6

Summary and concluding remarks

6.1 Summary

In this thesis we performed a systematic study of the adsorption of unsaturated hydrocarbons on metal surfaces. We used DFT-based methods and periodic models. The characterisation of the surface structures, adsorption modes and nature of the adsorbate-surface interaction along with the calculation of the relative stabilities, reaction energies and reaction barriers are key steps to understand surface phenomena. We want also to emphasize that the simulation of vibrational spectra can also play a decisive role in heterogeneous catalysis. Our work was aimed at complementing experimental observations and providing additional data, so that complex surface processes could be unravelled.

We focused our attention on three systems: propyne adsorbed on copper, platinum, palladium and rhodium (**Chapter 3**); the dehydrogenation reaction of propylene to propylidyne on platinum (**Chapter 4**) and the selective hydrogenation of 1,3-butadiene to butane on platinum and palladium (**Chapter 5**).

The objectives and the main conclusions of this work are:

In **Chapter 3**, we present a systematic study of the adsorption of propyne on several metal surfaces: Cu(111), Pt(111), Pd(111) and Rh(111). First of all, we determined the most favourable adsorption sites and their relative stabilities. The agreement between our results and the experimental data available is fairly good. We found that propyne adsorbs on Cu(111) with its molecular plane perpendicular to the metal surface and bisecting a Cu–Cu bond (di-σ/di-π adsorption mode). On the other hand, on Pt(111), Pd(111) and Rh(111), it prefers to sit on a 3-fold hollow site, with the molecular plane tilted away from the surface normal and the C≡C axis parallel to a metal-metal bond (di-σ/π). The decomposition of the adsorption energy in its main contributions helped us to rationalise the variation in adsorption energy observed for Cu (–98 kJmol^{-1}), Pd (–161 kJmol^{-1}), Pt (–197 kJmol^{-1}) and Rh (–226 kJmol^{-1}). On the Pt and Rh surfaces, the strong activation of the molecule and the high surface-adsorbate interaction cause propyne to be susceptible of decomposition. These results are well in line with the experimental evidence.

The analysis of the projected density of states (PDOS) enabled us to understand the unique adsorption behaviour of propyne on Cu(111). We found that the differences arise from the unique adsorbate-surface interaction. On this surface, the interaction takes place mainly through the sp-metal band whereas on Pt, Pd and Rh the interaction takes place via the d-band.

Besides, our calculations allowed us to corroborate and complete the experimental band assignment and confirm the adsorption site preference for propyne on Cu(111) and Rh(111). E.M. McCash and co-workers have assigned the band at 1361 cm^{-1} in the spectrum of propyne on Cu(111) to the C≡C stretching mode. This assignment has given rise to a controversy because it violates the metal surface selection rules (MSSR). Our calculations support and complete this assignment. We proposed that this mode strongly mixes with the CH_3 symmetric deformation. This coupling enhances the dynamic dipole moment perpendicular to the surface (in the z direction) and makes this mode active. However, on methyl deuteration this coupling disappears but the C≡C stretch is still intense. Our calculations demonstrated that this is due to the special nature of the propyne-Cu interaction.

For the system propyne/Rh(111), we concluded that the Rh surface is mainly covered with species adsorbed in a di-σ/π fashion. The simulated HREELS spectrum matches very well with the experimental one performed by G. A. Somorjai and co-workers. Frequencies and band intensities are well reproduced except for the feature at ~1100 cm^{-1}. This feature is clearly weaker in the simulated spectrum than on the experimental one. The presence on the surface of a small fraction of di-σ/di-π adsorbed species explains this difference.

The good agreement between the theoretical and experimental frequencies and intensities enabled us to predict the RAIRS spectrum of propyne on Pt(111) and Pd(111). To our knowledge, these spectra are not available in the literature.

In **Chapter 4**, we investigated the intermediates of the dehydrogenation of propylene to propylidyne on Pt(111). First of all, we studied the adsorption of propylene on Pt(111). For this molecule, we found two stable adsorption structures: bridge (di-σ) and top (π). The adsorption on bridge (–87 $kJmol^{-1}$) is more stable than the adsorption on top (–51 $kJmol^{-1}$). After determining and characterising the adsorption structure of this molecule, we investigated the possible reaction intermediates. Our study allowed us to obtain the adsorption site, geometry and relative stabilities of propylidyne and several C_3H_x (x=3–7) intermediates that may potentially be involved in the propylene-to-propylidyne transformation (1-propyl, 2-propyl, propylidene, 1-propenyl, 2-propenyl, propyne, propenylidene and propynyl). Our calculations showed that the Pt(111) surface tends to stabilise sp^3 bound intermediates. They also indicate that the dehydrogenation of propylene to propylidyne is favoured because the propylidyne moiety is the most stable surface species. Moreover, we computed the reaction energy for the possible elementary steps involved in the dehydrogenation reaction. Our calculations indicate that the propynyl intermediate formation is not energetically favoured and, therefore, this species may not be involved in the direct transformation of propylene to propylidyne.

Besides, we simulated the vibrational spectra for propylene, propylidyne and all the C_3H_x (x=3–7) intermediates. The results for propylene and propylidyne are in reasonable agreement with the experimental data. Unfortunately, the information available for the possible reaction intermediates is scarce. F. Zaera and co-workers have studied the changes in the IR spectrum of propylene on Pt(111) between ~230–300 K. They observed that the spectrum at ~260 K presents a signal at 2890 cm^{-1} that cannot be assigned to propylene either to propylidyne and, therefore, it belongs to a new species. Moreover, in the 1100–1500 cm^{-1} region all the features correspond to propylene or to propylidyne. Our best guesses are propylidene and 1-propenyl.

We also studied the surface structure and stability of a propylene-sulphate complex on Pt(111). We showed that the formation of this intermediate is energetically favoured and provided a theoretical support to the experimental observations. We proposed the surface structure for this alkyl-sulphate complex and demonstrated that the interaction of propylene with sulphate species activates the hydrocarbon molecule up to a large extent. Moreover, we showed that the simulated IR spectrum of the adsorbed alkyl-sulphate can be very useful to the identification of this surface species. The peaks at 1078 and 1047 cm^{-1} and the splitting of the SO_4 group frequencies of the sulphate unit are the fingerprint of this intermediate.

We studied the selective hydrogenation of 1,3-butadiene to butenes on Pt(111) and Pd(111) in **Chapter 5**. First of all, we studied the adsorption of 1,3-butadiene and butenes on Pt(111) and Pd(111). Despite the different electronic behaviour of Pt and Pd surfaces, the same adsorption modes with close adsorption energies have been found for 1,3-butadiene and butenes on both metal surfaces. For the 1,3-butadiene molecule the preferred adsorption structure has been characterised as a tetra-σ mode with the four C atoms bounded to four neighbour Pt atoms. In this surface structure the carbon chain remains almost parallel to the surface. The most stable adsorption mode for the butenes is the di-σ-mode. In the optimised geometry the C=C bond lies parallel to the metal surface and the alkyl groups point outwards the surface. Nevertheless on Pd(111) the molecules are less distorted than on the Pt surface. Moreover, the π adsorption modes are less destabilised with respect to the σ ones on Pd(111). In consequence, the energy difference between the di-σ and π modes is clearly smaller on palladium. We showed that the different selectivity observed on Pt(111) and Pd(111) for this reaction cannot be satisfactory explained by the single comparison of the relative stabilities of 1,3-butadiene and 1-butene on these metals. Our calculations suggested that the different selectivity observed arises from the reaction intermediates. We analysed the possible reaction pathways and computed the activation barriers. The pathway leading to the butan-1,3-diyl radical is competitive with those leading to butene on Pt(111). Indeed, the difference in energy activation is only 5 $kJmol^{-1}$. The formed butene desorbs as long as butadiene is present on the surface. The di-radical intermediate can be further hydrogenated, leading to the formation of butane as a primary product. This is in good agreement with the partial selectivity (60 %) to butene observed in experiments. On Pd(111), the butan-1,3-dyil radical is also stabilised but this effect is clearly smaller than on Pt. The difference in activation energy leading to 1-butene and butan-1,3-dyil is large enough (~30 $kJmol^{-1}$) to exclude the formation of this intermediate. Hence, our calculations predict a full selectivity to butene on Pd(111) in agreement with experiments.

6.2 General conclusions

The chemistry of unsaturated hydrocarbons at metal surfaces assumes a daunting complexity because of the huge number of possible surface structures. The great variety of species arises from the availability of large ensembles of atoms. Periodic DFT calculations proved once more to be an excellent partner of experiment. These methods permitted us to calculate adsorbate energetics, structure and spectra. Moreover, they provided detailed information on the elementary reaction steps, in terms of thermochemistry, reaction pathways and activation barriers.

The main conclusions about the studied systems can be divided in five groups:

- Chemisorption energy of molecules and molecular fragments

Calculations permitted us to obtain the adsorption energies on different adsorption sites for different unsaturated hydrocarbons adsorbed on metals. The decomposition of the adsorption energy in its main contributions (the distortion energy of the surface, the distortion energy of the molecule and the interaction energy) enabled us to rationalise the results obtained.

We also computed the relative stabilities for possible reaction intermediates. To obtain the adsorption energies for reaction intermediates is a key step in the study of the possible reaction pathways.

- Structure of adsorbates

We obtained the geometries and preferred adsorption site for propyne, propylene, 1,3-butadiene and butanes on several metal surfaces. Our results are in good agreement with the experimental data available. Therefore, we conclude that we can use calculations to predict the unknown structures.

Moreover, calculations demonstrated once again to be very useful to characterise weakly adsorbed structures and short-lived reaction intermediates. These species are extremely difficult to isolate and characterise by experiments because it is necessary to work in very restrictive conditions (usually UHV and very low temperatures).

- Nature of the adsorbate-surface interaction

Calculation of the projected density of states (PDOS) allowed us to rationalise the chemisorption energies and corroborate the conclusions obtained from the decomposition of the adsorption energy.

- Computed spectra and assignment of vibrational bands

The simulation of vibrational spectra of adsorbed molecules enabled us to corroborate and complete dubious band assignment and study the effects of the coupling between modes in the spectrum.

Moreover, simulation of vibrational spectra also demonstrated to be useful to determine the adsorption site preference.

The good agreement between the theoretical frequencies and intensities and experimental data available enabled us to predict the vibrational spectra for some molecules.

Frequency calculations also demonstrated to be useful to facilitate the identification of reaction intermediates. The computed values can be used as fingerprint of these short-lived molecules.

- Selectivity control

We confirmed that DFT calculations are a powerful tool to give some insights in the factors that control selectivity. The detailed investigation of all the possible reaction pathways and the calculation of the reaction barriers can play a crucial role in understanding the surface processes.