and a broad band at lower frequency (below 2000 cm^{-1}), attributed to several bridged CO species [27–29]. Both on the ex-nitrate and ex-chloride Ni–Pd bimetallic samples (2Ni0.6Pd(n) and 2Ni0.6Pd(cl)) the band of linearly adsorbed CO is rather broader (compared to the corresponding Pd monometallic sample) with a maximum at 2080–2070 cm^{-1} and an evident shoulder at about 2050 cm^{-1}. This indicates that both the components due to Pd–CO and Ni–CO linear species are present under this band. Therefore, it can be suggested that both Ni and Pd are on the surface of silica-supported Ni–Pd bimetallic catalysts. It is highly probable that the degree of interaction between Ni and Pd is rather low and these metals tend to form separate aggregates, as also suggested by the TPR spectra of figure 2.

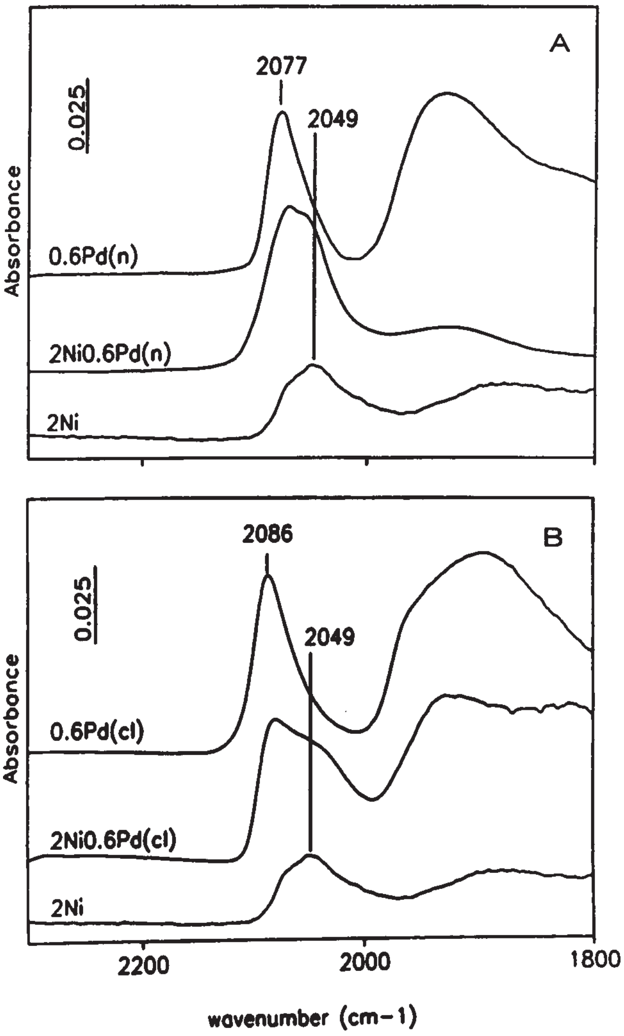

Figure 4. FT-IR spectra after admission of CO and following outgassing at room temperature on mono- and bimetallic Ni–Pd catalysts.

The activity data previously discussed have shown that the catalytic behaviour of the Ni-based bimetallic catalysts towards the methane dry reforming depends both on the second metal added to Ni and the precursors used for the sample preparation. Addition of Ru to Ni caused an improvement in the performance of the Ni-based catalyst, with the best results obtained on the ex-nitrate Ni–Ru catalyst. This sample showed, in fact, a much higher activity and stability compared to the Ni monometallic sample. It must be underlined that the reaction rate measured on this bimetallic sample is remarkably higher (one order of magnitude) compared to that of Ru and Ni monometallic samples thus excluding that just an additive effect can explain the increased activity.

On addition of Pd to Ni the catalytic performance of Ni/SiO_2 is not improved (especially in terms of deactivation rate, which is found to increase). On the basis of the characterization results obtained in this work (FT-IR spec-

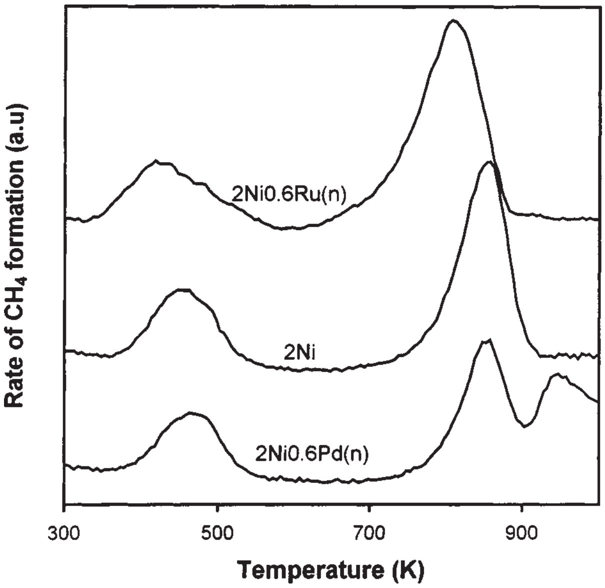

Figure 5. Temperature-programmed surface reaction (TPSR) of carbon with H_2 on ex-nitrate Ni-based catalysts. Carbon was produced in the decomposition of CH_4 at 673 K for 5 min.

tra, H_2 chemisorption and TPR measurements) we propose that the changes in the catalytic behaviour observed on the Ni-based bimetallic catalysts are strictly related to the different metal–metal interactions occurring on the catalysts. In the case of Ni–Ru catalysts a strong Ni–Ru interaction appears to take place with formation of Ni–Ru bimetallic particles which have a surface mainly covered by nickel. This probably can be explained considering that Ru nucleation centres are formed first and then Ni atoms are deposited on top of them. This can justify the increase in the metallic dispersion of Ni, remarkably when the ruthenium precursor used favours the formation of small Ru particles (as in the case of ex-nitrate samples). As widely reported in the literature [3,14–16], a higher Ni dispersion should lead to a decrease in the deactivation rate of the catalysts.

On the other hand, on Ni–Pd catalysts Ni and Pd tend to form separate aggregates with a very low interaction degree between them. Therefore, addition of Pd to Ni/SiO_2 causes a relevant increase in the deactivation rate of the catalysts compared to the Ni monometallic sample. Pd atoms, in fact, are located on the surface and, therefore, favour the formation of inactive coke on the catalyst. This hypothesis seems to be confirmed by the analysis of figure 5, which displays the TPSR spectra relating to the hydrogenation of surface carbon on the ex-nitrate catalysts. The figure shows that 2Ni0.6Pd(n) presents a less reactive carbon species (peak above 900 K) compared to the 2Ni sample. On the 2Ni0.6Ru(n) sample an opposite behaviour is observed. The hydrogenation of the surface carbon, in fact, starts at a lower temperature compared to Ni and Ni–Pd catalysts. This suggests that the carbon species formed during the methane dry reforming reaction on the surface of the 2Ni0.6Ru(n) sample present a high reactivity. This should decrease the amount of inactive carbonaceous species accumulated on the surface, thus limiting the deactivation of the catalyst.

4. Conclusions

On the basis of the catalytic activity and characterization data reported in this paper the following conclusions can be drawn:

(a) Addition of Ru or Pd to Ni/SiO_2 strongly influences the catalytic performance towards the reaction of dry reforming of methane.

(b) The catalytic behaviour of the Ni-based bimetallic catalysts strongly depends both on the second metal and the precursor used. The best results in terms of activity and stability are obtained on the ex-nitrate Ni–Ru sample.

(c) The different catalytic performance between Ni–Ru and Ni–Pd bimetallic samples is mainly related to the different degree of metal–metal interactions occurring on the catalysts. The strong improvement in the activity and stability observed in the case of ex-nitrate Ni–Ru catalysts has been attributed to the formation of Ni–Ru bimetallic clusters with a surface mainly covered by nickel. This leads to an increase in the metallic dispersion of Ni and favours the formation of a more reactive intermediate carbonaceous species, thus limiting the deactivation of the catalyst.

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