



A semiempirical theoretical study of Ni/ α -Al₂O₃ and NiSn/ α -Al₂O₃ catalysts for CH₄ reforming

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Abstract

In order to investigate the nature of Ni supported on α -Al₂O₃ and its modification with Sn in methane reforming reactions, a theoretical study was carried out. A molecular orbital approach of the extended Hückel type was performed to obtain the formation energies of postulated adsorbed and reacted species of CH₄, H₂O, O₂ and CO₂ on a model of Ni and NiSn surfaces resembling Ni/ α -Al₂O₃ and NiSn/ α -Al₂O₃. Three different known planes of fcc Ni were considered: (1 1 1), (0 0 1) and (1 1 0). Possible adsorbed and reacted species of CH₄, H₂O, O₂ and CO₂ on Ni with Ni all around, Sn fully rounded by Ni and Ni near a Sn were discussed using reaction energies. The interaction NiSn in Ni clusters has been claimed to be of interstitial substitution-type in alloys. The (1 1 1) plane is the most reactive for adsorption. In agreement with experimental work, methane activation on Ni is the controlling step in reforming of methane with CO₂ (R), partial oxidation with O₂ (POM) and mixed reforming using CO₂ and O₂ (MR). Sn near a Ni changed the adsorption properties of it. Favoured reactions for Sn rounded by Ni on (0 0 1) and (1 1 1) planes are the adsorption of CO₂ and formation of a Sn–CO bond and the generation of Sn–H bonds from methane and water dissociation. The theoretical results are discussed in the context of previously published experimental data.

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1. Introduction

Most syngas is obtained using traditional methane steam reforming process. Some alternative routes like partial oxidation of methane (POM), CO₂ reforming (R) and mixed reforming (MR) including O₂ and CO₂, may be of increased practical importance depending on desired H₂/CO molar ratio and other fac-

tors, such as the energetic consumption. Nickel catalysts are widely used in the industrial reforming processes.

There are a lot of reports about experimental characterisation of these Ni/ α -Al₂O₃ supported catalyst [1] but the literature about theoretical characterisation of these reactions is limited. There are some reports about H₂ interaction with Ni clusters and other studies about magnetic and electronic properties of clusters of pure Ni of different sizes, using sophisticated methods like DFT. The local spin-density approximation (LSDA) was used for exchange and correlation effects and the

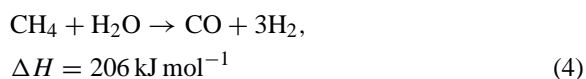
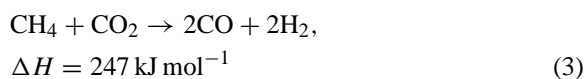
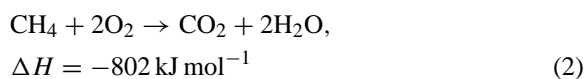
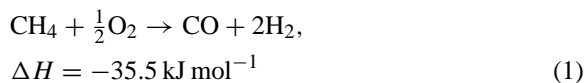
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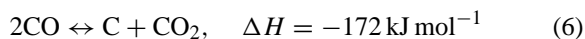
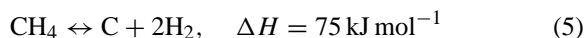
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inner cores were replaced by nonlocal pseudopotentials in the report of Reuse and Khana about calculation on clusters of Ni of sizes from 2 to 13 atoms [2]. Riley et al. have published chemical probe experiments using adsorption free energies of H₂O, NH₃ and N₂ to discuss icosahedral symmetry of Ni clusters in some cluster-size ranges [3]. Uncertainties still exist about the structure of Ni clusters for different sizes. A number of those clusters may have ground states that do not belong to any of the usual morphologies: icosahedral, decahedral and close packed. The icosahedral structures are preferred for the clusters with 13 and 55 atoms whereas for clusters of 19, 23, 24 and 38 atoms the fcc structure is favoured [4].

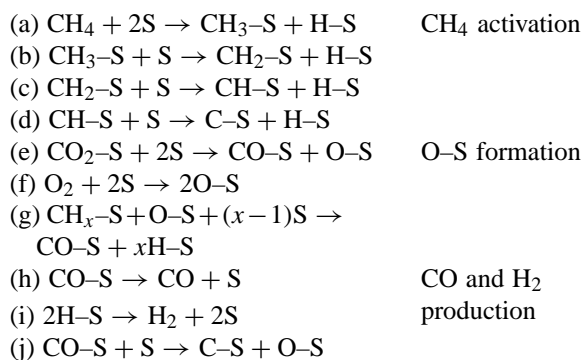
Related to the reactions of natural gas reforming for syngas obtention, there are a lot of reports about the different proposed mechanisms [5]. A one step or direct transformation (reaction 1) and a two step mechanism for the POM reaction (CH₄ + O₂), [5] have been proposed. The latter consists of a first step in which the total combustion takes place (producing H₂O and CO₂) and a second step in which the remaining methane reacts with the combustion products in classical reforming, (see reactions (2)–(4)). For R reaction a mechanism involving dissociation of CO₂ and CH₄ is suggested [6].



Besides these reactions, other undesirable ones are possible, as those that lead to the formation of carbon. The high temperatures of the reforming reactions through cracking of methane (reaction (5)) and/or the Boudouard reaction (reaction (6)) favour the deposits of carbon on the catalytic surface. This last one is an exothermic reaction which is penalised by temperatures higher than 600 °C.



Deactivation on Ni-based catalysts by coke formation is the most important deactivation mechanism in the process to syngas obtention. Some strategies are based in the usage of basic supports like CaO and the addition of Cu, but the carbon formation is not avoided [7,8]. Tin is recognised as a stability promoter against coke formation in many processes like aromatization and dehydrogenation of paraffins. A recent report about the effect of selective addition of tin on α -Al₂O₃-supported Ni catalysts via surface-organometallic-chemistry and their performance in POM, R and MR reactions has been published by Nichio et al. [9]. The authors prepared catalysts with low Sn contents and high resistance to carbon formation, maintaining activity and selectivity similar to Ni monometallic catalysts when Sn/Ni bulk <0.025. The reaction scheme that allows to explain the experimental results obtained by Nichio et al. is the following [9]:



The stages (a)–(d) correspond to the activation of methane to coke formation through successive C–H cracking steps. These steps must take place on sites formed by ensembles of several metallic atoms. If the C–S species are of the type C–Ni₃ seven Ni atoms are required per active site for carbon formation. Taking into account that the catalysts NiSn have atomic-surface Sn/Ni ratios of 6–20%, it is acceptable to suppose that small amounts of tin deposited selectively on Ni are enough to destroy many active sites for coke formation. On the contrary, the formation of synthesis gas passes through stage (g) where CH_x-S reacts with O–S species to give CO–S and H–S, which are finally desorbed to the gaseous phase as syngas (CO + H₂). Since CH_x-S corresponds to a partially dehydrogenated species (x = 1, 2 or 3), the activation stage

of methane also requires ensembles of several nickel atoms, but these ensembles are not necessarily of the same size than the ones needed for carbon formation. This may explain why only concentrations of tin over $\text{Sn}/\text{Ni}^{\text{bulk}} > 0.025$ (which implies a superficial atomic concentration of 50% approximately in Sn), inhibit the formation of synthesis gas. Some recent papers suggest that for R reaction performed on Ni/ Al_2O_3 catalysts, the number of hydrogen atoms contained in the superficial species $\text{CH}_x\text{-S}$ is between 2 and 3 ([9], and references therein). If this is the case, syngas formation would proceed on active sites composed of ensembles of three or four Ni atoms, and so, the promoting effect of tin atoms in intimate contact with nickel would be similar to what is proposed by Rostrup-Nielsen and Alstrup [10], Rostrup-Nielsen [11] for the case of partly sulphur poisoned nickel catalysts.

The present work is related to the experimental work of Nichio et al. [9]. Based on these experimental results, the goal is the study the adsorption and dissociation of the reactive molecules (O_2 , CH_4 , H_2O and CO_2) on the Ni and NiSn structures in its reduced form, when $\text{Sn}/\text{Ni bulk} \leq 0.01$. Due to their importance, the reactions leading to carbon will be evaluated, according to the reactions presented in Eqs. (5) and (6).

2. Theoretical model

The theoretical studies applied to catalysis may be classified in semiempirical, ab initio and the DFT methods. The extended-Hückel-modified method (EHMO)–semiempirical–was selected to perform the study of Ni and NiSn/ $\alpha\text{-Al}_2\text{O}_3$ catalytic systems.

The EHMO was widely used by Hoffman et al. to study electronic structure of transition metal complexes; it provides useful qualitative trends in systems with near a hundred (or more) atoms. The electronic structures and derived properties are established from electron equations for the molecular orbital. In this formalism, the non-diagonal elements of the Hamiltonian of the system are proportional to the overlap matrix elements. More recently, in order to improve the traditional extended Hückel Hamiltonian some corrections were introduced by Chamber et al. [12] and Juan and Hoffman [13].

The total energy of a selected adsorbed or reacted species on a Ni or NiSn cluster is a sum of an attractive and a repulsive term. The attractive energy is related to the electrons in the valence level i with an occupancy n_i . The repulsion energy is originated between all the possible pairs nucleus i –fixed atom j . The reported adsorption energies are calculated as the energy of the adsorbed molecule minus the sum up of the energies of the adsorbate and surface at infinite distance each other. Reaction energies involving reordering of adsorbate structures are calculated as product energies minus reactive energies. Depending on what is being compared, different energies can be obtained. If the adsorption is activated; therefore, the energy increases and later decreases whereas the adsorbate is approaching to surface and activation energies can be calculated. The difference between the stable situation of the adsorbate at equilibrium distance to surface and the energies of surface and adsorbate far away from each other is the adsorption heat. The higher the adsorption energy, the stronger the surface-adsorbate bond. The more negative the energy is, the more favourable. The reported data of adsorption heat are only of qualitative value and no significance must be extrapolated. Only the changes and the trend in changes can be analysed.

Because the EHMO is a semiempirical method, experimental parameters are needed for calculations. We have used reported ionisation potential obtained from spectroscopic data [14]. Since for the level 4p only theoretical data are available in literature, we have taken the data of Hartree–Fock–Slater [15]. Parameters used in this work for Ni, Sn, C, O and H are presented in Table 1.

Table 1
Huckel parameters

| | | | |
|----|----|----------------------------|--------|
| H | 1s | 1.000 | –13.60 |
| C | 2s | 1.154 | –19.65 |
| | 2p | 1.451 | –11.80 |
| O | 2s | 2.163 | –31.6 |
| | 2p | 2.750 | –16.78 |
| Sn | 5s | 2.12 | –16.15 |
| | 5p | 1.82 | –8.32 |
| Ni | 4s | 2.10 | –7.80 |
| | 4p | 2.10 | –3.70 |
| | 3d | 5.75 (0.5683) ^a | –9.90 |
| | | 2.00 (0.6292) ^a | |

^a Coefficients for double expansion of orbitals.

The program used to calculate the energy of the different species, was the ICONC originally developed by Chamber et al. [12], which takes into account repulsive terms that are not originally present in the EHMO. In the present work, calculations were carried out with a modified version of ICONC. This version has been tested in previous works dealing with the adsorption of CH_4 and NO on Pd catalyst [16,17] and for VO_x formation on $\gamma\text{-Al}_2\text{O}_3$, TiO_2 and SiO_2 [18,19].

Due to the semiempiric nature of this method, comparison with experimental data is the way to check the validity of these models. The main result is the possibility to find some reactions at surface that are more probable than others.

3. The models

The catalysts are all supported on $\alpha\text{-Al}_2\text{O}_3$. The size of metallic phases gives us tools to examine the particles of reduced Ni as the catalytic sites, being the support a dispersive medium. The average particle sizes (measured by TEM) are 16.5 nm and 17.5 nm for Ni and the best NiSn catalysts, respectively [9]. Therefore, considering 2.505 \AA as the Ni–Ni distance a maximum of 66–67 atoms are exposed in a line of an ideal squared particle, a situation far away of the actual one. We considered the three planes of Ni structure fcc because of the lack of data about the surface actual structure in these reduced supported catalysts. In this way, the selection of 24/25 atoms in the exposed plane

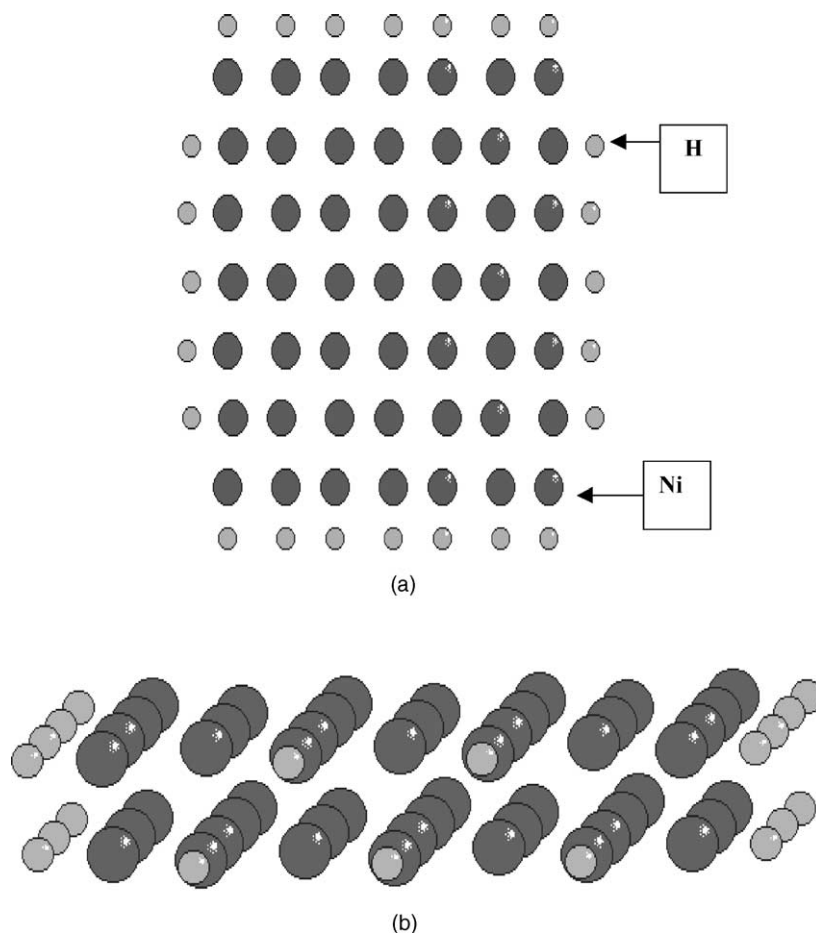


Fig. 1. Plane (001) Ni: (a) upper view; (b) lateral view, showing the first and second row. The H are depicted because they are needed in the calculation.

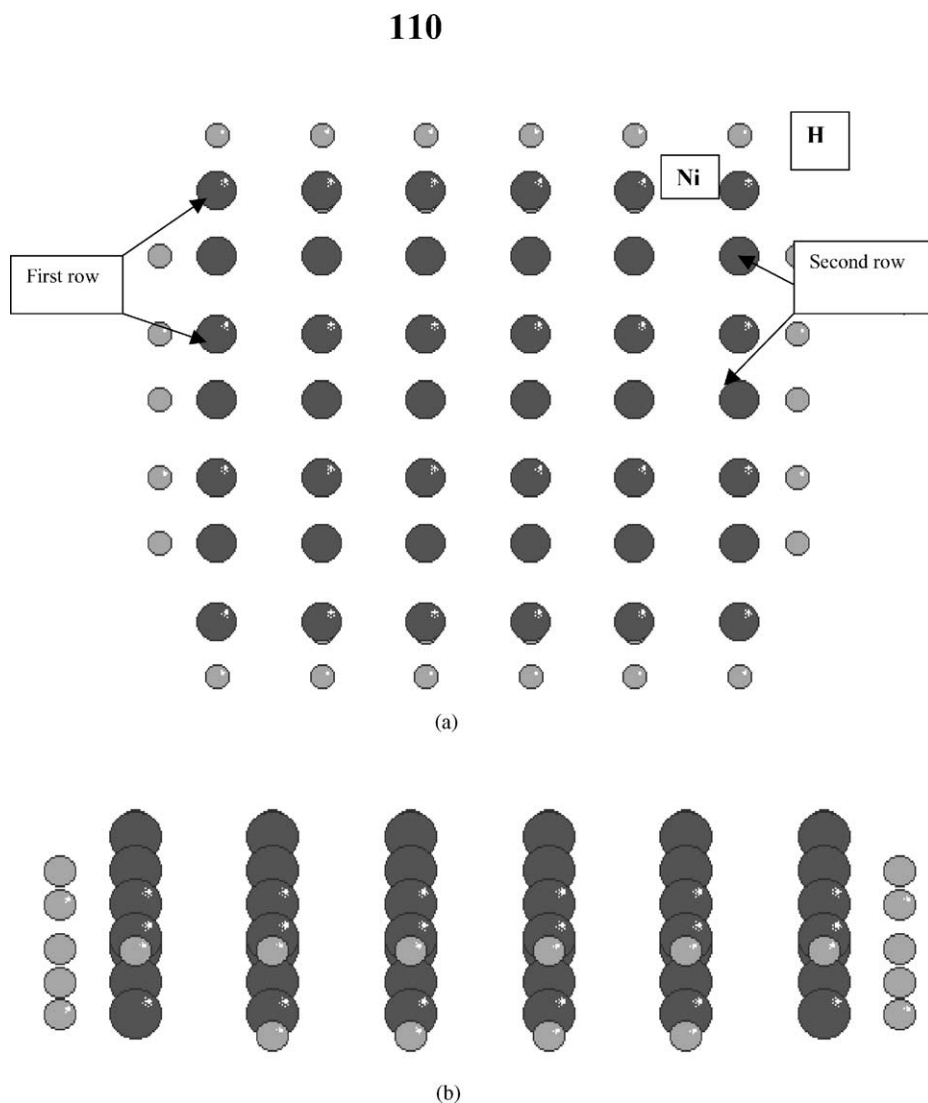


Fig. 2. Plane (110) Ni: (a) upper view; (b) lateral view, showing the first and second row. The H are depicted because they are needed in the calculation.

is adequate to study small molecules adsorption and dissociation avoiding border effects (Figs. 1–3).

The replacement of a Ni by a Sn in all these planes resembles the structure of NiSn catalysts at low coverage (see experimental data reported in reference [9]). For the NiSn catalyst, the Sn/Ni at surface is 0.06, whereas the Sn/Ni at bulk is 0.003. Therefore, replacing 1 Ni by Sn of 24/25 total exposed atoms leads to 0.0416/0.04 for Sn/Ni and replacing 2 we obtain 0.0833/0.08 for Sn/Ni. Each Sn atom affects four Ni

at surface in (001) and (110) planes and three Ni in (111). We need more than 5 Sn for 24/25 atoms at surface to achieve Sn–Sn interaction.

In all cases, to avoid border problems, H were placed to complete the co-ordination of borderline Ni atoms. Table 2 shows the characteristics of the used models for the different Ni and NiSn planes.

The NiSn clusters were modelled with exactly the same number of atoms than the Ni cluster, but a Ni at the centre of the first exposed row was replaced by a

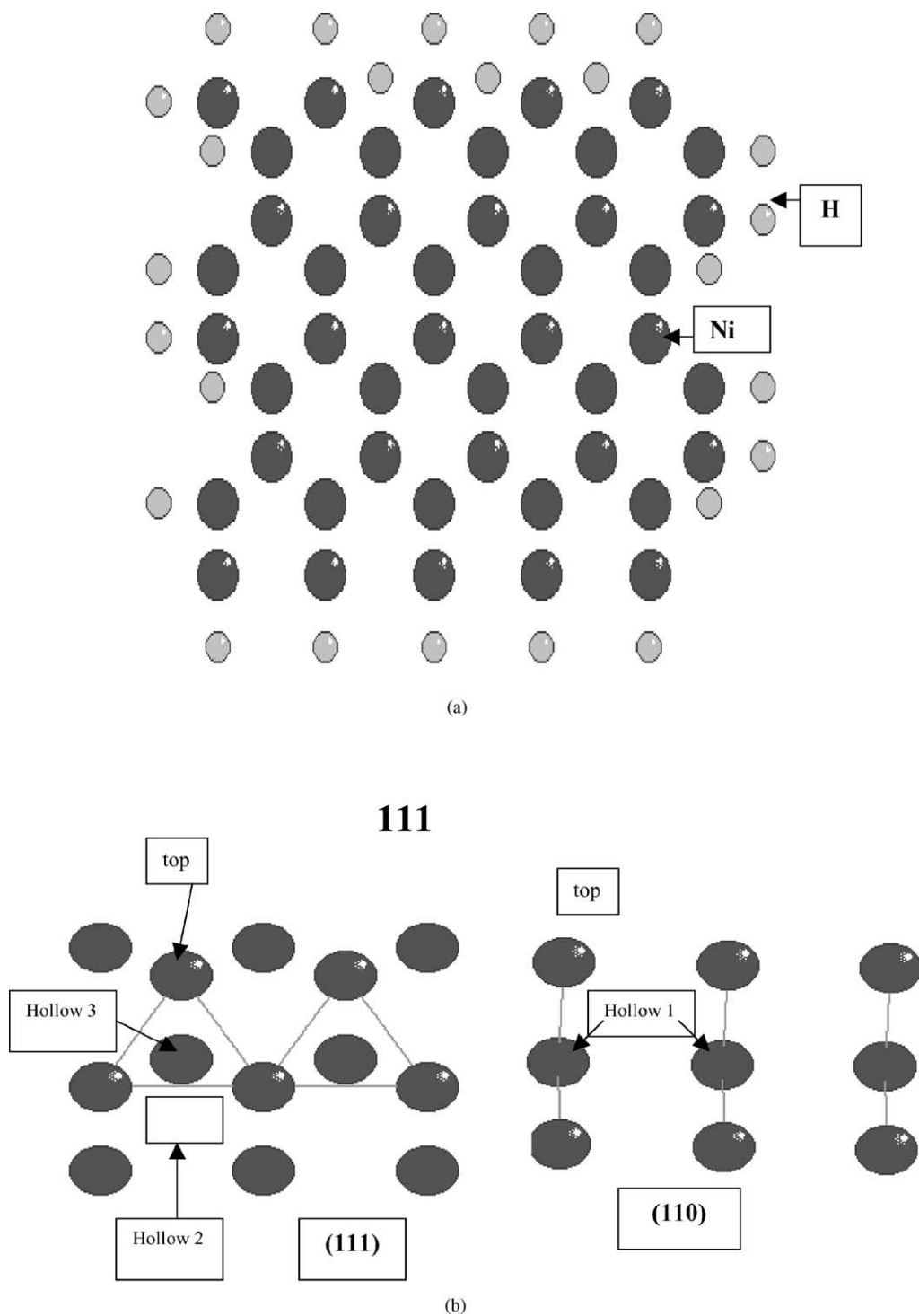


Fig. 3. Plane (111) Ni: (a) upper view; (b) hollow and top sites in (111) and (110) planes.

Table 2
Atoms in planes of fcc Ni cluster

| Plane | Model |
|---------|--|
| (0 0 1) | With 73 atoms: 24 H and 49 Ni, in two rows: first of 25 atoms and the second of 24 atoms (Fig. 1). |
| (1 1 0) | With 72 atoms: 30 H and 42 Ni, in two rows: first line of 24 atoms and the second of 18 atoms (Fig. 2). |
| (1 1 1) | With 73 atoms: 28 H and 45 Ni, in two rows: first of 25 atoms and the second of 20 atoms (Fig. 3). In Fig. 3 the different kinds of hollow sites are depicted. |

Sn atom. This structure resembles that provided by interstitial substitution alloys. The intimate NiSn interaction has been studied by temperature programmed reduction (TPR) [9,20]. A decrease in 100 °C in TPR peaks for NiSn/ α -Al₂O₃ (Sn/Ni at surface = 0.06) is found and related to reduction peaks in Ni/ α -Al₂O₃. In clusters NiSn two different situations were evaluated: adsorption on Ni close to Sn and adsorption on Sn.

3.1. CH₄

The adsorption was considered by the H side (form a) or by the three Hs of methyl (form b) on the (0 0 1) plane and only in the preferred form b for (1 1 0) and (1 1 1) planes (see Fig. 4). The distance C (CH₃)-Ni (surface) was optimised to obtain the energetic minima in all cases. The dissociation of CH₄ was evaluated in

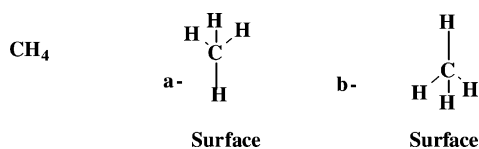
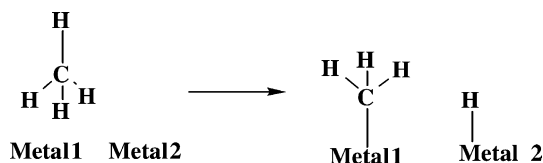


Fig. 4. Adsorption of methane on Ni surfaces.



Metal configuration :Metal 1 = Metal2 =Ni
Metal1 =Ni, Metal2 =Sn
Metal1 =Sn, Metal2 =Ni

Fig. 5. Dissociation of methane in Ni and Ni–Sn catalysts.

its first step of dehydrogenation: formation of metal-H and metal-CH₃ groups (see Fig. 5). These distances were modified in order to obtain the energetic minima. In case of NiSn clusters, the H–Sn versus CH₃–Sn dissociation species were evaluated.

3.2. O₂

The metal configuration to study O₂ dissociation is shown in Fig. 5.

3.3. CO₂

When CO₂ dissociates, leaves a (CO)-metal and a O-metal groups at surface. In this case, it was considered the bonding from the O and from the C side of CO.

3.4. H₂O

Dissociation of water leaves at surface H* and HO* species. In the two-step mechanism for POM total oxidation occurs and later CH₄ reacts with H₂O. Therefore, water is proposed to remain on surface and to react further with dissociated CH₄.

4. Carbon formation

Carbon formation was considered from methane dissociation and from CO dissociation (reactions 4 and 5). In case of CO dissociation, the needed step of change from perpendicular to parallel adsorption of CO was considered. The reaction of CO formation from CH₂ and O at surface was modelled, to compare CO versus C formation. When CO is produced from CH₂, it is parallel to surface and therefore desorption would be easy.

5. Results

Associative and dissociative adsorption results are presented. Associative adsorption is the adsorption of the whole molecule without broken bonds.

5.1. Ni cluster

5.1.1. CH₄ adsorption and dissociation

The adsorption of methane on fcc Ni planes is clearly preferred in form b (H–Ni distance: 2.03–1.83 Å) in Ni (1 1 0) plane (see Fig. 6). The adsorption energy is near –1.00 to –0.86 eV for this form, whereas it is only –0.30 eV for form a (H–Ni distance 1.91 Å).

On (1 1 1) plane, three different sites were evaluated: Ni top, Ni h2 and Ni h3. Three Ni atoms are involved in the methane adsorption and geometrically, each H interacts with each Ni and the resulting adsorption is strong. For total dehydrogenation we need five Ni atoms. Ni(1 1 1) plane is the most reactive and the most easily deactivated by C formation from CH₄, CO₂ or CO decomposition [21].

The order in adsorption energy for methane in Ni(1 1 1) plane in form b is.

Table 3

Adsorption and dissociation of CH₄ (eV) on Ni

| | (001) | (110) | (111) |
|---------------------------------------|-------|-------|-------------|
| Adsorption in form b-TOP | –0.89 | –0.83 | –1.01 |
| Adsorption in form b-HOLLOW | – | –1.11 | –1.03/–1.31 |
| H (CH ₃)-Surface-A-HOLLOW | – | 2.4 | 1.83/1.72 |
| Dissociation | –3.34 | –4.14 | –4.54 |
| H-Surface-A | 2 | 1.3 | 1.3 |
| C(CH ₃)-Surface-A | 2 | 2 | 2 |

Ni h3(1 1 1) ≫ Ni h2(1 1 1) > Ni top(1 1 1)

In case of Ni(00 1) plane the methyl–Ni surface and Ni–H distances at energetic minimum are 2 Å. The dissociation reaction is favoured instead adsorption without dissociation. For (1 1 0) and (1 1 1) planes the dissociation is strongly favoured (–4.14 and –4.53 eV, respectively, see Table 3).

5.1.2. O₂ adsorption and dissociation

For the (00 1) plane we evaluated adsorption of O₂ in perpendicular and parallel ways. The approach of O₂ can be perpendicular or parallel up to 2.50 Å from Ni, after this, the parallel orientation is preferred (see Table 4).

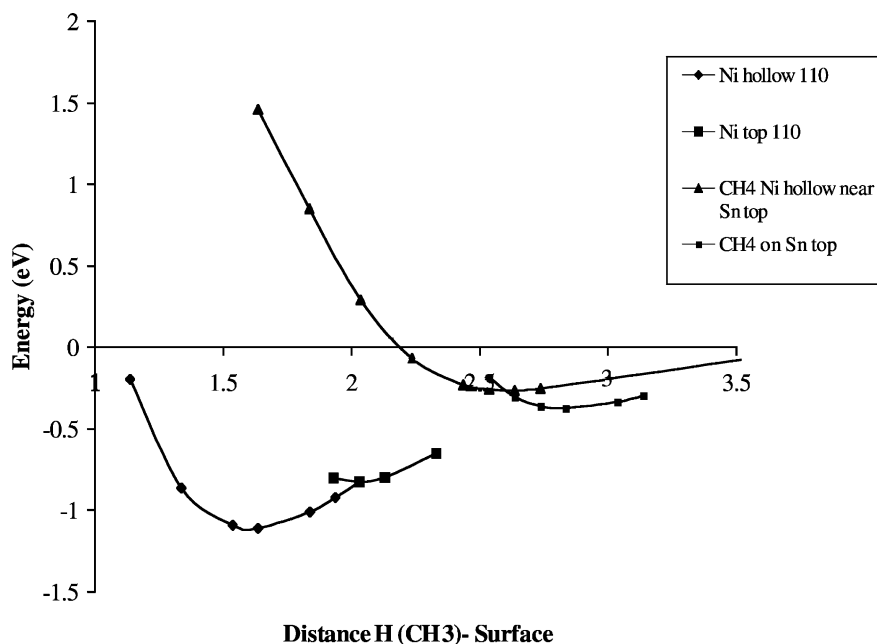


Fig. 6. Methane adsorption on Ni(1 1 0) and NiSn(1 1 0)-to avoid confusion, only the most important fraction of the curves are depicted.

Table 4
Adsorption and dissociation of O₂ (eV) on Ni

| | (001) | (110) | (111) |
|----------------------|--------|--------|-------------------|
| Adsorption in TOP | -14.64 | -14.6 | -14.88 |
| O-Surface-TOP | 1.3 | 1.3 | 1.3 |
| Adsorption in HOLLOW | - | - | -15.46/-15.31 |
| O-Surface-HOLLOW | - | - | 1.3 |
| Dissociation | -15.53 | -14.68 | -15.59 |
| | | | 1O in Ni h2 -13.4 |
| | | | 1O in Ni h3 -11.6 |
| O-Surface-A | 1.3 | 1.3 | 1.3 |
| O-Surface-A | 1.3 | 1.3 | 1.3 |

Dissociation of O₂ is energetically favoured for (111) and (001) planes, whereas for the (110) plane the energy for the dissociation reaction is somewhat lower (-15.60 eV versus -14.68 eV). Dissociative adsorption of O₂ is preferred to associative adsorption in (001) plane by almost -0.9 eV. In case of (111) and (110) planes, differences are not important.

5.1.3. CO₂ adsorption and dissociation

The distance Ni top-C(CO₂) in all planes is 1.5 Å. The highest adsorption energy is found for the (111) plane on Ni top and Ni h3 (-8.70 eV) whereas for (110) plane is the lowest (-7.98 eV). Far away from the surface, the linear CO₂ geometry is preferred and later the angular CO₂ geometry is adopted (see Table 5).

Dissociation of CO₂ leaves a CO molecule at 1.5 Å from surface Ni and the O 1.3 Å away from Ni. The highest energy is found for (111) plane (-16.37 eV) whereas for (110) and (001) planes is near -15.8 and -16.24 eV. Adsorbed CO molecules are oriented with C on Ni surface and O away, in agreement with experimental studies.

Table 5
Adsorption (as carbonate) and dissociation of CO₂ (eV) on Ni

| | (001) | (110) | (111) |
|--------------------------------|-------|-------|-----------|
| Adsorption TOP | -8.4 | -7.99 | -8.7 |
| CO ₂ -Surface-A-TOP | 1.5 | 1.5 | 1.5 |
| Adsorption HOLLOW | - | - | 8.7/-8.67 |
| Dissociation | -16.2 | -15.8 | -16.4 |
| O-Surface | 1.3 | 1.3 | 1.3 |
| C(CO)-Surface | 1.5 | 1.5 | 1.5 |

Table 6
Adsorption-dissociation of H₂O (eV) on Ni and Ni-Sn

| | (001) | (110) | (111) |
|-----------------|-------------|-------------|----------------------|
| Adsorption TOP | -0.08 | -0.51 | -0.51 |
| Ni-O | 2.4 | 2.4 | 2.4 |
| Dissociation | -9.7 | -9.1 | -8.93 |
| Ni-H | 1.3 | 1.3 | H hollow-1.94 |
| Ni-O | 1.7 | 1.7 | 2.5 |
| Adsorption NiSn | +0.20 | 2.0 | -0.07 |
| Sn | -0.51 | 1.34 | -0.76 |
| Ni near Sn | Sup-O = 2.4 | Sup-O = 2.4 | Sup-O = 2.4 |
| Dissociation | -11.15 | -10.9 | No minimum on Sn top |
| Sn-H | 1.3 | 1.3 | >3 |
| Ni-O | 1.7 | 2.4 | |

5.1.4. H₂O adsorption and dissociation

On (001) plane water distance to Ni surface at the adsorption step is 2.4 Å. The adsorption energy of H₂O is rather low (-0.08 eV). Dissociation of H₂O is easy on this plane (-9.70 eV). For (111) and (110) planes, the adsorption and dissociation energies for H₂O are very similar (see Table 6).

Adsorption step is energetically favoured in the following order: CH₄ ≪ CO₂ ≈ O₂. The dissociation step is energetically similar for CO₂ and O₂, whereas for CH₄ is almost four times lower. Water dissociation is favoured on the three planes of Ni in the following order: Ni(111) < Ni(110) < Ni(001), but not adsorption. Figs. 7 and 8 show the sites for Methane, O₂ and CO₂ adsorption on Ni(110) and Ni(111).

5.2. NiSn cluster

5.2.1. CH₄ adsorption and dissociation

Methane adsorption by the three Hs of methyl (form b) is selected because of the results on Ni clusters. On (001) plane, for Ni close to Sn, the adsorption energy for methane is +0.21 eV and the H-Ni distance is 2.13 Å. The adsorption energy on Sn achieves +2.15 eV at so long distances from surface, such as 2.5 Å.

On (110) plane, looking at Ni close to Sn, the adsorption energy of methane achieves -0.26 eV for form b (Ni-H bond distance = 2.64 Å). On Sn top the minimum is found at even higher distance 2.84 Å

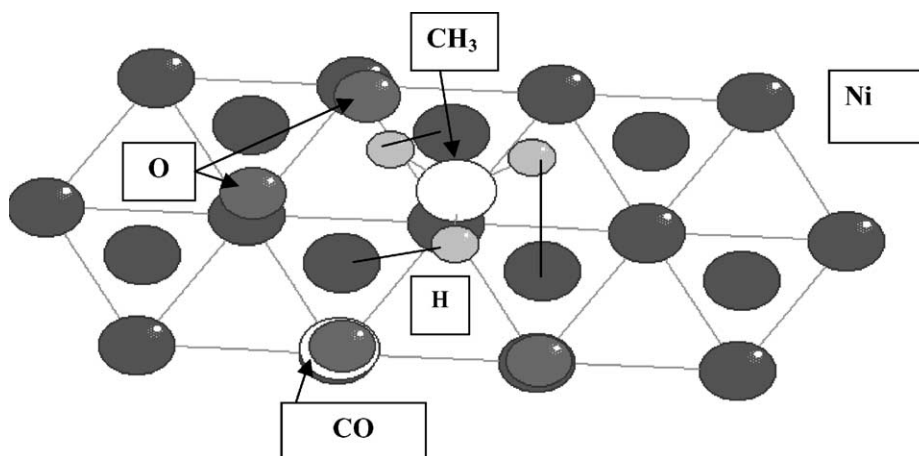


Fig. 7. Adsorption sites for methane, O_2 and CO_2 on Ni(111). In mixed reforming, positions for methane dissociative adsorption, CO_2 dissociative adsorption and O_2 dissociative adsorption (111) plane. The lines indicate the interaction of H from methyl with the second Ni row. C formation (from methyl on Ni top) without O_2 present would be geometrically favored on this plane. The same arise from CO, placed instead methyl group.

(-0.37 eV). On the (1 1 1) plane, no minimum is found for methane adsorption. Form (b) of methane adsorption shows an energy of -0.27 eV. This is a very weak adsorption and therefore no reaction will take place on Sn. There is no way in which the methane can react so far away from surface ($Sn-H(CH_4) = 3.23$ Å) (see Table 7).

5.2.2. O_2 adsorption and dissociation

Sn decreases the adsorption energy of O_2 in almost 0.7 eV. The adsorption of O_2 on Sn does not show a minimum on the three planes. No O_2 dissociation on Sn rounded with Sn atoms was considered to take place. The dissociation energy of O_2 on Ni close to Sn is lower than dissociation on Ni. When O_2 is adsorbed on a Sn with a Ni close to Sn, the second

O interacts with Ni and at the dissociation step the first O can remain bonded the Sn, with an equilibrium distance Sn–O for the minimum of 3 Å. In this sense, the O bonded to Sn is a reactive O, that can jump to the next Ni with an equilibrium distance for the minimum near 1.3 Å. Besides it can react with an incoming methane molecule. On NiSn cluster, O from dissociation is placed at 3 Å from Sn or even more. This O can migrate to the Ni close to Sn (see Table 8).

5.2.3. CO_2 adsorption and dissociation

Sn enhances the adsorption and dissociation of CO_2 , especially at (001) and (111) planes. Distances Sn–CO varies between 1.5 Å for (001) and (111) planes and 1.7 Å from the (110) plane. The

Table 7
Adsorption and dissociation of CH_4 (eV) on Ni–Sn

| | (001) | (110) | (111) |
|----------------------------|------------------------------|-------------------------------------|-----------------|
| Adsorption in form b-TOP | On Ni = 0.21 On Sn = 2.15 | On Ni = -0.264 On Sn = -0.37 | On Sn = -0.26 |
| H (CH_3)-Surface-A-TOP | 2.13 (Ni) On Sn > 2.5 Å | 2.636 (Ni) 2.836 (Sn) | 3.23 (Sn) |
| Dissociation | -4.23 | -4.23 | -5.88 |
| H-Surface-A | H–Sn = 1.3 | H–Sn = 1.3 | H–Sn = 1.3 |
| C(CH_3)-Surface-A | C–Ni = 2 | C–Ni = 1.5 | C–Ni = 1.5 |

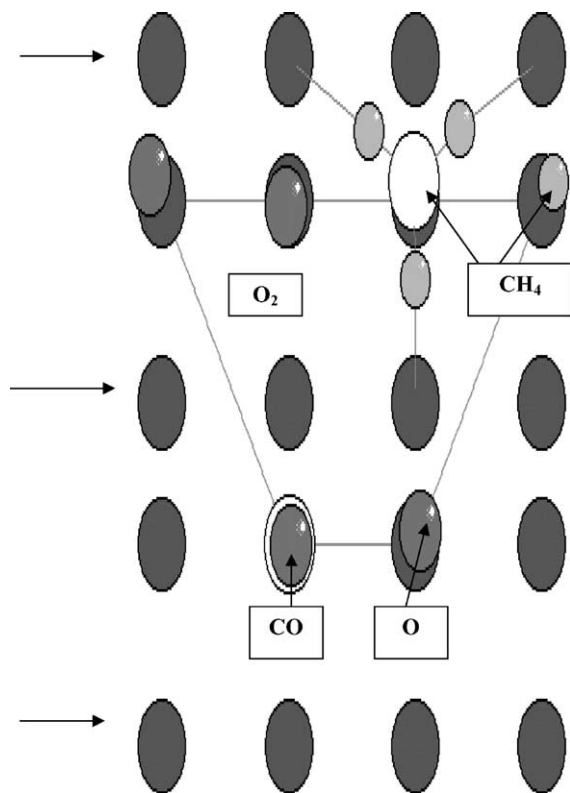


Fig. 8. Adsorption sites for methane, O and CO₂ on Ni(110). It is clear that the distances are higher for dehydrogenation of methyl group than in case of (111) plane. With arrows it is shown the second Ni row.

adsorption energies are 60% higher than Ni for these two planes on Sn, whereas dissociation reactions increase their energies by near 20%. The CO group remains on Sn, co-ordinated by the C side. The differences are between -2 and -3 eV favouring CO on Sn, being O on Ni (see Table 9).

Table 9
Adsorption (as angular CO₂) and dissociation of CO₂ (eV) on Ni close to Sn and Sn

| | (001) | (110) | (111) |
|---|-----------------------------------|------------------------------|-------------------------------|
| Adsorption TOP | (On Ni) -7.4 (On Sn) -13.2 | On Ni -4.4 On Sn -6.4 | On Ni -7.6 On Sn -13.3 |
| CO ₂ -Surface-A-TOP | 1.5 | 1.7 | 1.5 |
| Dissociation 1-from CO ₂ -Sn | -18.7 | -17.0 | -19.3 |
| O-Ni | 1.3 | 1.3 | 1.3 |
| C(CO)-Sn | 1.5 | 1.5 | 1.5 |

5.2.4. H₂O adsorption and dissociation

On Ni close to Sn, the adsorption energy increases, comparing it with that on Ni for (001) and (111) planes. The dissociation of water is favourable in case of H being located on Sn. The dissociation energies are near -11 eV (see Table 6).

We can conclude that the affinity of Ni surface for adsorbates is $O_2 > CO_2 > CH_4 > H_2O$, being the adsorption heat (a measure for ΔG at 0 K) near -110 kJ/mol for CH₄, -170 kJ/mol for O₂, -350 kJ/mol for CO₂ and -51 kJ/mol for H₂O calculated as the difference of the energy 3.0 or 3.5 Å far away from the surface minus the energy at the equilibrium distance. We must consider these values only in qualitative terms. In case of Sn, affinity decreases in order $CO_2 > CH_4 > O_2 \approx H_2O$ being the adsorption heat near -800 kJ/mol for CO₂, -12 kJ/mol for CH₄, 0 kJ/mol for H₂O and 0 for O₂.

5.2.5. C formation

On (001) and (110) planes step (c) and (d) are disfavoured when NiSn is considered. Step (b) is energetically preferable on NiSn for (001), whereas step

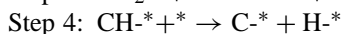
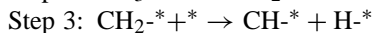
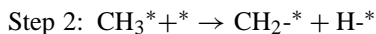
Table 8
Adsorption and dissociation of O₂ (eV) on Ni close to Sn and on Sn

| | (001) | (110) | (111) |
|-------------------|---|--|-------------------------------------|
| Adsorption in TOP | (On Ni) -14.01 (On Sn) ^a | On Ni -13.25 (On Sn) ^a | On Ni -11.4 On Sn ^a |
| O-Surface Ni-TOP | 1.3 | 1.3 | 1.3 |
| Dissociation | -18.7 , on two Ni and one Sn between -13.32 | -16.11 | -18.1 |
| O-Surface Ni-A | 1.3 | 1.3 | 1.3 |
| O-Surface Sn-A | 3 | 3 | 3 |

^a No minimum found-energy = -12.9 . Distances higher than 3 Å from surface.

(c) is on (1 1 1) plane. On this plane, the three steps are more favoured than on Ni. The model predicts the experimental fact: the (1 1 1) is the plane most easily deactivated by C formation.

Considering the steps of dehydrogenation.



EHMO calculations were done for the six planes of Ni and NiSn. Step 2 is favoured on NiSn(100) (−10.6 eV). Step 3 is important for NiSn(1 1 1) (−7.4 eV) and step 4 for Ni(00 1) (−4.4 eV).

Reaction of adsorbed CH₂ and O on surface to produce CO (step (g)) competes with the C formation (steps (c) and (d)). CO formation from CH₂ follows the order Ni (00 1)−15.8 eV > (1 1 0)−14 eV > (1 1 1)−4.1 eV. For coke formation the results for Ni are (00 1)−7.4 eV > (1 1 1)−4.5 eV > (1 1 1)−2.6 eV. The adsorption and first dissociation of methane are more difficult for (00 1) and (1 1 0) planes. These theoretical results are on line with the experimental fact that the (1 1 1) plane is catalytically the most important [20]. In this sense, the overall picture must be taken into account to relate these results with the experimental ones, being the particle size and therefore the preferred exposed planes the key point to understand activity. It has been published that on Ni/MgO the metal surface becomes resistant to coke formation, probably because the particles are small and finely dispersed [21] (see Table 10).

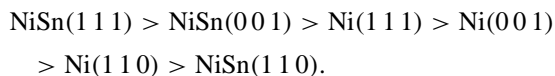
It is clear that the formation of CO it is favoured with respect to the deposition of C when Sn is added. Analysing the dissociation of CO to produce C-M for NiSn surfaces (Boudouard Reaction, reaction 6), we find that C remains on Sn and O goes to Ni.

Table 10
CO and C formation on Ni and on Sn in NiSn

| Plane | (00 1) | (1 1 0) | (1 1 1) |
|-----------------------------------|--------|---------|---------|
| CH ₂ → CO (Ni near Sn) | −4.8 | −4.9 | −3.04 |
| CH ₂ → C (Ni near Sn) | −4.6 | −1.9 | −3.9 |
| CO Sn−CO Ni | −8.6 | −15.3 | −6.3 |
| C Sn−C Ni | −6.8 | −11.0 | +0.1 |
| CH ₂ (Ni) → CO(Sn) | −13.4 | −20.2 | −9.3 |
| CH ₂ (Ni) → C(Sn) | −11.4 | −12.9 | −3.8 |

The calculation was done, taking into account the migration of the species at surface, when Sn is present.

The probability of C formation from CO shows the following order in planes.



The energies are in the range from −12.3 to −9.8 eV. The reaction similar or even more probable for NiSn(1 1 1) plane than in case of Ni(1 1 1). The reaction is disfavoured for NiSn (1 1 0) plane when it is compared to Ni(1 1 0). The CO desorption step is strongly unlikely for NiSn, comparing it with Ni. The desorption of CO leaving an O bonded to Ni implies a change in energy of 14.6/14.9 eV for Ni and 21.9/22.9 eV for Sn. Electronically, the desorption is not favoured. In this case the entropic factor can play a role. Because of this point, a Molecular Mechanic using MM2 techniques from Chem 3D 5.0 (Cambridge Soft) was used. The MM2 calculation results obtained using a cluster of near 20 Ni atoms or 19 Ni atoms and a Sn show that the entropic factor is very important when Ni and NiSn are compared. In this way, the difference for C formation involving Ni or Ni Sn is favouring C formation on Ni from CO decomposition by almost 6 kcal/mol, obtained from our calculations. Moreover, the MM2 results show different equilibrium distances for Ni−C from CO and Sn−CO. The distance is near 0.32 Å shorter when Ni is the adsorption site.

CO in formation at surface prefers to be located on Sn instead of on Ni, as for C. However, the biggest difference is for the (1 1 1) plane when Sn is present. Still in very low proportion, Sn clearly stabilises the formation of CO instead C. Migration of CO is possible, but not that of C [22], so there is no C formation on Sn. Neither CH₄ adsorption on Sn nor CH_x species migration towards Sn are possible (see Table 10).

6. Discussion

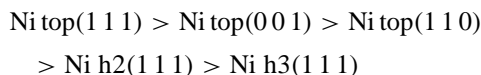
POM, R and MR reactions will be discussed, comparing Ni and NiSn catalysts models and considering the experimental results for Ni and NiSn catalysts (Sn/Ni < 0.06).

6.1. POM reaction (CH₄ + O₂)

Total dehydrogenation of methane is the classical proposed route for coke formation (steps a–d).

Methane adsorption is endothermic on Ni closer to Sn. In case of (1 1 0) plane the adsorption of methane is favored on Ni hollow 1. On this and the (1 1 1) planes, the adsorption energy of methane is near the same on Sn than on Ni near the Sn. When Sn is present, adsorption is preferred on Sn top only on (1 1 0) plane.

The feasibility of O₂ adsorption on the different surfaces follows the sequence.



The initial conversion in POM is near 85% for Ni catalyst at 700 °C and selectivity to CO₂ is near 20% [9]. CO formation from methane would take place in 4/5 Ni sites whereas carbon formation from methane takes place in 5 Ni sites (steps a–d). No changes arise in our case because we need one Sn in three to affect these reactions in a measurement level and we have 1 Sn in 24/25 in our model and near this at the low coverage of 0.06 Sn/Ni surface (between 1 and 2 in 25). We have than only 17% (one in six) of these ensembles of 3–4 surface atoms are affected in adsorption of methane or O₂ with Sn present at this level of Sn content. When the Sn/Ni surface molar ratio achieves 0.5 the activity decreases drastically to 6% in methane conversion. In this surface one Sn in three total atoms for reaction 1 implies 0.33 Sn/Ni at surface.

The results of Nichio et al. [9] show that coke formation is only 0.03% after 24 h on stream using Ni or NiSn. Only a minor fraction of dissociated methane form coke. Dissociated O in surface avoids this. No differences arise from NiSn at low coverage (0.06 Sn/Ni at surface) in coke formation. The H₂/CO ratio is the same, 2.5, after 1 h on stream for Ni and NiSn 0.06. A mixed one step–two step mechanism match exactly with this fact.

In summary, in POM, coke would be provided by methane decomposition, but the reactions stop at intermediate CH₂* production because of O presence and CO formation. The high affinity of Ni surface by O₂ explains this fact.

6.2. R reaction (CH₄ + CO₂)

We will analyse now the results for CO₂. When Sn is absent, dissociation of CO₂ to form CO is energetically more favoured than O₂ dissociation. The

C–Ni surface is close to 1.5 Å. In case of Ni–CO, back bonding could be important and CO can easily dissociate to produce C and two adsorbed O. In case of Sn, back bonding is not possible. Sn affects the nearest neighbours and the CO₂ is preferentially adsorbed and reacts on Sn. The reaction produces C and several Ni are affected. The presence of only 1 Sn in 20 that selectively adsorbs CO₂ is enough to avoid coke formation. Anyway, C is present, probably through CO dissociation and in minor amount from CH_x, when Sn is present. This fact is presented by Nichio et al., where almost no C formation is found for NiSn at so low coverages as 0.06, whereas for Ni is clear the C formation reaction measured by TPO/TGA (3.75% C after 24 h in stream at 700 °C). Proposed reaction producing C on Ni is step (d) whereas (j) is not considered to take place. These facts lead to higher amount of CO versus H₂. In this case, the experimental H₂/CO is 0.8. Dissociation of CO₂ explains the higher relative amount of CO for NiSn than for Ni. The H₂/CO must be higher when Sn is present and it is. In this line of reasoning step (e) seems to be more important in case of Ni than in case of NiSn. However, an additional deactivation reaction must be taken into account because the catalyst is further deactivated in R than in POM. In case of R we revised the original explanation of similar reactivity and active sites in Ni and NiSn. It seems that some kind of compensation effect is acting in case of R and therefore the ignition temperature is similar, but the active sites and mechanism could not be the same, especially because of the C formation results.

6.3. MR reaction (CH₄ + CO₂ + O₂)

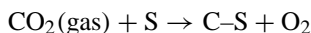
When Sn is present, reference [9] reports that lower amounts of C are produced after 24 h on stream at 700 °C in MR (0.05 versus 0.15% in case of Ni). When Sn is present reaction (2) takes higher importance.

Replacement of Ni by Sn follows the trend Ni(1 1 0) > Ni(1 1 1) > Ni(0 0 1). The (1 1 0) plane would be preferentially Sn substituted, whereas (1 1 1) and (0 0 1) would not. In the (1 1 0) plane, dissociation of CO to produce C is disfavoured by almost 1 eV. O₂ competes with methane in a stronger way than with CO₂. The ignition temperatures in case of Ni and NiSn for the R reaction are similar [9].

The energy for CO formation on Ni is half that when CO is placed on Sn, especially for (1 1 1) plane

(−4.1 versus −9.3 eV). This plane is supposed to be the one with higher concentration in particles of the size presented in reference [9].

Although at 700 °C, C formation is disfavoured from CO₂ decomposition versus CH₄ decomposition, the considered reaction is.



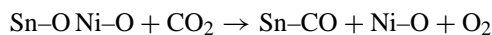
If the adsorption energy for O₂ is so strong, the reactions to be compared are the C formation from CO₂ decomposition (step e and lately CO dissociation) and from methane dissociation steps a–d. For MR, the C amount is 0.05%. We found that there is a barrier to surpass to achieve decomposition of CO on Ni of almost 140 kJ mol^{−1}, the change of orientation of CO at surface (from perpendicular to parallel).

The desorption of O₂ from dissociatively adsorbed O at surface is energetically disfavoured by almost +5.5 eV for the three planes of Ni. The reaction considered was.



CO₂ adsorption does not produce the O₂ desorption on Ni, but it does on NiSn (1Sn/24–25 total). The

reaction on this model would be.



The energies for this reaction on the planes are near −20 eV for (1 1 1) plane and −12.9 eV for (0 0 1). In case of NiSn(1 1 0) plane, this reaction has an energy of +8.22 eV.

7. Conclusions

1. In line with published experimental and theoretical data, EHMO predicts that methane adsorption is the least energetically favoured step of the reaction. Methane dissociation (but not adsorption) is favoured when Sn is present and Sn–H is produced.
2. The adsorption of O₂ on Ni is the strongest of all the adsorbates considered. Adsorption and therefore dissociation of O₂ is severely hindered on Sn. Sn changes the adsorption properties of Ni close to it. The Sn in top in the (1 1 1) plane is especially poor for O₂ adsorption in comparison to Ni. On these planes, the O₂ dissociation produces O–Ni

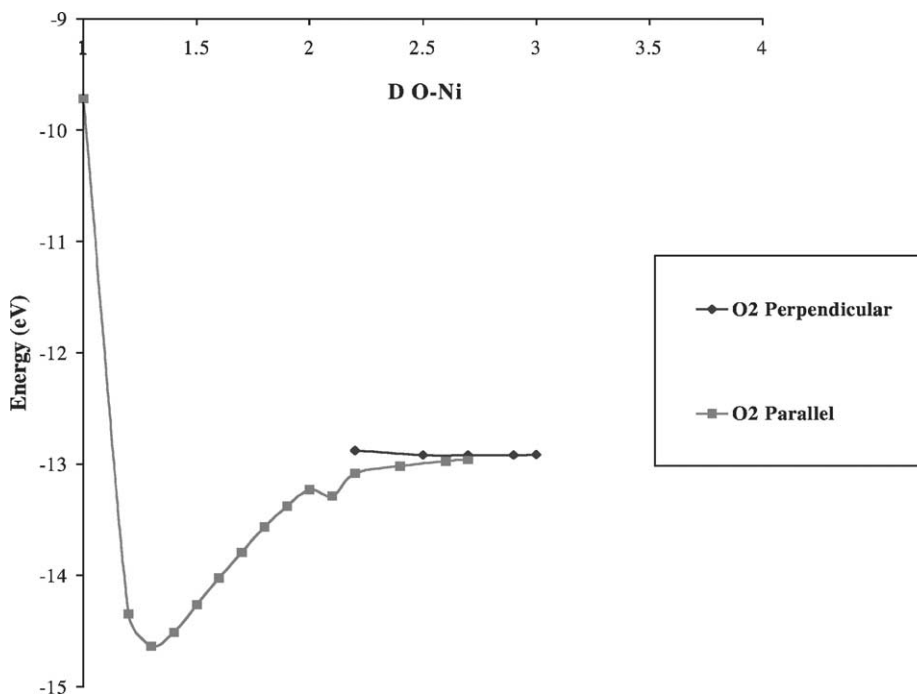
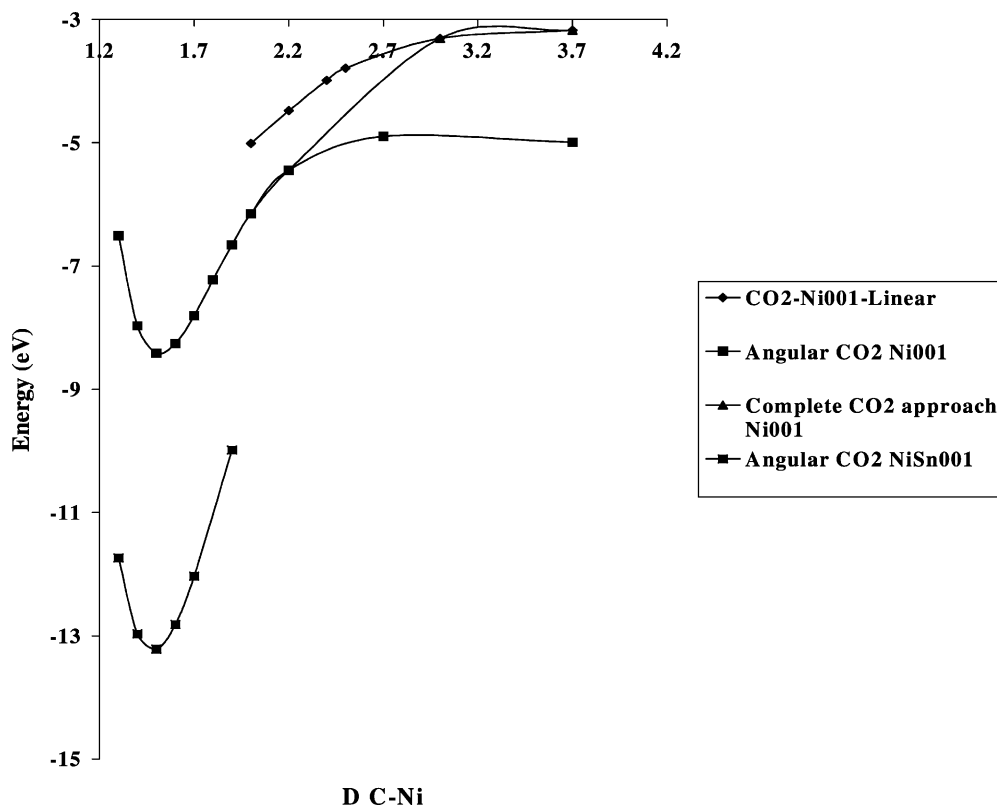


Fig. 9. Adsorption energy of parallel and perpendicular O₂ on Ni(001).

Fig. 10. Adsorption of CO₂ on Ni(001) and NiSn(001).

species separated by a Sn atom. The strong O adsorption prevents reactions of C formation to take place and H-surface species avoids Ni oxidation.

3. CO formation on Sn is the preferred reaction from CO₂ decomposition, especially for NiSn(1 1 0) and NiSn(1 1 1) planes.

4. All the reactions producing C-* from CO₂ seems to be of minor importance when Sn is present at these ratios Sn/Ni. The O concentration at surface from CO₂ dissociation when Sn is present could be enough high to avoid C formation. Lower importance of steps (c) and (d) of CH₃ dissociation

Appendix A

Carbon formation reactions from CH₄ (Figs. 9–11)

| | Plane | | | | | |
|--------|---------|-----------|---------|-----------|---------|-----------|
| | Ni(001) | SnNi(001) | Ni(110) | SnNi(110) | Ni(111) | SnNi(111) |
| Step 2 | -3.5 | -10.6 | -3.3 | -3.2 | -2.28 | -2.65 |
| Step 3 | -3.04 | -2.7 | -1.1 | -0.65 | -2.18 | -7.4 |
| Step 4 | -4.4 | -2.8 | -1.47 | -1.06 | -3.35 | -3.66 |

Step 2: CH₃* + * → CH₂* + H-*; Step 3: CH₂* + * → CH* + H-*; Step 4: CH* + * → C* + H*.

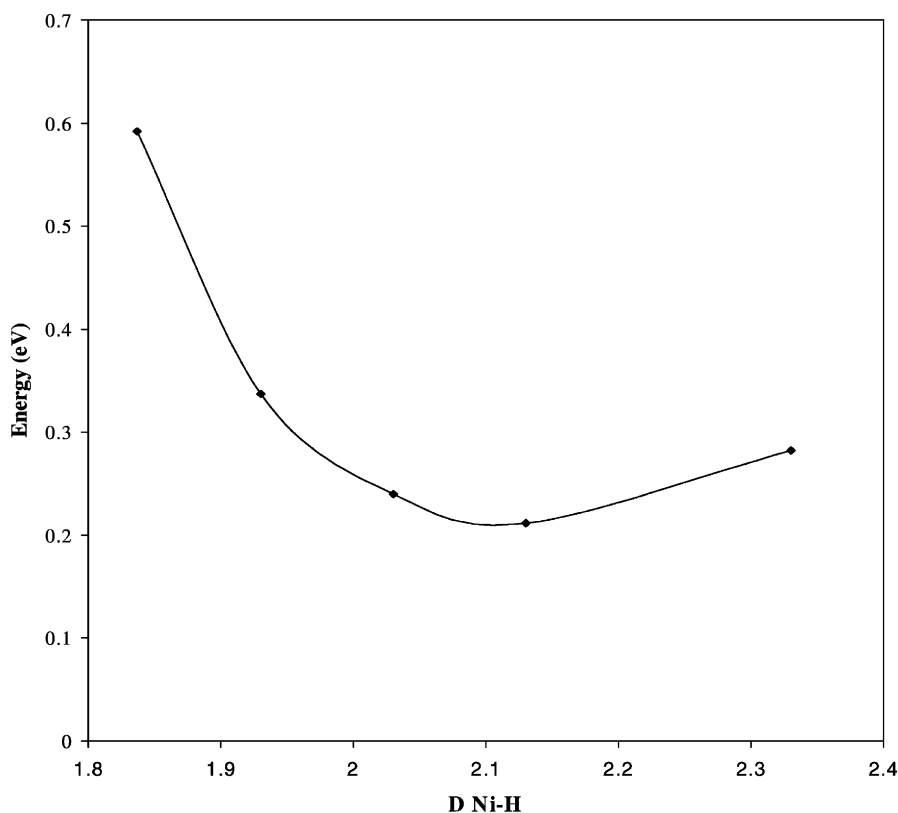


Fig. 11. Adsorption of methane on Ni close to Sn in (001) plane.

when Sn is present can explain experimental data (especially considering NiSn(1 1 0)).

5. Although C formation would be favoured by enthalpic changes, the entropic terms are in order to be non-spontaneous in case of Ni with Sn. The short Ni–CO distance is in line with further reaction to produce C when no Sn is added.

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