



Structure and stability of acrolein and allyl alcohol networks on Ag(111) from density functional theory based calculations with dispersion corrections

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ABSTRACT

The interaction of acrolein and allyl alcohol with the Ag(111) surface has been studied by means of periodic density functional theory based calculations including explicitly dispersion terms. Different coverage values have been explored going from isolated adsorbed molecules to isolated dimers, interacting dimers or ordered overlayers. The inclusion of the dispersion terms largely affects the calculated values of the adsorption energy and also the distance between adsorbed molecule and the metallic surface but much less the adsorbate–adsorbate interactions. Owing to the large dipole moment of acrolein, the present calculations predict that at high coverage this molecule forms a stable extensive two-dimensional network on the surface, caused by the alignment of the adsorbate dipoles. For the case of allyl alcohol, dimers and complex networks exhibit similar stability.

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1. Introduction

Competitive adsorbate–adsorbate and adsorbate–substrate interactions at surfaces are responsible for the formation of different superstructure patterns, from highly ordered self-assembled structures to complex disordered ones. The adopted molecular geometry and the activation of chemical bonds present in these surface arrays are critical aspects which are in direct relation with possible applications in nanotechnology as well as with the catalytic activity and selectivity of the resulting systems. Precisely, a relationship between coverage, molecular orientation and selectivity was recently proposed for the hydrogenation of acrolein (propenal). This simple aldehyde is often chosen as a prototype for the study of the chemoselective hydrogenation of α,β -unsaturated aldehydes to the corresponding unsaturated alcohols, widely used as pharmaceutical precursors and in the fragrance industry [1,2]. Suitable catalysts must be used for this reaction because thermodynamics favors the hydrogenation of the C=C bond. Experiments using high resolution synchrotron X-Ray Photoelectron Spectroscopy (XPS), Near Edge X-Ray Absorption Fine Structure (NEXAFS) and Temperature Programmed Desorption (TPD) have shown that the structure of acrolein adsorbed on Ag(111) strongly depends on the coverage and that at high coverage the structure has the C=C bond markedly tilted away from the surface [3]. From this experimental study, the structure proposed for the adsorbed acrolein at high coverage has the C=O

bond almost parallel (2°) to the surface but the C=C bond is tilted by 12° . This change of orientation with coverage is claimed to be responsible for the observed chemoselectivity. On the other hand, the same authors pointed out that, on the same surface, the desired product, the allyl alcohol, has a C=C angle tilted about 30° when it is coadsorbed with hydrogen at low coverage (at 0.3 ML of hydrogen) and changes to only 3° at high hydrogen coverage, bringing the C=C bond nearly parallel to the surface. Thus, the preference for the production of allyl alcohol from adsorbed acrolein, which is observed to be more favored at low H coverage, has to be attributed to the geometric orientation of the C=C bond of the reactant which hinders, at least partially, the attack by H.

Very recently, Wei et al. have investigated the hydrogenation of acrolein on silica-supported silver catalysts with various particle sizes (1–9 nm) [4]. They found that the selectivity to allyl alcohol and turnover frequency increased with increasing particle size. As the authors have pointed out, the results appear as somewhat unusual because the most active catalyst is also the most selective. Increasing the total pressure from 1 to 5 atm was also found to increase the selectivity and decrease the activation energy. These results also suggest that, on flat surfaces, a tilted orientation of acrolein, preferably at high coverage, is desirable for high selectivity and high activity.

In a previous work we have investigated the structure of acrolein adsorbed on Ag(111) using density functional theory (DFT) based calculation with the PW91 form of the Generalized Gradient Approach exchange–correlation potential [5]. Our calculations evidenced that, at low coverage, the preferred structure for adsorbed acrolein is parallel to the surface, in agreement with experiments. However, at higher

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coverage, we found that different complex networks are possible with different orientations with respect to the surface, which contrast with the above-mentioned NEXAFS results. Due to the fact that these experiments provide only average structural parameters, we concluded that the different calculated structures should be considered as input data to interpret NEXAFS experiments with similar coverage situations. Nevertheless, one must advert that our previous study neglected dispersion or van der Waals (vdW) interactions which have been found to play an important role in the adsorption geometry and energetics of adsorbed molecules, and intermolecular interactions as well [6–12]. This is because most of the commonly used DFT based methods rely on approximations of the electron exchange and correlation which do not properly describe the long-range vdW forces.

In the past few years, a considerable effort has been devoted to include vdW interactions in DFT based methods. The simplest approximation consists in employing an empirical correction, leading to the so-called DFT-D methods [13]. These are simply based on the addition of damped atom-pairwise dispersion corrections of the form $C_6 R^{-6}$, where C_6 represents a dispersion coefficient for a given atom pair and R is the distance between the atoms. The implementations of Ortmann et al., [14] Grimme, [15] and Tkatchenko and Scheffler [16] constitute widely used representatives of DFT-D methods. On the other hand, approaches aimed at providing a first-principles description of vdW interactions have also been developed. These methods are usually referred to as vdW-DF and can be computationally more demanding. Among these, a promising approximation is the one proposed by Dion et al. [17] and other functionals obtained by modifications of this one resulting in different vdW-DFT flavors, such as the rPW86-vdW, [18] optPBE-vdW and optB88-vdW, [19] and optB86b-vdW [20] although their performance is still not fully established and, in absence of experimental data, it is really difficult to justify a given choice. This is clear from the recent review by Prates-Ramalho et al. [21] on the performance of different methods aimed to account for van der Waals interactions between adsorbates and surfaces in density functional theory based methods. In fact, very recent work for the interaction of graphene with Ni (111) has shown that among a rather long list of functionals proposed to include van der Waals interactions, only optB86b-vdW and the empirical DFT-D of Grimme are able to provide a balanced description of the experimentally well-established physisorption and chemisorption states, the attachment strength of the latter on the Ni(111) surface, the graphene–Ni(111) separation, and the band structure of chemisorbed graphene [22]. Hence, in spite of some claims, that Grimme's DFT-D method is too empiric, it still appears to be robust enough to distinguish the two states for graphene on Ni(111) and, also, the exfoliation energy of graphite [22].

In the present work we report DFT based calculations for low and high coverage of acrolein and allyl alcohol on Ag(111) which include dispersion corrections for vdW interactions mainly through DFT-D, which is justified by the above arguments regarding the case of graphene on Ni(111), with some calculations carried out also with optB86b-vdW mainly for comparison purposes. We have already mentioned that these unsaturated aldehydes and alcohols are of interest in selective hydrogenation processes [23–27] and that experimental information for the geometric structures of these molecules on Ag(111) is at hand; [3] which can be taken as a reference. Our main objective here is to study geometries and relative stabilities of acrolein and allyl alcohol networks on Ag(111) and the effect of the dispersion interaction on these systems.

1.1. Computational details

Periodic slabs consisting of four layers of metal atoms interleaved with a vacuum width equivalent to five atomic layers were employed to determine adsorption geometry of adsorbed acrolein (denoted as ACR) and allyl alcohol (denoted as AOL). For the low coverage case, a $p(4 \times 4)$ supercell is used while for the high coverage situation

several structures are considered. The first one is represented by a $p(2 \times 2)$ cell which corresponds to a coverage four times larger than the one corresponding to the low coverage case modeled by the $p(4 \times 4)$ supercell. In this situation the adsorbed molecules are all equivalent and thus oriented in the same way (head-to-tail). Another possible structure arising from the interaction between adsorbed molecules involves a head-to-head type of contact and thus allows for the formation of dimers and more complex structures. To take into account these head-to-head interactions we use $p(5 \times 3)$ and $p(4 \times 2)$ cells containing explicitly two non-equivalent molecules initially placed in a head-to-head manner although the resulting structure is, in all cases, fully relaxed. Note, that in the $p(4 \times 2)$ cell with two adsorbed molecules the coverage is the same as in the $p(2 \times 2)$ cell with one adsorbate. However, in the former supercell different orientations of the two adsorbed molecule are possible whereas in the latter this is not the case because of the periodic symmetry. In the $p(5 \times 3)$ cell the coverage is such that the adsorbed molecules are also allowed to form dimers but rather separated from each other.

For each of the surface structures mentioned above, the energy was evaluated at DFT and DFT-D levels. Following our previous work devoted to ACR on Ag(111), [13] we used the PW91 exchange–correlation potential [28,29] version of the Generalized Gradient Approximation (GGA) for DFT based calculations without dispersion corrections. Since the empirical corrections to this GGA functional are not available, we used the DFT-D approximation suggested by Grimme using PBE [15]. Note, however, that the performance of PW91 and PBE is very similar even in the energy profile for surface reactions [30] and that, indeed, it has been very recently shown that these functionals provide the best overall performance for the bulk properties of the thirty transition metal elements [31]. In the DFT-D approach, the total energy is given by

$$E^{\text{DFT-D}} = E^{\text{DFT}} + E_{\text{disp}}, \quad (1)$$

where E^{DFT} is the Kohn–Sham total energy as obtained from genuine PBE and E_{disp} is an empirical dispersion correction given by

$$E_{\text{disp}} = -s_6 \sum_{i,j} f(R_{ij}) C_6^{ij} (R_{ij})^{-6}, \quad (2)$$

where $f(R_{ij})$ represents a damping function and the C_6^{ij} coefficients are obtained from atomic polarizabilities and ionization potentials. On the other hand, s_6 is a scaling factor which was optimized in 0.75 for PBE [15].

The one electron Kohn–Sham states were expanded in a plane wave basis with a kinetic cut off energy of 415 eV and the PAW method [32] was used to take into account the effect of the inner cores on the valence states. Suitable Monkhorst–Pack [33] meshes have been used to carry out all necessary integration steps in the reciprocal space. These are as follows: $5 \times 5 \times 1$ for the $p(2 \times 2)$ cell, $3 \times 3 \times 1$ for the $p(4 \times 4)$ cell, and $3 \times 5 \times 1$ for both $p(4 \times 2)$ and $p(5 \times 3)$ cells. The adsorbate-induced dipole moment in the vacuum region was eliminated following the method outlined by Kresse et al. [34] Both DFT and DFT-D periodic calculations were performed using the VASP code [35,36]. The adsorption energy (E_{ads}) was calculated with respect to the naked surface and to the gas phase molecule (the most stable conformer of ACR or AOL). In all cases, the structure of the adsorbed molecule(s) and the two topmost layer of the Ag(111) surface model have been fully relaxed; the other two metal layers were maintained fixed at the bulk geometry. This strategy is commonly used when studying the chemistry of metal surfaces, the case of ethylene partial oxidation on Ag(111) studied by different authors [37–40] provides a beautiful example of the appropriateness of this model which is also supported by low-energy electron diffraction studies which show slight relaxations of the first two interlayer distances with respect to the bulk distance, namely, -0.5% for Δd_{12} and -0.4% for Δd_{23} , and even smaller relaxation

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