Short communication

Inhibition of carbon formation during steam reforming of methane using thiol-coated nickel catalysts

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Abstract

n-Butanethiol-impregnated, micrometric, pristine Ni powder (Ni–C_4S) was tested as a catalyst for use in the steam reforming of methane, using X-Ray photoemission spectroscopy (XPS) and mass spectrometry (MS). The catalytic activities of both the pristine Ni and the Ni–C_4S powders were measured at 700 °C, under conditions that favoured (molar CH_4:H_2O ratio of 2:1), and did not favour (molar CH_4:H_2O ratio of 1:2) formation of surface carbon. The results show that: (a) Ni–C_4S demonstrates both high catalytic activity and stability during the 21 h duration test; (b) under conditions favouring the deposition of surface carbon, the Ni–C_4S retained both its efficiency and structural integrity, while the catalytic activity of the Ni was reduced by ∼70% and the catalyst pellets lost their integrity; (c) the amount of deposited carbon in the case of the Ni–C_4S catalyst was significantly lower than that observed for the Ni catalyst, in spite of the longer testing duration. It was concluded that the thiols pre-treatment of Ni surfaces, to be subsequently used in the production of catalysts supported SOFC anodes, can considerably increase their "active life span" this being a critical attribute in respect of their eventual commercialization.
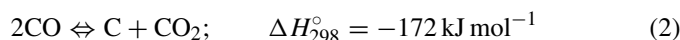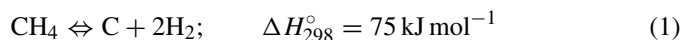© 2007 Elsevier B.V. All rights reserved.

Keywords: Carbon deposition; Steam reforming; Ni catalyst; *n*-butanethiol pre-treatment; CH_4; SOFC

1. Introduction

The catalytic steam reforming of methane is now in worldwide used as the main, large-scale, hydrogen production technology [1–3]. Recently, this reaction has become of increasing importance for the prior processing of fuel cell feedstock gas [4]. The metallic elements of the periodic tables', group VIII, are essentially all active catalysts for this reaction. Ceramic-supported nickel catalysts are both favoured and widely used in industry, because of their high activity, their relatively high active life span and their significantly lower utilisation costs, in comparison with the alternative precious metal-based, catalysts [3,5–21]. However, "catalyst aging"/deactivation, due to the formation of surface coke [5–11,22] is the major problem inhibiting the wide scale use of these materials. In fact, when in general hydrocarbons are exposed to high temperatures, the formation of superficial carbon deposits often occurs, due to the formation of C–C and C=C bond containing hydrocarbon chains, at the exposed catalyst surfaces. Thus, during the production of the synthesis gas from natural gas (NG), carbon deposits may be formed by the decomposition of the methane feedstock (1), or through the Boudouard reaction (2), the simplified reactions, as set out below, representing the formation of the various possible forms of carbon at the surface of the catalysts:

$$CH_4 \Leftrightarrow C + 2H_2; \qquad \Delta H_{298}^{\circ} = 75\,\text{kJ mol}^{-1} \qquad (1)$$

$$2CO \Leftrightarrow C + CO_2; \qquad \Delta H_{298}^{\circ} = -172\,\text{kJ mol}^{-1} \qquad (2)$$

Both the reforming and the coke deposition reactions are believed to be initiated by the same elementary hydrocarbon activation step [6]. Under the steam-reforming reaction conditions, the metal catalyst surfaces are covered by CH_x species, mainly generated by the dissociative adsorption of CH_4 or local hydrogenation of other CH_y species. At the surface of these catalyst(s), used in the steam gasification route, intermediate species are converted into CO and H_2, in competing with other possible reaction routes, such as dehydrogenation, polymerization, and rearrangement to produce highly stable aromatic and graphitic

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carbon species [8]. The latter groups are highly stable forms of carbon, being refractory towards gasification. Moreover, the atomic carbon species are relatively labile and may diffuse into Ni particles, thereby forming the refractory Ni carbides. In some cases, the dissolution leads to whisker carbon growth that eventually inhibits the material catalytic efficiency, destroying the catalyst structural integrity and ultimately plugging the reactor. Higher steam to carbon (S/C) ratios in the reactor feed can be used to control this carbon formation, but in commercial operations, this results in higher production costs. Modifications to the catalyst, through the introduction of alkali metals [23], or gold [24], can improve the catalyst carbon's resistance. Hydrotalcites and mixed oxides have also shown higher resistances to both coke formation [25], and to sintering [26] than is normally displayed by those commercial catalysts that are supported on alumina. For example, Chin et al. [27] have demonstrated that the addition of small quantities of gold to the surfaces of supported nickel catalysts is an effective means of retarding the formation of carbon during hydrocarbon steam reforming. Christensen et al. [28] have demonstrated that nickel, supported on hydrotalcite-derived materials, has both a smaller crystal size and a greater resistance to coke formation than the conventional $NiO/\alpha\text{-}Al_2O_3$ and $NiO/CaO\text{-}Al_2O_3$ materials. They have shown that the greater resistance to carbon formation could be due to a higher saturation concentration of carbon within the smaller nickel crystals. Rostrup-Nielsen [29] has shown that sulfur can be used to protect the catalyst against these carbon deposits. In fact, adsorbed sulfides generally poison the catalytic activity of the nickel through the occupation of the active Ni sites and conformational changes induced into the surrounding adsorbed sulfur atom "ensembles". Rostrup-Nielsen [29] suggested that the size of these "ensembles" was critical in allowing steam reforming to take place with minimal coke formation. Steam reforming is also considered to involve "ensembles" of three to four nickel atoms minimum, while actual carbon formation requires "atomic clusters" of six or seven atoms, minimum [29]. Complete coverage of the catalyst with sulfur results in its total deactivation. However, at sulfur coverage of about 70% saturation, carbon deposition could be effectively eliminated, without involving significant harm being done to the steam reforming catalytic activity [29]. In the present work, it has been demonstrated that the pre-treatment of pristine Ni micrometric powder, through impregnation under ambient conditions, and within a *n*-butanethiol organic solution, strongly protects the Ni catalyst from latent carbon formation and subsequent deposition, while, at the same time, preserving its catalytic activity for the steam reforming of methane reaction.

In previous publications [30–32], it has been revealed that Ni micrometric powders, "contaminated" with thiols containing less than six carbon atoms, show similar activity to the "pristine" catalytic activity of Ni in CH_4 steam reforming reactions. It has also shown that the sulfur has no effect on the catalytic activity of the catalyst during the reaction of reforming [32]. In this present work, a study has been undertaken involving a comparison of the catalytic activity of; (a) pristine and (b) *n*-butanethiol ($H\text{-}(CH_2)_4\text{-}SH$) pre-treated Ni powders, under reaction conditions selected to favour or not, the formation and deposition of

carbon; these conditions being the molar ratios of the reactants; – $CH_4/H_2O = 2{:}1$ and 1:2, respectively. The products of the CH_4 steam reforming, being conducted at the 1:2 (10 Torr, 20 Torr) and 2:1 (40 Torr, 20 Torr) CH_4/H_2O molar ratios, were monitored using mass spectrometry (MS), while the catalysts surface were analyzed by X-Ray photoemission spectroscopy (XPS).

2. Materials and methods

The catalyst employed in this study was a pure nickel powder, supplied by the Inco Co (Inco Ni 255), being initially produced by the thermal decomposition of nickel tetracarbonyl vapour [33]. The specifications and characteristics of this product can be found elsewhere [31]. The *n*-butanethiol ($H\text{-}(CH_2)_4\text{-}SH$) (Aldrich, 99%) and the methanol solvent (Aldrich, 99%), as employed in this work, are both liquids at room temperature.

The thiol pre-treatment of the Ni catalyst was effected by immersion of the pristine nickel powder into 10^{-3} M solutions of *n*-butanethiol/methanol (5 g of Ni in 100 ml of solution) at ambient temperature; the solutions containing excess thiol, at several orders of magnitude in excess, compared to the subsequent deposited monolayer quantities, this calculation being provided elsewhere [32]. The actual immersion (impregnation) time was 20 h. The allowed impregnation duration is sufficient to reach equilibrium conditions. In fact, in the previous published work [34], the authors have studied the evolution of the C–H stretch spectra of butanethiol films adsorbed on gold as a function of the time (1, 2, 3, 5, 15, 45 min and 15 h) of exposure to the 5 μM solution and they show that exposures beyond ≈45 min have no further effect on the IR-RAS spectra. In other study, Mekhalef et al. [35] have studied the effect of immersion time (15 min and 18 h) of *n*-alkanethiols on nickel polycrystalline substrates and have demonstrated that prolonged immersion times (18 h) in the neat *n*-alkanethiols are necessary to improve the organization of the chains. They explain these phenomena for their particular relevance for oxidizable metals if SAMs are to be used as a protective barrier against the diffusion of O_2 at the monolayer/metal interface. After the immersion, all such treated samples were rinsed with copious quantities of fresh methanol until thiols could no longer be detected in the rinsing solution. Finally, the treated samples were dried for 12 h at ambient temperature, followed by product characterization and reforming tests. The adsorption of *n*-butanethiol was confirmed by use of diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) (see Fig. 2 in Ref. [32]). Herein, the *n*-butanethiol pre-treated Ni catalyst is denoted as Ni–C_4S. X-ray photoelectron spectra (XPS) for the catalyst samples were acquired at ambient temperature, using a Kratos HS system, equipped with a mono-chromatized Al Kα (hν = 1486.6 eV) X-ray source, operated at 120 W and probing a 12,000 μm² area of the sample. The photoelectron kinetic energies were measured, using a hemispherical electrostatic analyzer working in the "constant pass energy mode". The background pressure within the analysis chamber was maintained at below 2×10^{-8} Torr. Survey scans (0–1200 eV) and high-resolution Ni(3p), S(2p), C(1s) and O(1s) spectra were obtained at pass energies of 160 and 40 eV, respectively. Correction for the charging effects was achieved by

referencing all of the binding energies with respect to the O(1s) core level spectrum in NiO (BE ≈ 529.1 eV [36]). The uncertainty in the peaks positions was estimated to be ±0.2 eV for all spectra. The analysis of the measured Ni(3p), S(2p), C(1s) and O(1s) high-resolution spectra envelopes was performed by means of curve-fitting synthetic peak components, using the XPSPEAK41 software. The raw experimental data were used without preliminary smoothing. Gaussian–Lorentzian product functions and Shirley background subtraction procedures were used to approximate the line shapes of the fitting components. Quantification of the carbon atomic percentages was obtained by an integration of the C(1s) core-level spectra, with the appropriate corrections for photo-ionization cross-sections.

The detailed description of the experimental setup and the protocol for catalytic activity measurements can be found elsewhere [31].

3. Results and discussion

Fig. 1 shows the mass spectrometer results for the steam reforming of methane at 1:2 (10 Torr, 20 Torr) CH_4/H_2O molar ratio, monitored for 20 h on pristine Ni catalyst, by following the partial pressures of H_2, CO, CO_2 and CH_4. The collected data show that the catalytic activity commences at approximately 325 °C (onset of hydrogen production). Fig. 1 shows that the hydrogen production increases as the temperature increases, the maximum yield being obtained at 500 °C. No noticeable modification in the hydrogen production rate was observed by increasing the reaction temperature, from 500 to 700 °C. The same trend was also observed for the CO and CO_2 products while the CH_4 underwent a decrease from 325 °C and continued to decrease as a function of temperature until 500 °C; at this temperature there was no measurable methane remaining and the conversion was considered to be complete (100%). These results are all in good agreement with those from thermodynamic calculations performed on the system at chemical equilibrium, as described in Ref. [31]. This also means that the reaction conditions chosen allow the state of equilibrium to be
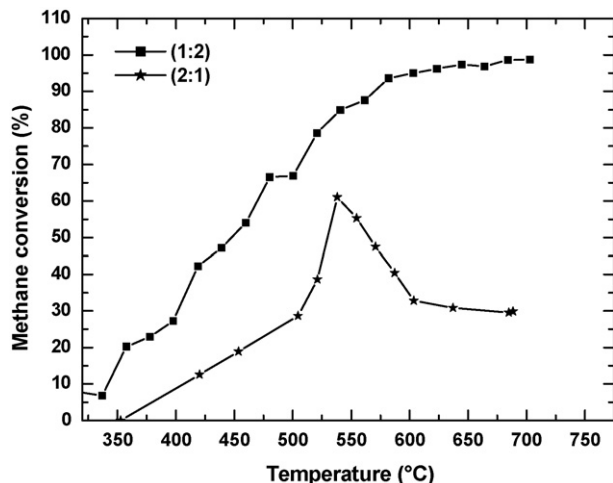
Fig. 2. Methane conversions, achieved over the unsupported Ni catalyst, as a function of the $CH_4:H_2O$ molar ratio and the reaction temperature. Reaction conditions: square symbols $CH_4:H_2O$ = 1:2 (10 Torr, 20 Torr); star symbols $CH_4:H_2O$ = 2:1 (40 Torr, 20 Torr). For all studies performed in these tests, the total gas pressure was 1.0 atm, pure Ar carrier gas being used to make up the balance.

reached and, under the same temperature conditions, the kinetics are sufficiently fast to achieve equilibrium at the chosen spatial velocity. The same experiment was also performed by changing the molar ratio from 1:2 to 2:1 (40 Torr, 20 Torr) CH_4/H_2O. Fig. 2 provides a comparison of the experimental CH_4 conversion over the nickel catalyst at the CH_4/H_2O molar ratios of 1:2 and 2:1. This figure shows that, at a CH_4/H_2O molar ratio of 1:2, the CH_4 conversion was 95 ± 2% at 700 °C. Moreover, at this temperature, the conversion remains constant with time. A different behaviour is to be observed for the $CH_4:H_2O$ molar ratio of 2:1. Under these new conditions, the CH_4 conversion increased with temperature up to 550 °C, where it then reached a maximum of ~60%, then decreased with additional temperature increases (e.g. ~30% of CH_4 conversion at T = 700 °C). This particular behaviour is inconsistent with the results of thermodynamic calculation, the latter predicting that, for a given $CH_4:H_2O$ molar ratio, higher reaction temperatures systematically lead to higher, theoretical equilibrium, methane conversions, as shown in Fig. 2 of Ref. [31]. This difference is most probably due to the earlier formation and deposition of carbon at the lower temperatures, the prior deposited carbon inhibiting the catalytic activity and contributing to this "anomalous behaviour". Fig. 3 shows the carbon deposition formed for two different $CH_4:H_2O$ molar ratios (1:2 and 2:1) over reaction temperature. As expected, it is also evident that the C(s) formation is highly affected by the $CH_4:H_2O$ ratio. For a $CH_4:H_2O$ molar ratio of 2:1, the increased carbon deposits on the catalyst can be obtained by increasing the reaction temperature, from 200 to 700 °C. However, over this same temperature range, no carbon was generated for a $CH_4:H_2O$ molar ratio of 1:2. Thus, at lower $CH_4:H_2O$ ratios, steam reforming of methane dominates the reforming system and the high excess of steam enhances the carbon gasification, which in turn suppresses the carbon deposition taking place on the nickel catalyst.
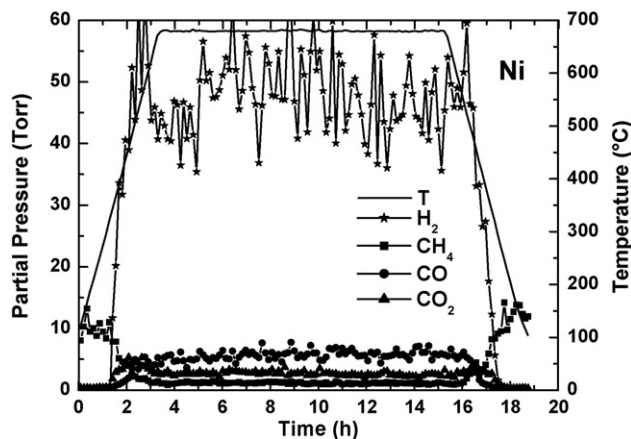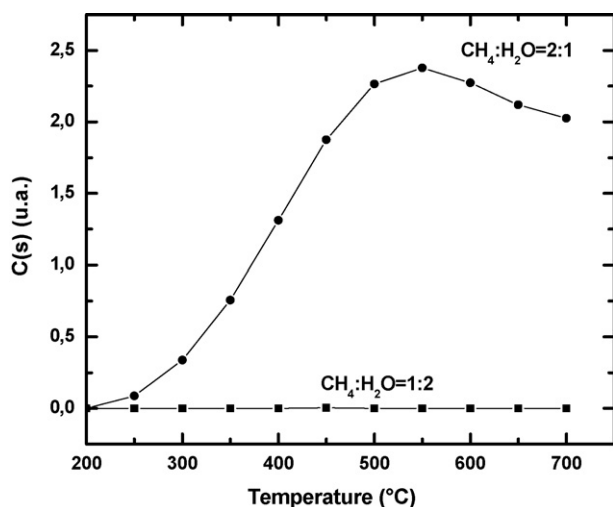

Fig. 1. Gas composition and temperature profiles vs. time on-stream for the steam reforming reaction, performed with an unsupported Ni catalyst. Reaction conditions: $P(CH_4)$ = 10 Torr, $P(H_2O)$ = 20 Torr, and $P(Ar)$ = 730 Torr.

Fig. 3. Effects of: (1) temperature and (2) CH_4:H_2O molar ratio, on the theoretical equilibrium values for the steam reforming reactor operating at 1 atm total pressure.

Fig. 5. XPS C(1s) spectra of (a) Ni–C_4S powder and (b) Ni–C_4S, obtained after their separate use in steam reforming tests. Reaction conditions: $P(CH_4) = 10$ Torr, $P(H_2O) = 20$ Torr, $P(Ar) = 730$ Torr, time of reforming = 20 h, and $T = 700\,°C$ for 12 h.

In the second part of the experimental work, pristine Ni powder was pre-treated with *n*-butanethiol and then used for the steam reforming of methane at a CH_4/H_2O molar ratio of 1:2; the reaction being monitored for a 20 h period. The CH_4/H_2O molar ratio of 1:2 was initially used to ensure attainment of chemical equilibrium, high conversion yields and absence of carbon deposition, while, at the same time, avoiding any limitations related to the reaction kinetics. Fig. 4 shows the results obtained through MS analysis, they are similar to those obtained with the pristine Ni powder (Fig. 1). In fact, hydrogen production was increased as the temperature increased. The temperature for the onset of hydrogen production was still at around 325 °C, with its maximum value at 500 °C. H_2 production remained stable over the experimental duration of 20 h, after the stabilization at $T = 700\,°C$. Methane conversion was at $94 \pm 2\%$ at 700 °C, and it also remained stable over time, as with the pristine Ni experimental run.
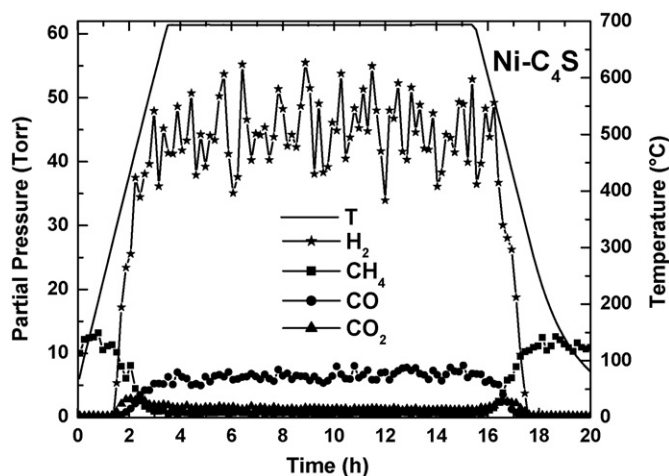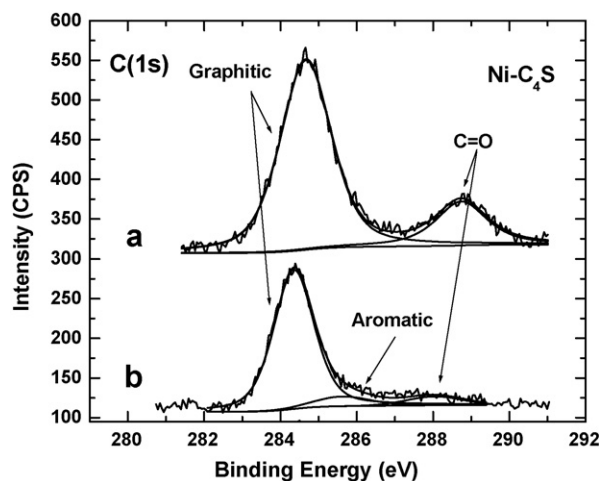

Fig. 4. Gas composition and temperature profiles vs. time on-stream for the steam reforming reaction performed with Ni–C_4S catalysts. Reaction conditions: $P(CH_4) = 10$ Torr, $P(H_2O) = 20$ Torr, and $P(Ar) = 730$ Torr.

Fig. 5 shows the XPS spectra of the C(1s) for the Ni–C_4S with before and after CH_4 steam reforming. From analysis of the near-surface atomic compositions for the nickel, pre-treated with *n*-butanethiol before the reforming reaction, the existence of two forms of carbon C(1s), located at ≈284.5 and ≈288.7 eV, was detected. The peak located at ≈288.7 eV is attributed to C=O. This originates from the Ni catalyst powder, which was produced commercially by the thermal decomposition of Ni(CO)$_4$ [33]. It is not known at this time if residual "chemisorbed" CO affects the binding of thiols to the Ni powder. The peak observed at ≈284.5 eV is attributed to graphitic (i.e. aliphatic) carbon, and originated from the *n*-alkanethiol molecule, previously chemisorbed on the catalyst surface. This assignment is consistent with the adsorbed thiolate [37–39]. In the case of Ni–C_4S after the steam reforming of methane, it was noticed that, besides those peaks observed for the nickel, pre-treated with *n*-butanethiol before steam reforming of the methane, a new peak, located at 285.6 eV, now appears. This new peak could possibly be attributed to an aromatic compound. The formation of aromatic–aliphatic carbon is obviously due to the pyrolysis of the pre-adsorbed *n*-butanethiol on the catalyst surface and cannot be attributed to the process feed gas ($CH_4 + H_2O$). Assignment and formation of aromatic–aliphatic carbon has already been discussed and confirmed in a previous study by these authors [32]. This present result shows that the used catalyst was "active" for the steam reforming of methane at a 1:2 CH_4/H_2O molar ratio over the entire 20 h(s) duration of the experiment. Additionally, it also shows that the catalyst was not affected by the adsorption of *n*-butanethiol.

The following experiment has been made to investigate the effect of *n*-butanethiol, on Ni catalytic activity during the steam reforming, and under conditions favouring the formation of carbon (CH_4/H_2O molar ratio of 2:1). For this purpose, the Ni–C_4S was tested for 21 h at a CH_4/H_2O molar ratio of 2:1 over a temperature profile ranging from 50 to 700 °C and returning to 50 °C (see Fig. 4), and involving a dwell time of 14 h at 700 °C.
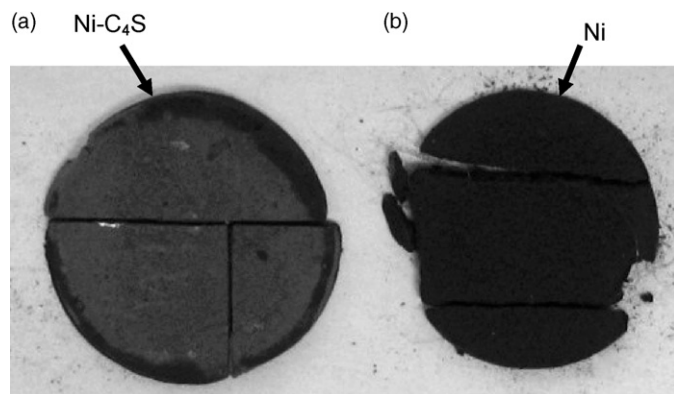
(a) Ni–C$_4$S

(b)

Fig. 6. Pellets obtained for (a) Ni–C$_4$S, after their use in steam reforming tests performed under the following conditions: $P(CH_4) = 40$ Torr, $P(H_2O) = 20$ Torr, $P(Ar) = 700$ Torr, time of reforming = 21 h, and $T = 700\,^{\circ}C$ for 13 h; (b) pure Ni, after their use in steam reforming tests under the following conditions: $P(CH_4) = 40$ Torr, $P(H_2O) = 20$ Torr, $P(Ar) = 700$ Torr, time of reforming = 9 h, and $T = 700\,^{\circ}C$ for 2 h.

The results are compared to those obtained with the pristine Ni that had earlier been tested under the same conditions, but only for 9 h (over the temperature cycle of 50–700–50 $^{\circ}C$, with a 2 h dwell time at 700 $^{\circ}C$;) the main difference being that this experiment lasted some 12 h less at the peak temperature of 700 $^{\circ}C$). Fig. 6 shows pellets of Ni–C$_4$S and Ni, after their use in the above-described experiments. The Ni pellet was now dark and friable, while the Ni–C$_4$S pellet had a color relatively similar to that of fresh Ni–C$_4$S, in spite of its treatment period of over 21 h. The results obtained by XPS confirm this observation. Figs. 7 and 8 show a comparison of the XPS C(1s) and Ni(3p) spectra between the Ni–C$_4$S and Ni catalysts, after their use in the steam reforming test at a CH$_4$/H$_2$O molar ratio 2:1 for 21 and 9 h, respectively. The analysis of the carbon C(1s) in Fig. 7b for the "used" Ni pellet shows that two types of carbon
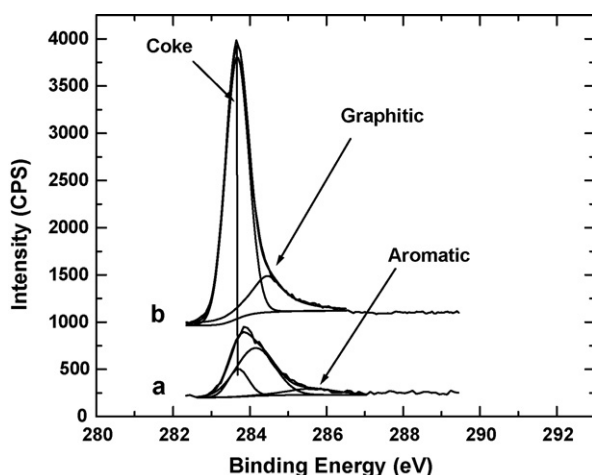

Fig. 7. XPS C 1s spectra of pellet materials (a) Ni–C$_4$S, obtained after their use in steam reforming tests under the following conditions: $P(CH_4) = 40$ Torr, $P(H_2O) = 20$ Torr, $P(Ar) = 700$ Torr, time of reforming = 21 h, and $T = 700\,^{\circ}C$ for 13 h; (b) pure Ni, obtained after their use in steam reforming tests under the following conditions: $P(CH_4) = 40$ Torr, $P(H_2O) = 20$ Torr, $P(Ar) = 700$ Torr, time of reforming = 9 h, and $T = 700\,^{\circ}C$ for 2 h.
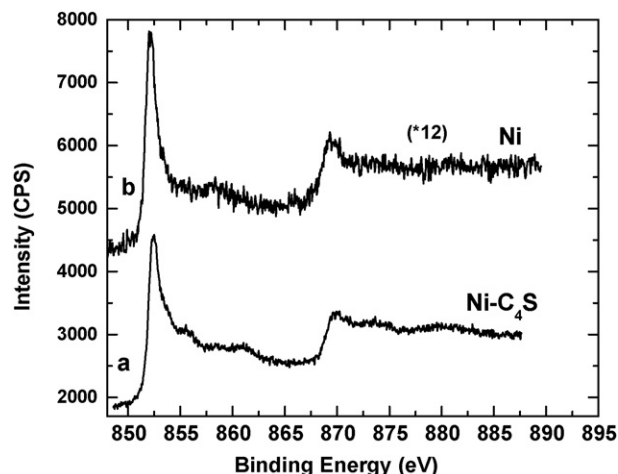

Fig. 8. XPS Ni(3p) spectra of test pellets (a) Ni–C$_4$S, obtained after their use in steam reforming tests made under the following conditions: $P(CH_4) = 40$ Torr, $P(H_2O) = 20$ Torr, $P(Ar) = 700$ Torr, time of reforming = 21 h, and $T = 700\,^{\circ}C$ for 13 h; (b) pure Ni, obtained after their use in steam reforming tests made under the following conditions: $P(CH_4) = 40$ Torr, $P(H_2O) = 20$ Torr, $P(Ar) = 700$ Torr, time of reforming = 9 h, and $T = 700\,^{\circ}C$ for 2 h.

can be identified in these spectra: (1) amorphous 'coke' which was earlier detected at 283.7 eV binding energies, as reported by Weckhuysen et al. [40] and Sexton et al. [41]; and graphitic carbon, at 284.5 eV binding energies [42]. However, analysis of the carbon C(1s) in Fig. 7a for Ni–C$_4$S shows that, besides the peaks observed for pristine Ni, another peak, located at 285.6 eV also appears. This peak could be related to an aromatic type of carbon contained in small molecules. Spectral "deconvolution" reveals the appearance of a new type of carbon (peak at 283.7 eV) in both experiments but in different quantities. This peak is associated with carbon deposited during the CH$_4$ steam reforming reaction at a 2:1 CH$_4$/H$_2$O molar ratio. On the other hand, comparison of XPS Ni(3p) spectra between Ni–C$_4$S and Ni shows that the signal for Ni, as pristine nickel, is lower than that for Ni–C$_4$S, by a multiplying factor of 12 (Fig. 8). However, for the carbon phase, the opposite effect is observed. In order to evaluate the carbon formation tendency for the two tested catalysts, the following calculation has been undertaken:

$$X = \frac{\text{area (carbon at 283.7 eV)}}{\text{area (Ni(3p))}} \times \frac{\text{sensitivity of Ni}}{\text{sensitivity of carbon}}$$

The result shows that, for the Ni–C$_4$S, we have a C/Ni atomic ratio of approximately 0.2, while the same C/Ni atom ratio is 29 in the case of the pristine Ni catalyst, even if the latter was used for 12 h less than the Ni–C$_4$S. Thus, it can be concluded that the quantities of carbon deposited are some 145 times lower when the Ni powder employed is pre-treated with n-butanethiol.

Although it is believed that the partial S coverage of the Ni surface is mainly responsible for this improved catalysts preservation, the exact mechanism is still unknown and additional work on the matter is needed. The elucidation of this mechanism can lead to new ways of preparing more efficient and durable catalytic formulations.

4. Conclusion

This work brings forward some experimental proofs for the decrease in the carbon formation tendency during CH_4 steam reforming, by pre-treating the unsupported Ni catalyst with *n*-butanethiol. The catalytic formulation tested was obtained by immersion of pristine Ni powder in solutions of butanethiol/methanol at ambient temperature. The steam reforming of CH_4 at CH_4:H_2O molar ratios not-favouring (1:2) and favouring (2:1) the surface carbon formation, was used to evaluate the effect of the *n*-butanethiol pre-treatment. It has been found that the quantities of carbon deposits for the *n*-butanethiol pre-treated catalyst is two orders of magnitude lower than that obtained over pristine Ni, under the same conditions of temperature and pressure. This result, obtained by calculations using XPS, is supported by the differences of color and texture observed in the respective pellets of pristine Ni and Ni–C_4S.

Acknowledgements

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