

A DF-vdW Study of the CH₄ Adsorption on Different Ni Surfaces

Silvia González¹, Francesc Viñes², Juan Fernando García¹, Yody Erazo¹, Francesc Illas²

1) *Departamento de Química, Universidad Técnica Particular de Loja, San Cayetano Alto, Loja, Ecuador. Ap. P. 1101608, GETNano, Grupo Ecuatoriano de Estudios Experimentales y Teóricos de Nanosistemas.*

2) *Departament de Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/Martí i Franquès 1, 08028 Barcelona, Spain.*

Abstract

A systematic density functional (DF) theory based study of methane (CH₄) adsorption on the three lowest-index Miller Ni surfaces plus two stepped Ni surfaces is presented. A standard GGA type functional (PBE) has been used to compute the total energy and the van der Waals (vdW) contribution included to properly describe the weak molecular interaction of CH₄ with the Ni metal surfaces. The surfaces are represented by a periodic supercell approach and several sites and molecular orientations have been explored with one, two and three H atoms pointing towards the surface. Although all adsorption energy values are small, taking into account dispersion terms allows one to distinguish the effect of the surface structure on methane adsorption.

Introduction

Since some years ago the use of hydrogen as fuel have been suggested as a good alternative as energy source because its oxidation releases a high amount of energy and the gas emissions are inoffensive [1]. However, its synthesis is required [2,3] because there are not natural sources. Methane as hydrogen source is an excellent alternative because is present in natural deposits and it can be obtained as a product of degradation of biomass. Almost all processes for obtaining hydrogen from methane require a C-H bond cleavage. This bond is highly stable (432 kJ mol^{-1}) in the gas phase [4], and, hence, a catalyst is required to dissociate it. Thus, the catalytic methane dissociation on transition metals has become a quite interesting topic and, even more, its adsorption, since it is the mandatory previous step to the molecular breaking, which oftentimes bias the posterior steps. Hence it has been studied using diverse experimental techniques [5-13] and theoretical methods [14-28].

Among the different transition metals, Ni is the most typical catalyst for methane decomposition [5,29]. Hence it is not surprising to find that Ni has been extensively theoretically studied for methane dissociation catalysis. For instance, Density Functional (*DF*) methods employing different exchange-correlation functionals, in particular those within the Generalized Gradient Approximation (*GGA*), have been used to describe the methane adsorption on metallic surfaces [30,31]. However, this interaction is known to be weak and dominated by dispersion terms and, consequently, the GGA calculations do not reproduce this trend. In fact, using the revised version of the Perdew-Burke-Ernzerhof (*rPBE*) functional a value of 5 kJ mol^{-1} was predicted for the adsorption energy of CH_4 on Ni(111) [30]. A stronger adsorption (36 kJ mol^{-1}) was found on a defective surface involving a Ni adatom [17]. Nevertheless the weak interaction of CH_4 with metallic surfaces using GGA functionals hinders a more detailed analysis of different molecular configurations or site structures and the differentiation among diverse types of surfaces becomes difficult.

To contribute to the better understanding of the interaction of CH_4 with different types of Ni surfaces, here we report a systematic theoretical study of the adsorption of this molecule on a variety of well-defined surfaces models and using a GGA-based functional which includes a description of the van der Waals (*vdW*) forces. We will show that this type of approach describes very well the weak interaction between methane and Ni, with results close to the experimental ones. Moreover, to analyze the effect of coordinatively

unsaturated sites, we considered the interaction of CH₄ with the lowest-index Miller Ni surfaces (111), (110), and (100) and the two stepped surfaces, the (533) and the (577).

Surface Models and Computational Details

Methane adsorption on pristine (111), (110), and (100) Ni surfaces, and on stepped Ni(533) and Ni(577) surfaces has been studied using density functional calculations either neglecting or including dispersion terms (see below) carried out on periodic slab models and making use of the VASP code [32,33]. In order to decouple the effect of dispersion on the interaction of methane with the Ni surfaces and on the Ni substrate itself, the slab models were constructed using the PBE [34] optimized lattice parameter of 3.848 Å for Ni in good agreement to the experimental value of 3.80 Å [35] indicating that the contribution of dispersion to the intermetallic bonding, already overestimated by the PBE functional by ~10% [36], is not dominant. This is not surprising since PBE has been shown recently to provide a balanced description of the 30 transition metal elements [36].

Slab models consisting of at least three metallic layers have been constructed. A vacuum region with a width larger than five metallic layers (12 Å) has been placed in the normal direction to the surface to avoid interaction between the repeated slabs. A (2×2) supercell has been used for Ni(100), a (3×2) was used for Ni(110), a (3×3) for Ni(111), a (3×1) for Ni(533) and finally, a (2×1) supercell was used for Ni(577) surface (Figure 1). In all cases the structures include eight to nine surface metal atoms leading to a similar coverage in all the studied surfaces. Note that stepped models result from the combination of lowest-index Miller surfaces: the Ni(533) surface is a combination of (111) terraces with steps with an arrangement of a (100) plane and, in the Ni(577) case, the (111) terraces combine with (110) steps.

The interaction of methane on the different surface models has been studied by placing the corresponding species just on one side of the slab, the first metallic layer of the slab was relaxed in response to the presence of the CH₄ molecule and the rest, two atomic layers were fixed at their atomic positions. All calculations included a dipole correction as implemented in VASP. Three different CH₄ orientations were considered with one, two, or three H atoms pointing towards to the metallic surface.

The exploration of the preferred adsorption sites has been carried out by means of total energy DF theory based calculations and subsequent geometry optimization employing the optPBE functional approach due to Klimeš *et al.* [37-39]. In this method a

modified exchange implementation of the vdW-DF is used whereas other proposals exist as described in a recent review [40]. However, the performance of the different functionals including dispersion terms is still to be fully assessed and a considerable amount of work has been devoted to the interaction of benzene with metal surfaces which is taken as a benchmark system [41]. Interestingly, optPBE provides a good agreement between average experimental adsorption energy and calculated values for benzene on various metallic surfaces [42,43] even if the experimental measures need also to be taken into account with caution. It is also rewarding to see that for this reference system, results predicted by optPBE agree with the, in principle, more sophisticated but not yet broadly used, DFT-VDw^{surf} method [41,44] and with more accurate calculations such as those obtained from the random phase approximation [41] which, in turn, are in agreement with calorimetric measurements [41]. Moreover, optPBE has been extensively used to study the interaction of water with metallic surfaces providing quite satisfactory results [45]. Therefore, it is expected that, even if a direct comparison to experiment is not possible here which makes it difficult to estimate error bars in the calculated properties, the general trends will be correctly described which is the main goal of the present study.

The Kresse and Joubert [46] implementation of the Projector Augmented Wave (*PAW*) method [47] was used to reproduce the effect of the atomic cores on the atomic electronic density of valence electrons. The Kohn-Sham [48] one-electron wavefunctions were expanded in a basis set of plane waves with kinetic energy up to 415 eV. The geometry optimization of all minima was carried out using a conjugate gradient algorithm. A 3×3×1 Monkhorst-Pack **k**-points grid was used to sample the Brillouin zone of the surface unit cell [49]. All employed parameters were tested using tighter values, yet changes were not significant. Due to the magnetic nature of Ni the polarized spin formalism has always been used except obviously for the gas phase CH₄ molecule. Harmonic vibrational frequencies have been obtained from the Hessian matrix constructed by finite differences of each molecule nucleus displaced in the three spatial coordinates by 0.01 Å and used to properly characterize the final optimized structures as true minima in the potential energy surface. For these structures, the adsorption energy was calculated the following equation;

$$E_{ads} = E_{sur} + E_{CH_4} - E_{CH_4/sur} \quad (1)$$

where E_{ads} is the adsorption energy, $E_{CH_4/sur}$ is the energy of the methane molecule interacting with the metallic surface, E_{sur} is the corresponding energy of the bare surface,

and E_{CH_4} is the energy of the isolated molecule. Note that, within this definition, the more positive the adsorption energy, the stronger the bond to the surface. The adsorption energy was subsequently corrected for the Zero Point Energy (*ZPE*) and the resulting values are denoted as E_{ZPE} .

In order to provide results comparable to the experiments, the desorption temperature was calculated using the Redhead method, based on the Arrhenius equation:

$$r_{des} = Ae^{-\frac{E_{ZPE}}{RT}} \quad (2)$$

where, r_{des} is the desorption rate constant, A is the preexponential factor, T is the desorption temperature, R the gas constant and E_{ZPE} is the desorption energy of methane corrected by *ZPE*. The rate constant and the pre-exponential factor are considered constants with standard values of $1 \cdot 10^6$ and $1 \cdot 10^{10}$, respectively. Note, however, that the reported desorption temperatures should be taken as a gross estimation.

The CH_4 adsorption on the different metallic surfaces was studied assuming that the incoming molecule adsorbs at a given site of the surface, either top, bridge, three- or four-fold sites on low-index surfaces, and additionally at steps, terraces, or edge sites of stepped surfaces. All possible sites on each surface were explored depending of the atomic arrangement of the surfaces.

Results and Discussion

Before discussing the results of the CH_4 adsorption, let us briefly analyze the isolated molecule case: The calculated bond distance of C-H is 1.095 Å, in excellent agreement with the measured value of 1.086 Å [50]. Regarding the vibrational frequencies, four normal modes (ν_1 , ν_2 , ν_3 , and ν_4) with A_1 , E , F_2 , and F_2 symmetry, respectively. The PBE calculated frequencies are located at 2966, 1529, 3063, and 1311 cm^{-1} , respectively which, within a deviation less than 100 cm^{-1} , agree with the experimental values with values of 3025.5, 1582.7, 3156.8, and 1367.4 cm^{-1} [51]. The small differences arise, on one hand, from the neglect of anharmonic component on the vibrations, and, on the other hand, due to the intrinsic accuracy of the employed method.

Let us focus now on the adsorption of CH_4 on the Ni surfaces. In all the encompassed adsorption sites, the geometry of the adsorbed molecule is very similar to that of methane in vacuum, the C-H bond distance is around 1.100 Å, except in few cases that is almost 1.110 Å, in particular in Ni(110) surface and the stepped surfaces. These

slight elongations could be related to an activation of C-H bonds and an eventual breaking. However such a small elongation must be treated with caution, and it is not unexpected since it is fully consistent with the weak character of the interaction.

For the most stable, less active Ni(111) and more studied surface [6,17], initial and final adsorption sites, calculated adsorption energy values, vibrational frequencies, and geometric parameters are summarized in Table 1, while a sketch of the most stable adsorption site is presented in Figure 2. From the values encompassed on Table 1 one clear point is that the inclusion of vdW description strengthens the bond to the Ni(111) surface, especially when comparing present estimations to previous GGA calculations. However, the resulting interaction is still in the 5-8 kJ mol⁻¹ range even if the vdW contribution to the adsorption is almost 50%. On the other hand, the quite low adsorption energy and the multitude of available surface conformations results in an extremely high mobility of methane adsorbed on the Ni(111) surface although this will only be the case at quite low temperatures (Table 1). In fact, methane is unlikely to be adsorbed on Ni(111), unless cryogenic temperatures are applied, in concordance with the extremely low sticking coefficient measured for this system [51].

The situation is sensibly different for the more open Ni(110) and Ni(100) surfaces, whose results are found in Tables 2 and 3, respectively, and the most stable conformations are depicted in Figure 2. On both surfaces the adsorption energy is 2-3 times increased with respect to that obtained for the densely-packed Ni(111) surface, with adsorption values ranging 15-19 kJ mol⁻¹. Similarly to the Ni(111) there is a wide bunch of possible and accessible adsorption conformations, and despite the increase on the bonding strength, it is still considered a physisorption, and when attached, methane would likely to easily diffuse over these two surfaces. In any case the present results agree with a higher methane reactivity of Ni(110) and Ni(100) compared to Ni(111), as found in single crystal surface science experiments [52].

The defective surfaces are presumably more active and in the case of the Ni(533) surface this statement is partially true (Table 4). The adsorption energy values are larger than on the Ni(111), but similar to those of Ni(100) which is not surprising since the Ni(533) surface has steps with an atomic arrangement similar to those Ni atoms in the Ni(100) surface. Therefore, the calculated adsorption energy values for these two surfaces are similar although the value for Ni(533) is slightly increased by ~2 kJ mol⁻¹, a finding easily explained in terms of the lower coordination of the Ni atoms at the steps, and also by

the fact that the strongest adsorption situation on this stepped surface corresponds to an step edge line (Figure 2). However, as in the cases discussed above, there is still a high variety of easily reachable conformations. Here it is important to point out that results in Tables 1 to 5 include the initial and final configuration from the geometry optimizations. In some cases more than one initial starting point converge to the same final structure but, because of the convergence thresholds, the final structures may display some very small numerical differences. These could have been removed but keeping them allows one to have an idea of the numerical accuracy and, at the same time, provides information about the final state for each initial configuration.

In the particular case of the Ni(577) surface, the situation is similar to that of the above-explained cases. Here the adsorption energies are comparable to those of the Ni(100) and Ni(533) surfaces with similar estimated desorption temperatures so that the adsorption can be still considered physisorption. As discussed for Ni(533), the preferred adsorption sites are located at the step edge line, with many possible accessible conformations, Figure 2 displays a sketch of the most stable one. The enhanced activity seems to join the stability of (111) terraces with the higher-activity of low-coordinated atoms at the (110) steps. One can perhaps argue that this is related to the higher activity of Ni nanoparticles, containing a significant number of low-coordinated sites.

The analysis of the vibrational frequencies reported in Tables 1 to 5 for the adsorbed molecule on Ni(111), Ni(110), Ni(100), and Ni(533) shows little differences; the calculated vibrational frequencies for the adsorbed molecules are all very similar to those of the free molecule. Hence, the ν_4 vibration results essentially unaffected whereas ν_2 and ν_3 normal modes feature 5-10 cm^{-1} red shifts. The exception is the ν_1 frequency, because the interaction with the surface affects the molecule vibration by red shifting it by $\sim 35 \text{ cm}^{-1}$ which is in nice agreement with the experiments of Maroni *et al.* [53] using molecular beam and Raman techniques and with the calculations of Prasana *et al.* [54] and Halonen *et al.* [55], who pointed out the importance of this vibration as the CH_4 molecule approaches the surface. A particular case is the interaction of the molecule with Ni(110) at the top site and the CH_4 oriented with one H atom pointing towards the surface which results in noticeable elongation of the C-H bond distance, $\sim 1.11 \text{ \AA}$, and the ν_1 mode is shifted by more than 100 cm^{-1} with respect to free molecule, suggesting the proclivity of this state for eventually contributing to breaking the C-H bond. Interestingly, the Ni(577) surface displays a completely different behavior which is not unexpected in the view of the

larger interaction with methane. Here, the ν_1 mode is reduced by $\sim 30 \text{ cm}^{-1}$, but the other vibrations are blue shifted, the ν_2 mode by $\sim 30 \text{ cm}^{-1}$ and ν_3 and ν_4 by 60 cm^{-1} .

Conclusions

The interaction methane with several Ni surfaces has been studied by periodic density functional calculations explicitly including dispersion terms. The interaction is always weak and can be safely classified as physisorption. Nevertheless, including dispersion terms have important qualitative consequence since it permits to distinguish the different surfaces. Hence, the interaction of methane with these surfaces decrease in the order $\text{Ni}(577) > \text{Ni}(533) \sim \text{Ni}(110) \sim \text{Ni}(100) > \text{Ni}(111)$. The calculated vibrational frequencies are very similar to those of the gas phase molecule but with some noticeable shifts which can measured.

Acknowledgements This work was supported by the Spanish MICINN grant CTQ2012-30751, the *Universidad Técnica Particular de Loja* (Ecuador) and, in part, by the *Generalitat de Catalunya* (grants 2009SGR1041 and XRQTC). F.V. thanks the MINECO for a postdoctoral *Juan de la Cierva* grant (JCI-2010-06372), and F.I acknowledges additional funding through the 2009 ICREA Academia award for excellent in university research.

Figure 1. Top and side views of the employed Ni surfaces, where blue balls point to the location of the Ni atoms of the upmost layer and the gray balls denote the metallic atoms of the second layer of each surface.

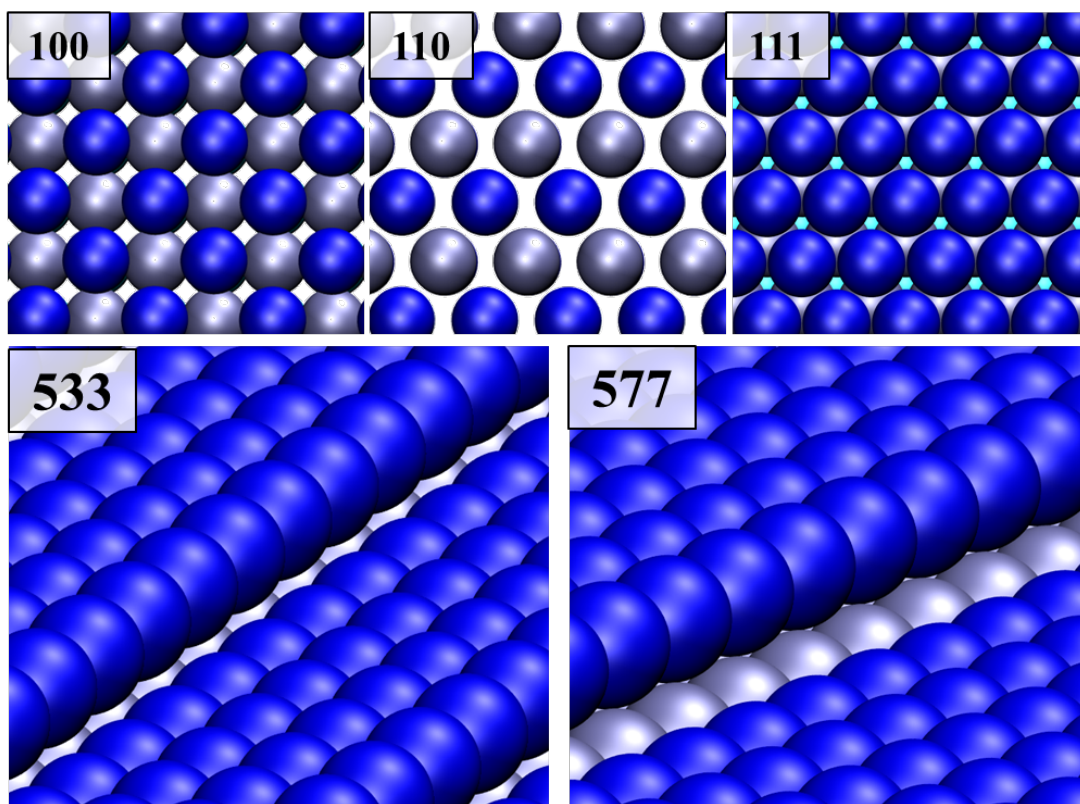


Figure 2. Molecular orientations and adsorption sites of methane on the different Ni surfaces.

