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Theoretical aspects of heterogeneous catalysis: Applications of density functional methods

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Abstract

The progress in applications of density functional methods to problems of materials for heterogeneous catalysis as well as to their adsorption properties and reactivity is overviewed. Transition metal surfaces (Cu, Ru, Pd, Pt, Pd/Zn, Pd/Pt), metal oxide surfaces (MgO, NiO) and supported d-metal particles (atoms, Pd nanosize clusters) are taken as examples of catalytic substrates. Reactants/adsorbates considered range from single atoms, diatomic molecules, ammonia and small unsaturated hydrocarbons to more complex such as carbonate and urea molecules. Results of cluster- and slab-model density functional calculations chosen from various theoretical and experimental groups illustrate impressive achievements of the past decade in selected aspects of theory in heterogeneous catalysis. Also, some problems and limitations of the density functional description are alluded.
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1. Introduction

Surface science and heterogeneous catalysis have long been the research fields where *quantitative* information was derived almost exclusively by means of the rich arsenal of sophisticated experimental techniques [1–4]. However, during the past decade, amazing progress has been achieved in the performance of first-principles electronic structure methods due to both the unprecedented growth of the available computer power and crucial developments of computational methods and algorithms. In particular, the method based on density functional (DF) theory [5,6] recently became an extremely powerful and efficient tool in chemistry [7]. Currently, DF studies are widely used to generate and rationalize various kinds of observables characterizing complicated systems of importance for surface science and heterogeneous catalysis. These data successfully complement the experimental results and some of them would otherwise be very difficult (or even impossible) to obtain or hard to interpret [8–17].

In the following, we shall overview the opportunities and limitations of modern DF methods to quantify structural, binding and spectroscopic parameters of catalytic relevant surface complexes as well as to characterize both the thermodynamics and kinetics of surface reactions taking place on catalytic materials. To this end, we selected, from the literature, a series of representative case studies that deal with adsorption and reactivity properties of transition metal surfaces, metal oxide surfaces and supported metal particles. Both very recent and older studies are included in our account to get a feeling of the dynamics of the rapidly developing field of surface science and heterogeneous catalysis tackled from first principles.

Quantum mechanical ‘‘computer experiments’’ to simulate solid surfaces and surface complexes are nowadays performed with the help of two types of models. The first, more physical ones represent surfaces in terms of a unit cell

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periodically repeated in two- or three-dimensions [18]. To describe perfect surfaces of single crystals in such a periodic approach, unit cells containing a rather limited number of atoms usually suffice. However, any distortion of the surface periodicity, by a defect or an adsorbate, requires a significant increase of the size of the unit cell, which results in a higher computational cost. Otherwise, such surface irregularities repeated periodically would be too close to each other. Fortunately, the current accessibility of high-performance computers and efficient software makes such an increased computational demand affordable and slab models are becoming very popular in theoretical studies in catalysis [11,13].

The alternative cluster model approach [19–22] is immanent to cases where periodicity is completely absent. This rather common chemical situation is exemplified by surface complexes at a very low coverage. In the cluster model, one attempts to represent a part of the surface of the material under study by a finite moiety (cluster) built of a limited number of atoms. Such a cluster may (or may not) be embedded in an environment medium mimicking the rest of the infinite system and treated at a less sophisticated level than the most interesting central part of the model. Results of cluster model calculations depend on the size and shape of the most rigorously described ''active'' part of the model as well as on the accuracy of how adequately the environment is represented. Provided cluster models of a surface system are validated to deliver ''converged'' calculated observable values with respect to sufficiently large size and accurately imposed boundary conditions, they may offer some advantages. For instance, cluster models treat complexes on solid surfaces in terms of localized states, using the conventional chemical language of molecular orbitals (MO), exactly as if one were simply considering a molecule formed by two fragments. This is particularly useful for clarification of the surface reactivity. The vast arsenal of quantum chemical codes, schemes and tools is readily applicable for cluster model studies [8–10,12,14–17].

This paper is organized as follows. In Section 2, we exemplify structural assignments of adsorption complexes on metals by a combination of experimental vibrational spectroscopy data and DF model cluster results for NO and NH species on Ru(0 0 0 1) followed by somewhat more complex systems such as carbonate or urea on metal electrodes. In Section 3, we provide examples of the difficulties of DF theory to accurately predict adsorption energies. To this end, we outline a recently opened discussion on the so-called CO/Pt(1 1 1) puzzle—failed attempts of DF approaches to reproduce the subtle adsorption energy differences for CO on various surface sites of Pt(1 1 1). We also discuss the problem of the adhesion of metals to oxide surfaces and provide some comments on the problems encountered by a DF description of particular classes of open-shell systems, namely adsorption properties of CO, NH_3 and NO on NiO(1 0 0) and Ni-doped MgO(1 0 0). Section 4 is devoted to novel three-dimensional nanosize cluster models that open a way to obtain size-converged values of adsorption energies (being most delicate observable) and enable a realistic representation of supported model metal catalysts. In Section 5, the problem of N_2 activation on Ru(0 0 0 1) is considered, that emphasizes importance of surface defects in catalysis. Section 6 deals with the catalytic trimerization of acetylene on atomic Pd particles supported on MgO and the catalytic coupling of propyne on a metal surface. Both are recent examples of rather complex heterogeneously catalysed reactions. Finally, some conclusions and outlook are presented.

2. Structure, bonding and vibrations of adsorption complexes on metal surfaces

Vibrational spectroscopy ''fingerprints'' play a notable role in ''bridging'' theory and experiment for clarifying the microscopic picture of surface phenomena. Two examples presented below illustrate potential of vibrational spectroscopy to structurally characterize, in combination with calculated DF results, adsorption complexes on transition metals. These are followed by two more examples showing how DF cluster and periodic model calculations help to assign vibrational spectra of adsorbates in electrochemical environment.

2.1. Adsorbed NO and ON Species on Ru(0 0 0 1)

Low-temperature molecular adsorption of NO on transition metals (TM) gives rise to complicated vibrational spectra due to the presence of several states with different bonding configurations [23]. High-resolution electron energy loss spectroscopy (HREELS) data for NO/Ru(0 0 0 1) system were analysed in a combined experimental and DF study carried out a decade ago [24]. The goal was to examine, which of the conceivable structures of molecular NO adsorbed on a clean Ru(0 0 0 1) surface causes the HREELS peaks observed at a low coverage. Special attention was paid to resolve the origin of the peaks in the extremely low frequency region, $\sim$1130 cm^{-1}, i.e., red-shifted by as much as $\sim$750 cm^{-1} with respect to a free NO molecule.

Small clusters Ru_n ($n \leq 13$) were employed to model three-fold hollow, bridge and on-top adsorption sites on the Ru(0 0 0 1) surface (Fig. 1). DF calculations were performed in economic local density approximation (LDA) providing accurate geometries and vibrational frequencies [7]. Not unexpectedly, NO adsorption in the three-fold hollow (μ_3) positions with the N atom directed towards the substrate was calculated to be accompanied by a significant weakening of the NO bond. This is due to many-orbital donor–acceptor interactions involving the four HOMOs of NO, among which the 1π and $2\pi^*$ orbitals are of particular importance. The Pauli repulsion between

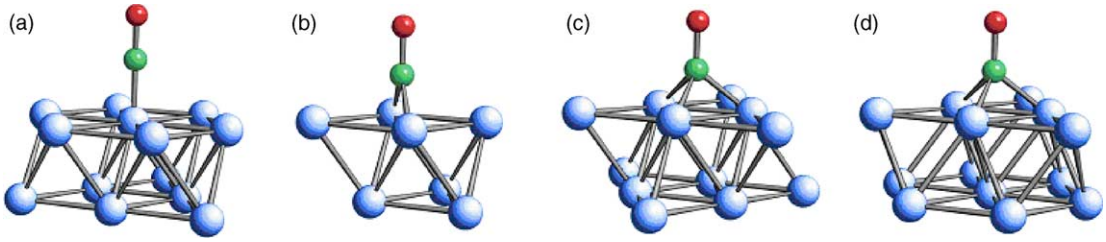

Fig. 1. Cluster models of NO adsorption at various positions of the Ru(0 0 1) surface: (a) on-top, Ru_{13}(7,6)–NO; (b) bridge, Ru_7(4,3)–NO; (c) fcc three-fold hollow, Ru_{12}(6,6)–NO and Ru_{12}(6,6)–ON; (d) hcp three-fold hollow, Ru_{13}(6,7)–NO and Ru_{13}(6,7)–ON. The main rotational axis of the substrate clusters is that along which the NO adsorbate is assumed to approach the surface, either N- or O-end down.

the adsorbate and the substrate contributes to increase the N–O force constant. A balance of these two effects results in a vibration of the μ_3-NO/Ru(0 0 0 1) species measured at 1400 cm^{-1} and calculated at 1407–1437 cm^{-1}. The small difference between the calculated N–O frequencies of the nearly iso-energetic two types of μ_3-NO adsorption complexes at fcc and hcp sites agrees with the experimental finding that no splitting of the peak at 1400 cm^{-1} takes place. Calculations for the three-fold sites favour an orientation of the NO adsorbate almost perpendicular to the surface.

On the basis of the calculated frequency at 1160 cm^{-1}, the very puzzling low coverage mode observed at 1130 cm^{-1} was assigned to the N–O stretch of the μ_3-ON species coordinated at three-fold hollows in an unusual *isonitrosyl* fashion, via the oxygen atom. This structure is characterized by a longer distance, weaker covalent interactions with the metal and a reduced Pauli repulsion between the adsorbate and the substrate. The latter effect enables one to rationalize both the significantly lower frequency and the reduced intensity of the N–O mode in this case compared to the common μ_3-NO adsorption complexes. A similar bonding orientation has been proposed to explain the vibrational spectrum of NO on a Ag(1 1 1) surface [25,26].

The ON/Ru(0 0 0 1) adsorption state exists neither as a single nor as a major phase. It makes a direct experimental proof of the formation of μ_3-ON/Ru(0 0 0 1) isonitrosyl difficult, at least without surface extended X-ray absorption fine structure (SEXAFS) measurements for which a synchrotron radiation source is required. However, by analysing the calculated peculiarities, an alternative experiment was proposed to identify the anomalous μ_3-ON/Ru(0 0 0 1) structure. Namely, a difference of the ionisation potentials of the 4σ-MO in the μ_3-ON complexes and all other studied adsorbed NO species by about 0.8 eV had been predicted. Thus, a shoulder due to 4σ-level of μ_3-ON had to be detectable by photoelectron spectroscopy at low coverages, when the both complexes are present at the surface. This feature is expected to disappear at a higher coverage, $\theta > 0.5$, typical for the vanishing of the HREELS peak at ~1130 cm^{-1}. A subsequent photoelectron spectroscopy examination of this argument indeed revealed the predicted changes in the pertinent spectral area, thus, corroborating the presence of the non-classically bound μ_3-ON/Ru(0 0 0 1) complexes.

After the NO/Ru(0 0 0 1) publication [24], coordination compounds with isonitrosyl ON ligands were proposed to exist as a metastable isomer of mononitrosyl Ru [27] and Fe [28] complexes. This light-induced state, extremely long-living at low temperature, had been previously considered as a (puzzling) electronically excited state. This assignment was revisited by direct X-ray structural determinations [27,28] and resulted in a new rationalization as a structural isonitrosyl isomer. These metal complex isomers with an ON ligand were manifested by notably lower N–O frequencies compared to the parent classical nitrosyl compounds. Despite the difference between the metastable isonitrosyl complexes with a terminal coordination of the ligand and the adsorption systems, the results just outlined [27,28] are pertinent to the observations of NO complexes on Ru surface [24]. Indeed, the light-induced origin of the metastable isonitrosyl surface species would imply a notable intensity dependence of the vibrational peaks of the N–O stretch, assigned to the surface isonitrosyls, on the type of the spectroscopic excitation sources, e.g., HREELS versus infrared (IR).

2.2. NH on Ru(0 0 0 1)

NH_x species on metals participate in many key chemical reactions, e.g., in extremely important catalytic synthesis of ammonia [29] (see also Section 5). A combined DF and vibrational spectroscopy study of NH/Ru(0 0 0 1) complexes [30] is outlined in the following. It disclosed that a vibrational feature has been commonly but erroneously used as a ‘‘fingerprint’’ for identifying the presence of adsorbed NH species on metals.

Identification of the adsorbed NH_x intermediates, including the smallest NH species, appeared to be a complicated task. Formation of NH on a Ru(0 0 0 1) surface by the decomposition of formamide [31], hydrazine [32] and in the reaction between adsorbed N and H atoms [33] has been reported. The conclusion that a tilted (bent) NH is present on the Ru surface was solely based on HREELS data and on the assignment of the energy loss peak at 1350 cm^{-1} (the Ru–N–H bending mode) to a fingerprint of a bent adsorbed NH species. The observation of this band together

with the stretching modes N–H (3310–3360 cm^{-1}) and Ru–NH (570–690 cm^{-1}) let a major argument for formation of NH/Ru complexes. Actually, the interpretation of the band at 1350 cm^{-1} was merely supported by its closeness to the IR frequencies ascribed to the bending mode of organic imides and transition metal imido-complexes, despite that the bending mode M–N–R of coordination compounds is not characteristic, and thus, not suitable for deriving structural information [34]. To reach at an unequivocal clarification of the crucial aspect of the NH/Ru(0 0 1) system, whether the HREELS band at ~1350 cm^{-1} is indeed, as it was commonly accepted, a manifestation of the Ru–N–H bending vibration– cluster model DF calculations and new Fourier transform infrared spectroscopy (FTIR) experiments with significantly improved spectral resolution were required [30].

The calculations showed that isolated NH species can adsorb on the Ru(0 0 0 1) surface with the N–H axes either along the surface normal (three-fold hollow) or tilted (on-top) [30]; the former (upright) structure is energetically favoured. For both μ_3 and on-top adsorbed NH species, frequencies of the Ru–N–H bending mode were calculated to emerge below 800 cm^{-1}. This is much lower than the experimental value ~1350 cm^{-1} that at the time of the investigations [30] was unanimously assigned to the bending mode and used as the strongest argument for tilted adsorption imido-complexes on Ru and other metal surfaces [31–33]. These theoretical findings were corroborated by high-resolution IR absorption measurements of the N + O + H(D)/Ru(0 0 0 1) layer in the spectral range 600–4000 cm^{-1} [30]. The IR spectra revealed a band at 3320 cm^{-1} assigned to the N–H stretch of the adsorbed NH species, but, in line with the upright orientation of adsorbed μ_3-NH species found in the DF calculations, no other bands inherent to NH/Ru(0 0 0 1) complexes were detected. Thus, the assignment of the HREEL frequency measured at ~1350 cm^{-1} in previous studies as a manifestation of the bending mode Ru–N–H had to be rejected. The novel observation that the 1350 cm^{-1} mode was formed much more slowly than the N–H stretching mode supported this revision. That no isotopically shifted mode was found after replacing H by D implied that either the D-derived mode of the new species was below the detection level, or that the spectral feature at ~1350 cm^{-1} is not related to vibrational modes of any H-derived moiety. Recent HREELS study of NH/Ru(1 1 $\bar{2}$ 0) complexes [35] revealed the absence of vibration peaks around 1350 cm^{-1}. Moreover, bands at such low frequencies as ~700 cm^{-1} have been observed and interpreted as bending modes of adsorbed μ_3-NH.

2.3. Adsorbates in electrochemical environment

The application of surface science techniques in electrochemistry has triggered important developments. In particular, the preparation of well-defined single crystal electrode surfaces [36,37] together with the application of spectroscopic techniques such as in situ FTIR has permitted to study adsorbates in electrochemical environment in a rather straightforward way [38–40]. Most often, the interpretation of IR spectra of this kind of systems is based on the comparison with the corresponding spectra of molecular complexes [41]. Model calculations are of great help to interpret the corresponding spectra on more sophisticated grounds and, as shown in the pioneering work of Bagus et al. [42,43] for CO and CN on Cu(1 0 0), cluster models are particularly well suited to investigate the effect of external electric fields. These earlier calculations were of Hartree–Fock (HF) type and hence permitted to understand solely the basic mechanisms but not to make quantitative predictions. As illustrated in the previous examples, DF cluster model calculations have reached a level of accuracy that enables one to make accurate predictions of the structure and chemical bonding of molecules adsorbed on surfaces. Furthermore, nowadays also more elusive properties, such as the Stark tuning rate of CO and OH on Pt(1 1 1) [44], are becoming accessible for high-level cluster model description.

Cluster model DF calculations have also been very useful to assign the ''in situ'' spectroscopic features of CO adsorbed on Pd/Pt(1 1 1) bimetallic single crystal electrodes [45]. For more complex adsorbates such as carbonate on Pt(1 1 1), based on DF cluster model calculations Markovits et al. have shown that the comparison to spectra of molecular complexes is not always straightforward and can lead to erroneous assignments [46]. These authors have also found that the vibrational frequency of the highest normal internal mode of A_1 symmetry can be assigned by comparison to the spectrum of carbonato molecular complexes, whereas, this comparison is not possible for other normal modes because of the presence of the surface. Hence, some normal modes are transferable from the complex to the surface adsorbed molecule, whereas, others are not. However, in reality, the situation is actually less simple because of the presence of other species; for instance, coadsorption of bicarbonate moieties introduces further complications. In this case, the interpretation of the corresponding spectrum requires a high level of accuracy. This can be achieved by making use of periodic models and contemporary generalized-gradient approximation (GGA) exchange–correlation potentials [47]. Nevertheless, it is important to emphasize that in many cases, the complex–surface analogy works very well. This has been found precisely to be the case, e.g., for urea on Pt(1 1 1) [48]. The impossibility to know beforehand the degree of fulfilment of this rule is actually what makes DF model calculations so useful.

3. Accuracy of calculated adsorbate–surface interactions

3.1. The CO/Pt(1 1 1) puzzle

In the previous section, it has been shown that even the early DF cluster model calculations were reliable and very helpful for tracing the relations between vibrational

frequencies and structure of adsorption complexes. However, no successful attempts were (and were able to be) undertaken at that time to accurately reproduce the energetic of surface complexes on metals (and other kinds of substrates), for two major reasons. On the one hand, because of the substantial overbinding in the LDA scheme [7] and, on the other hand, because of the significant cluster size-dependence of calculated adsorption energies found for moderate cluster sizes [19,49]. The former is thought to be almost overcome by the impressive accuracy increase achieved by recently proposed GGA functionals and hybrid approaches [7]. The cluster size-convergence problem also appears to be solved (see more details in Section 4) and periodic approaches became readily available. It is nowadays expected that even subtle relative adsorption energy differences on metals of about 10 kJ mol^{-1} can be correctly reproduced by contemporary DF calculations. The cluster size-dependence can be greatly reduced for sufficiently large models as shown precisely for CO on the Pt low-index surfaces [50].

As outlined in the following, problems with fulfilment of such high-energy accuracy expectations for one of the touchstone systems of surface science, CO on Pt(1 1 1) [51], initiated unprecedented discussion in which a significant part of the theoretical chemistry community has become involved [52–57]. Results of periodic plane-wave DF calculations on the adsorption system of low-coverage CO on Pt(1 1 1) surface, performed by several groups with the state-of-the-art slab models, were reported in a paper published in 2001 [51]. It was shown there, that even using modern GGA exchange–correlation functionals and essentially eliminating the convergence issue of the results with respect to various computational parameters, both all-electron and pseudopotential calculations lead to a qualitatively erroneous conclusion. Namely, the DF studies revealed a preference of CO to occupy (in the low-coverage regime) hollow adsorption sites of Pt(1 1 1) and not the atop sites [51]. It is in apparent contradiction with reliable experimental data obtained for this adsorption system by low-energy electron diffraction analysis [58,59], vibrational spectroscopy measurements [60–62] and theoretical simulations [63,64] of scanning tunnelling microscopy results [64,65], all favouring the atop adsorption positions of CO on Pt(1 1 1) at low coverage over the three-fold hollow sites.

This failure indicates preference of adsorbed CO to low-coordination sites on transition metals and implies a general drawback of DF methods to correctly represent the experimentally observed situations. It is especially important for two reasons. First, the CO/Pt(1 1 1) system is one of the most thoroughly studied benchmarks, having an immediate relation to reactivity of such an ubiquitous catalyst as platinum. Second, DF calculations are concluded yet not to ''be viewed as a ''black box'' simulation tool'' [51]. Even after reaching numerical convergence and re-examining precision of various approximations involved, successful prediction of most stable adsorption sites is claimed to be not guaranteed for moderately small energy differences.

The latter remark deserves closer attention since the corrugation of the potential energy surface (PES) for CO/Pt(1 1 1) is certainly weak and its accurate representation is a stringent test for a computational method. In fact, PES empirically determined for CO/Pt(1 1 1) based on fitting measured vibrational spectroscopy data [62] gives, by extrapolating to zero coverage, a binding energy preference of CO on the atop site as little as 6 kJ mol^{-1} with respect to the bridge complexes; no infrared line of CO on three-fold hollow sites has been observed [62]. Thus, the CO/Pt(1 1 1) problem under consideration deals with subtle energy differences of the order of 10 kJ mol^{-1}.

One more peculiarity of the CO/Pt(1 1 1) systems, which has not been addressed *explicitly* by plane-wave calculations [51], is a strongly relativistic character of such a heavy element metal as Pt and of the chemical bonds it forms. Whereas, plane-wave studies often rely on sufficient accuracy of the structure and energetics of adsorption complexes involving heavy elements, that is provided by relativistic pseudopotentials [51,52], methods utilizing localized basis sets currently offer more opportunities to *directly* take relativistic effects into account [55,66,67]. Interestingly, that examination of the relativistic corrections to CO adsorption energies on Pt(1 1 1) slab, undertaken at the FP-LAPW level, revealed even a stronger trend in relativistic calculations to favour three-fold hollows against the atop sites [51]. This effect was assigned to the long lattice constant of Pt optimised at nonrelativistic level, which is notably, by 23 pm larger than the relativistic value and by 30 pm larger than the experimental one.

As already mentioned, soon after Ref. [51] appeared, several attempts have been undertaken in the framework of periodic models to find the reasons for the CO/Pt(1 1 1) puzzle and to solve the problem. For instance, the influence of the error on the CO adsorption energy on Pt(1 1 1) and the site preference brought by pseudopotential approximation and exchange–correlation functionals has been carefully examined [52]. The authors suggested that the discrepancy between the experimental and DF site preference is mainly due to GGA that treats bonds of distinct orders with different precision. A combined DF study of a series of cluster and periodic models of CO on Pt(1 1 1) [53] confirmed that the site preference obtained for cluster models of increased size (at variance with small cluster models that are not adequate for reliable description of chemisorption) is in agreement with the results of periodic calculations [51], i.e., in disagreement with experiment. The new insight gained from the cluster model studies was that employment of hybrid functionals (with a part of the non-local Fock exchange) leads to an increased stabilization of the atop site relative to the three-fold one [53]. Indeed, the atop site becomes most favourable in slab-model calculations with the B3LYP hybrid functional [57]. The energetic preference of the three-fold hollow site was assigned to inadequate representation of

the HOMO–LUMO splitting [53]. In a similar way, in a periodic slab-model study [54] the site preference was shown to depend on a subtle balance of the interaction of HOMO and LUMO of the adsorbed CO with the substrate. The proper (experimentally observed) site preference on Pt(1 1 1) should come out of calculations performed with exchange–correlation functionals that repair the well-known problem of HOMO–LUMO separations underestimated in contemporary DF methods [54].

Decisive progress in addressing the CO/Pt(1 1 1) puzzle has been reached in slab-model DF investigations [55], very thoroughly performed using a linear combination of atomic-centred numeric and Slater orbitals. The calculated PES of CO on Pt(1 1 1) was found in agreement with experimental results, with the atop site being energetically preferable. Thus, it was convincingly shown that DF relative adsorption energies obtained at GGA level with the currently accessible precision of ± 10 kJ mol^{-1} should be considered qualitatively accurate for the CO/Pt(1 1 1) system as well. The key difference of the study [55] compared to other periodic studies mentioned above [51–54] is that it included relativistic effects in an accurate fashion by using the zeroth-order regular approximation (ZORA); a subsequent publication of periodic model results on CO/Pt(1 1 1) corroborated importance of accurate explicit account of scalar relativistic interactions in this system [56]. Another important conclusion of that ZORA work is that convergence of DF/GGA relative energetics for all adsorption sites to better than ± 10 kJ mol^{-1} represents a formidable task. Hence, that the DF/GGA data for CO site preference on metals disagree at this accuracy bar with experiment is neither a convincing proof nor a disproof of the failure of current DF methods. However, a more critical conclusion is reached when examining the DF description of the interaction of NO with a magnetic metal oxide system such as NiO(0 0 1) (see Section 3.3).

Thus, one can conclude that for adsorbates on metal surfaces and for cases involving such very low energy differences between competing sites, the favourable view of the DF/GGA method is supported by the opportunity to use other, more reliably computed observables (e.g., vibrational frequencies) to discriminate between the preferred sites on the basis of agreement or disagreement of these observables with the measured values. Finally, a clear need of more work to be done to validate various approximations used to account for relativistic effects in periodic plane-wave DF calculations has been pointed out [55]. Solutions of the latter problem are readily available at the level of cluster models [66,67], which however commonly impose other accuracy limitations due to slow size-convergence of the adsorption energies on metals [19,68,69]. An efficient way to essentially eliminate these convergence problems, and thus, to bring the cluster model approach to a highly accurate level is presented in Section 4. In the following two issues are discussed which provide evidence of further limitations of current DF methods.

3.2. The strength of metal–oxide interaction

The interaction of metal atoms and clusters with oxide surfaces has been the subject of a large number of experimental and theoretical studies. In particular, the interaction of isolated metal species on MgO(0 0 1) provided a very suitable playground for theoretical studies. The first systematic study of the interaction of nine TM atoms on the regular sites of MgO(0 0 1) has been undertaken by Yudanov et al. [70]. These authors have found that the Ni triad is the only one for which relatively strong interface bonds are formed. The adhesion energy is larger for the interaction of the metal atoms directly on top of surface oxygen anions and reaches values of about 80 kJ mol^{-1} per atom (when BLYP GGA exchange–correlation functional is used) or more; W being the only other metal atom considered, which exhibits a similarly strong bond. This moderately strong binding was explained through hybridisation arguments, the metal s and d orbitals mix and the resulting hybrid orbitals have a more favourable interaction with p orbitals of the surface oxygen. Cluster model DF calculations suggest that the TM atoms considered [70] can be classified into two groups, atoms which tend to form relatively strong chemical bonds with the surface oxygen anions of MgO (Ni, Pd, Pt and W), and atoms which interact very weakly with the surface, with BLYP adsorption energies of the order of 30 kJ mol^{-1} or less (Cr, Mo, Cu, Ag and Au). In any case, DF calculations show that the TM/MgO(0 0 1) interaction is not accompanied by any significant charge transfer from the metal to the regular, defect-free surface. This is because of the strong ionic character of this substrate the oxygen centres at the regular surface sites of MgO(0 0 1) are almost completely reduced and are not able to oxidize adsorbed metal atoms. Recent DF studies [71] of 17 various single TM atoms on regular O^{2-} sites of MgO(0 0 1) with BP86 and PBEN functionals supported this qualitative picture of the interactions. However, one has to point out that adsorption phenomena at oxide surfaces can be substantially different when occurring at defect sites, which appear to be ubiquitous, but will not be touched in this article. We mention that Markovits et al. [72] addressed the problem of the spin state of the adsorbed 3d TM atoms. Overall, it is found that the binding energy of single metal atoms along the series resembles the cohesive energy of the bulk metals; this strongly supports the above interpretation of the metal–support interaction, namely that the mixing of TM s–d states has a key contribution to the final interaction energy.

The trends described above are based on GGA or hybrid DF calculations and, as in the case of CO on Pt(1 1 1) commented in the previous subsection, one may wonder about the accuracy of the computed adhesion energies. In fact, earlier theoretical calculations for Cu on the regular, defect-free MgO(0 0 1) surface have shown a very large variation of the calculated energy values depending on the

method used. Cluster model calculations predicted values as different as ~0 and ~140 kJ mol^{-1} at the HF [73] and LDA [74] levels, respectively. This dispersion of results does also appear when using different DF methods [75]. Moreover, significant discrepancies were found between the binding energies obtained with ''classical'' quantum chemistry approaches, i.e., wave-function methods, and those based on DF theory. To understand the origin of these differences, Cu and Pd atoms on MgO(0 0 1) were taken as examples for closer inspection. A wide series of quantum mechanical calculations of increasing complexity – based either on wave-function or DF methods – were carried out for embedded cluster models of increasing size. For both instances, it was found out that the convergence of the model was achieved with a rather small amount of the substrate material [75,76]. In the case of Cu on MgO, it was also possible to compare results with periodic plane-wave DF calculations [77]. It has been concluded that HF adsorption energies are extremely poor and result in a negligible binding after correcting for the basis set superposition error. It was also found that, not unexpectedly [7], LDA largely overestimates the interaction energy; the latter decreases when using GGA functionals and is further reduced when employing a hybrid scheme. An interesting conclusion of these theoretical studies is that the interaction energy calculated with wave-function methods was converging to the B3LYP (hybrid) value, provided that enough electronic correlation is included with a large enough basis set. Very recently, calculations on the interaction of metals with simple oxide surfaces have indicated that one of the most likely terms responsible for the overbinding observed in the LDA calculations might be caused by the presence of a severe self-interaction [78,79]. When these terms are appropriately corrected for, the values of LDA and GGA are more similar [78]. For additional details concerning the interaction of metal atoms with the MgO(0 0 1), the reader is referred to recent reviews [17,80].

3.3. Difficulties encountered in describing simple adsorbates on NiO(1 0 0)

Simple adsorbates such as NH_3, CO and NO on NiO(1 0 0) and Ni-doped MgO(1 0 0) surfaces have been studied in detail [81–84]. Their structure has been determined experimentally with a high degree of accuracy. Hence, it offers a unique opportunity to test the performance of current DF methods. Photoelectron diffraction on NiO(1 0 0) thin films evidences that NO is bound with a Ni–N distance of 188 pm and a tilt angle of 59° from the surface normal [81]; CO binds almost normal to the surface with a Ni–C distance of 207 pm [81,82]; a similar distance, 206 pm, is measured for NH_3 [81,82]. Thermal programmed desorption (TPD) on NiO single crystals shows that the desorption energy of NO, 55 kJ mol^{-1}, is about twice that of CO, 29 kJ mol^{-1} [83]. A very rough estimate from TPD spectra of NH_3 adsorbed on NiO thin films [84] suggests that this molecule is the most strongly bound, with a desorption energy of about 80 kJ mol^{-1} [81,82]. Moreover, IR spectra on NiO powders show that while the frequency of adsorbed NO is red-shifted compared to that of the gas phase molecule, $\Delta\omega = -71$ cm^{-1} [85], the opposite is found for CO, the corresponding vibrational stretch is slightly blue-shifted, $\Delta\omega = +9$ cm^{-1} [86]. A very important point is that Ni^{2+} ions diluted in a MgO matrix behave in a very similar way as Ni^{2+} ions in the extended NiO surface. In fact, the CO vibrational frequency is virtually the same in the two systems [85,87]; also, the desorption temperatures of NO adsorbed on Ni-doped MgO and NiO are very similar [88–90]. The physical reason behind these similarities is that the bonding of CO and NO to the Ni ion is very local and does only marginally depend on the matrix in which the ion is included. A key feature of the NO molecule adsorbed on NiO/MgO solid solutions is that the electronic structure revealed by electron paramagnetic resonance (EPR) measurements do only show a single unpaired electron in the 3d shell of Ni (formally $Ni^{+}3d^{9}$) [91]. Note that this implies the transfer of one electron from the NO $2\pi^{*}$ molecular orbital to the Ni(3d) AO, which in this way is reduced from Ni^{2+} to Ni^{+}.

The bonding of the three above mentioned molecules to NiO and Ni-doped MgO has been studied in detail [92–94] using both DF and explicitly correlated wave-function based methods. Likewise, selected calculations have been carried out within the cluster approach and compared with the corresponding data computed for periodic slab models. The results of these investigations are in a way disappointing since it is shown that DF observables exhibit a strong dependence on the exchange–correlation functional used. Even more, in some cases, DF predictions provide a qualitatively wrong picture of the interaction. Functionals which furnish most accurate values for NH_3/NiO and CO/NiO systems are inadequate to describe the bonding in NO/NiO and vice versa. A correct solution requires explicitly correlated wave functions generated by complete-active-space SCF (CASSCF) and second-order perturbation theory (CASPT2) approaches [95,96] or the multi-configuration CEPA (MC-CEPA) method [97]. However, the large number of electrons involved in the correlation treatment and the stronger dependence of this kind of calculations on the Gaussian basis set results in too large error bars in the bonding properties remain. For NH_3 and CO the failure is connected in part to the well-known limitations of current DF methods to describe dispersion forces [7]; for NO, the problem is related to the presence of open-shells which indeed is connected to the breakdown of current DF implementation (LDA or GGA) to describe magnetic interactions [98] and to properly describe the electronic structure of charge transfer insulators such as NiO [99–103] resulting in a concomitant dependence of the predicted band gap on the exchange–potential used [104].

4. Metal nanoclusters

4.1. Models of single crystal surfaces and supported catalysts

Many parameters of adsorption complexes on metals (and other substrates), e.g., those characterizing the interaction mechanism, structural and vibrational spectroscopy features, exhibit rather low sensitivity to the size of the substrate cluster models [19–22]. This enables one to successfully employ the cluster approach to sufficiently accurately estimate a variety of observables required to rationalize experimental data for surface complexes, relying on small to moderate cluster models. Even metal substrates featuring highly polarizable electrons and the absence of localized bonds, common for chemical compounds, can be adequately represented by cluster models, if the central issue to address is not a precisely calculated adsorption energy (the latter often shows notable oscillations with size and shape of the cluster models, that mimic the surface electronic structure insufficiently [19,50,68,69,105,106]). These cluster models may yield different results for the Pauli repulsion between adsorbate and substrate, depending on whether pertinent cluster orbitals localized at the adsorption site are occupied or empty. The discrete density of states is an inherent feature of clusters that prevents a correct description of the polarizability of metal surfaces, and thus, hinders cluster size-convergence of adsorption energies. The form of conventional moderately large cluster models may become particularly critical. These models are inherently ''two-dimensional'' with substrate atoms from two or three crystal layers usually taken into account; thus, a large fraction of atoms at the cluster boundaries lack proper coordination.

In order to compute also the size-converged adsorption energies, a new strategy was proposed to use three-dimensional nanosize cluster models terminated by low-index crystal planes [107] (Fig. 2); these ''nanocrystal'' models comprising up to a hundred atoms (or even more) can be chosen to exhibit computationally advantageous (but not mandatory) high-point group symmetry. A series of octahedral clusters Pd_{55} to Pd_{146}, with the geometry fixed as in Pd bulk, has been calculated at all-electron scalar relativistic level, focusing on the interaction of CO with the three-fold hollow sites on Pd(1 1 1) facets [107]. It was examined, how different adsorption parameters vary with cluster size and how these values of cluster models relate to adsorption properties of the corresponding site at the Pd(1 1 1) surface. Starting from the model Pd_{79}, the calculations yielded CO adsorption energy varied in a range of 5 kJ mol^{-1} only [107]. Thus, the nanoscale models consisting of ~80 Pd atoms basically no longer exhibit size effects for adsorption properties. This very important finding indicates that convergence of adsorption energies on a single crystal metal surface can be reached with moderately large compact cluster models, which avoid the drawbacks of conventional cluster models where a significant fraction of metal atoms at the boundaries are insufficiently coordinated. The adsorption energy from the ''converged'' cluster models is essentially in *quantitative* agreement with energies calculated from periodic slab models, provided the same exchange–correlation functional is used in both calculations [107].

Moreover, the models just discussed [107] enable a realistic description of adsorption properties and reactivity of the so-called supported model catalysts which are notably less complex than industrial metal catalysts on oxides. To prove that these nanosize clusters can adequately represent supported model catalysts [3], the adsorption of CO on nanosize Pd particles was studied theoretically, using DF calculations, and experimentally, by means of infrared reflection absorption spectroscopy (IRAS) and sum frequency generation (SFG) [108]. The model clusters – three-dimensional crystallites of about 140 Pd atoms – were chosen as octahedral fragments of the fcc bulk, exhibiting (1 1 1) and (0 0 1) facets. Various types of adsorption sites were probed by CO: three-fold hollow, bridge and atop positions at (1 1 1) facets; four-fold hollow and atop sites at (0 0 1) facets; bridge positions at cluster edges; atop positions at cluster corners and on single Pd atoms deposited at regular (1 1 1) facets [108].

Adsorption properties of the small (1 1 1) cluster facets were calculated to be similar to those of an infinite (1 1 1) Pd surface. However, the strongest CO bonding was found on bridges at cluster edges. The adsorption energy atop of low-coordinated Pd centres (kinks) was also calculated larger than that for atop sites of (1 1 1) and (0 0 1) facets. In the combined study [108], vibrational spectra of CO adsorbed on supported Pd nanocrystallites of different size and

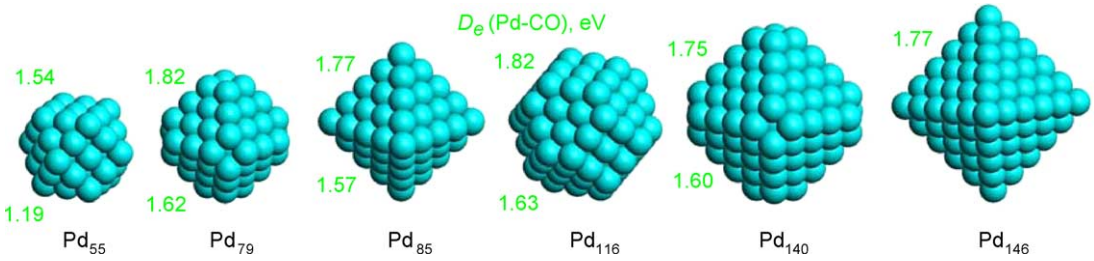

Fig. 2. Summary of the calculated adsorption energies of CO molecules on three-fold hollow sites of the (1 1 1) facets of the cluster models Pd_{55}–Pd_{146} at the fixed bulk-terminated (upper numbers) and optimized (low numbers) geometries.

structure (well-faceted and defect-rich) measured using IRAS and SFG were correlated with the theoretical results. A characteristic absorption in the region 1950–1970 cm^{-1} accompanying CO adsorption was assigned, in line with the theoretical data, to vibrations of bridge-bonded CO at particles edges and defects. The DF data under discussion helped to substantiate interpretation of the experimentally observed differences in CO adsorption on alumina supported Pd nanoparticles of varying size and ordering degree [108]. This study demonstrated a new opportunity for modern powerful theoretical tools based on DF schemes to provide insights into structure and properties of such important systems as model supported metal catalysts.

A further application of the nanosize cluster models to materials relevant to catalysis is a DF GGA scalar relativistic study of surface/subsurface impurities of light atoms H, C, N and O bound to Pd nanoclusters [109]. Models were investigated with single atoms adsorbed at three-fold hollow sites in the centre of each of the eight hexagonal (1 1 1) facets of the cuboctahedral clusters Pd_{79} and Pd_{116} [109]. For the Pd_{79} cluster, the atoms were also allowed to "migrate" from their fcc surface hollow sites to the interstitial octahedral hole sites underneath; similarly, migration to subsurface tetrahedral holes from hcp sites was modelled with the Pd_{116} cluster. These models provided insight into the relative stability of surface and subsurface atomic species as well as the activation barriers for migration from surface to subsurface positions. Such considerable transformations of various catalysts, induced by strongly bound atomic deposits, are expected to occur under reaction conditions. Subsurface C species occupying octahedral holes below the surface three-fold fcc sites of the cluster Pd_{79} are calculated to be almost iso-energetic with adsorption complexes at fcc surface sites, with binding energies 677 and 664 kJ mol^{-1}, respectively [109]; these very strongly bound impurities bear significant negative charge of about $-1e$. Among other atoms considered only H is predicted to exhibit (under a suitable experimental conditions) a notable propensity to diffuse subsurface of Pd(1 1 1) facets. The calculations yielded a moderate activation barrier of ~60 kJ mol^{-1} for diffusion of atomic C from surface fcc sites to octahedral subsurface sites; for diffusion of H, the barrier height is about the same.

4.2. Bimetallic catalysts

Bimetallic systems, usually supported nanosize particles [110], are even more challenging for an accurate theoretical description than just addressed monometallic species. Considerable amount of work on bimetallic systems has been carried out using slab models and plane-wave basis sets [111–116]. These DF calculations have been of great help to rationalize many qualitative trends and in particular have established such trends. However, from the discussion above, it is clear that infinite surfaces may exhibit different chemistry than finite particles. To support this statement, it is enough to realize that some of the sites present on the nanoparticles are not present on the extended surface. Also, most of these sites are the most chemically active. Therefore, various authors have attempted to use cluster models to study the adsorption and reactivity of bimetallic particles of different sizes and compositions. For instance, the dissociation of H_2 has been studied on PdCu and RhCu bimetallic systems [117,118] and the adsorption of CO on the latter has also been considered [119]. One of the important conclusions of these investigations is that bimetallic particles tend to preserve the atomic structure of the bulk and, also, that in these alloy systems a single Pd or Rh atom can be active to dissociate molecular hydrogen. However, both cases require the presence of other Pd or Rh atoms below the surface, i.e., forming Pd or Rh microclusters that are surrounded by the other component of the binary alloy. This result stresses the importance of electronic or ligand effects in the activity of these bimetallic surfaces towards molecular hydrogen activation.

More recently, a theoretical research of the active component of novel Pd/ZnO catalysts for methanol steam reforming has been reported [120]. Focusing on systems with low Zn concentrations, iso-structural bimetallic cuboctahedral nanoclusters $Pd_{132}Zn_8$, $Pd_{116}Zn_{24}$ and $Pd_{108}Zn_{32}$ were investigated as local models of the catalysts [120]. The calculated average cluster cohesive energy was found to decrease gradually with increasing number of Zn atoms: each Zn atom destabilizes the cluster by ~100 kJ mol^{-1}. CO probe molecules adsorbed at hollow Pd_3 sites in centres of the (1 1 1) cluster facets, were used to explore how the adsorption properties of bimetallic species change with respect to those of the reference monometallic cluster Pd_{140} [107]. Calculated CO adsorption energies manifest a weakening of the adsorbate–substrate bonds when Zn atoms are located in the subsurface layer of the $Pd_{140-n}Zn_n$ clusters; however, Zn atoms in the surface layer affect the CO adsorption energy only marginally. Interestingly, that quantification of CO adsorption energy using moderately large cluster models Pd_kZn_1, built in a conventional two-dimensional fashion, revealed a different (even counterintuitive) trend [120]. Absence of correlation of calculated CO adsorption energies with C–O vibrational frequencies was traced back to the different nature of these properties: adsorption energies are global characteristics, whereas, the frequencies are mainly determined by the local environment of a site.

Finally, one aspect central for catalytic applications of the three-dimensional nanocluster models introduced in this section needs to be emphasized. Namely, these models expose both regular adsorption sites present on ideal surfaces (in general less active) and adsorption sites on defects (inherent and deliberately constructed) that exhibit enhanced chemical activity. Defects alone, as outlined in the following section, often are responsible for catalytic performance of a material under scrutiny. This aspect is advantageous for comparative theoretical analysis of the reactivity of various regular and defect sites on metal catalysts in the framework of the same nanocluster model;

symmetry lowering of these models, required for such reactivity studies, which are not restricted by the shape of adsorption complexes, appears to be computationally affordable nowadays [121].

5. Role of surface defects in ammonia synthesis: N_2 activation on Ru(0 0 0 1)

The human population has been almost quadrupled in the past century. Continuation of this unprecedented growth up to now would not have been at all possible without a not always properly appreciated activity: the Fritz Haber's synthesis of ammonia, production of which is increasing more rapidly in the last fifty years than the population of the world [122]. The availability of ammonia and fertilizers allowed to the world's population to have enough to eat (unfortunately, only on the average). Paramount importance of ammonia makes its catalytic synthesis – on both the classical iron and more recently designed ruthenium-based catalysts – probably one of the best understood complex chemical processes, nowadays, despite numerous problems still to be solved [123]. Dissociation of dinitrogen molecules is known to be the kinetically determining step in the ammonia synthesis. DF calculations of N_2 dissociation on Ru surfaces, in combination with experimental results, made a crucial contribution to the understanding that the reaction is totally dominated by defects (step sites) [124].

Activation barrier of N_2 dissociation over Ru catalysts determined by measuring the dissociation rate ranges from 30 to 60 kJ mol^{-1} [125,126] in agreement with the dissociation probability measured over different Ru surfaces [127]; time-of-flight thermal desorption data are also in line with the barrier height of the order of 60 kJ mol^{-1} [128]. At variance, DF calculations featured a dissociation barrier of 130 kJ mol^{-1} [128] or, even larger, when more accurate exchange–correlation functionals were employed [129]. A possible rationalization of this difference between the experimental and theoretical results is that the thermal experiments actually measure the rate of N–N bond breaking at the few step sites on the single crystal surfaces instead of quantifying the dissociation process on the terrace sites. In such a case, if steps indeed determine the reactivity of the flat single crystal Ru surfaces with respect to N_2 cleavage, the defect sites also should dominate on the catalysts nanoparticles.

In order to investigate whether steps might be responsible for the low barrier of N_2 dissociation on Ru, plane-wave slab-model calculations [124] were performed at an accurate GGA level [130]. On the Ru(0 0 0 1) surface, the barrier for N_2 dissociation has been calculated as large as ~185 kJ mol^{-1} (or ~170 kJ mol^{-1} after corrections for the zero-point energy). These values are certainly much too high to explain the measured barrier height for N_2 dissociation on various Ru samples 30–60 kJ mol^{-1} [125–127]. However, if only ~1% of Au monolayer is adsorbed on Ru(0 0 0 1), which has been shown to preferentially decorate the steps [131], the nitrogen coverage was suppressed, and therefore, the N_2 dissociation rate was decreased dramatically (by nine orders of magnitude), corresponding to the activation barrier of 125 ± 20 kJ mol^{-1} [124], which is much closer to the calculated barrier on the terrace of Ru(0 0 0 1). The only reasonable interpretation of this very strong effect is that the N_2 dissociation observed on clean Ru(0 0 0 1) surface was dominated by less than 1% steps which are blocked by Au deposition. Indeed, calculated DF potential energy diagram for N_2 dissociation at a step revealed notably lower barriers than for the flat surface, with the lowest value being ~40 kJ mol^{-1} which is very close to the experimental value observed without deposited Au [124].

The step sites favoured the transition state structure for N_2 dissociation so strongly because here the two N atoms do not have to share any Ru atoms as nearest neighbours (as is the case for the transition state on the flat surface). The main difference in the barrier height is, therefore, caused by the fact that five Ru atoms are associated with the transition state complex at the step site rather than four on the terrace [124]; in this way, the former species avoids the indirect repulsive interactions responsible for the high barrier on the terrace [129]. Furthermore, enhanced reactivity of the step atoms compared to those on terraces gives an additional lowering of the barrier.

Thus, experimental and theoretical DF studies [124] have shown that steps totally dominate N_2 dissociation even on "flat" Ru(0 0 0 1) surface due to a high barrier on the terraces and a combined electronic and geometric effect favouring dissociation at steps on the surface. This very important finding can most probably be generalized for other reactions on metal and metal–alloy catalysts (see, e.g., Refs. [13,132–134]).

6. Examples of catalytic reactions

In this section, we will describe two cases that exemplify the power of DF methods to describe rather complex catalytic reactions. The first example concerns the trimerization of acetylene, a reaction which is known to occur on various TM surfaces [135–137]. However, the case to be discussed here involves supported Pd atoms. The second example is related to the previous one, involving the coupling of alkynes (in this case propyne) on an extended metal surface. The presence of the third carbon atom in the reactant molecule completely changes the chemistry and different products are obtained depending on the metal surface examined [138].

6.1. Acetylene trimerization on supported Pd atoms on MgO

Small supported noble- and TM-particles represent a novel type of catalyst, performance of which can be tuned by changing their size, almost atom-by-atom. Such model

catalysts have been employed to study the cyclization of three acetylene molecules to benzene. For that, size-selected Pd_n species ($n \leq 30$) produced by a laser evaporation source were ''soft landed'' on MgO thin films [139,140]. Temperature programmed reaction spectra for the cyclotrimerization of acetylene reveal that on Pd_1, Pd_2 and Pd_3 benzene is formed at 300 K. Another desorption peak of benzene is observed at 430 K on Pd_7. For Pd_8 the latter feature becomes equally strong as the peak at 300 K and from Pd_{30} clusters benzene mainly desorbs at 430 K. No benzene is detected on a clean MgO(1 0 0) surface at these experimental conditions. Such size-dependent reactivity of the metal clusters makes them very attractive to rationalize structure–property relations. The finding that already Pd atoms catalyse formation of benzene [140] motivated DF studies of the activity of Pd atoms as a function of their location on the MgO support [141].

The propensity to catalyse the acetylene trimerization is manifested by the ability of Pd atom to bind two C_2H_2 molecules, to activate them and to bind the C_4H_4 intermediate. The first acetylene molecule is calculated to be bound to a free Pd atom by ~200 kJ mol^{-1}, whereas, the second one is bound twice as weak, by 96 kJ mol^{-1} [140]. The C_4H_4 intermediate is even more strongly bound to the Pd atom than two adsorbed C_2H_2 molecules. A single adsorbed acetylene molecule is more activated than the second one, implying that the electron density on Pd is essential for promoting the activation. The next step, $Pd(C_4H_4) + C_2H_2 \rightarrow Pd(C_4H_4)(C_2H_2) \rightarrow Pd(C_6H_6)$, requires that the Pd atom coordinates and activates the third acetylene molecule. Yet, C_2H_2 interacts very weakly (<30 kJ mol^{-1}) with $Pd(C_4H_4)$ and the structure of this third molecule is not deformed by the interaction. This shows that, unlike the experimental finding for Pd_1/MgO, isolated Pd atoms cannot catalyse the cyclotrimerization.

Therefore, the interactions with the support are crucial for the reactivity of Pd atoms. One could assume that either positive or negative charge of supported Pd atoms causes their activation. The bonding of acetylene to a d-metal is described as σ donation from its filled bonding orbital to empty states of the metal and π back-donation from the occupied d orbitals of the metal to empty antibonding π^* orbitals of C_2H_2 [142,143]. Both mechanisms result in weakening of the C–C bond and distortion of the molecule. Calculations showed that both negative and positive charge artificially added on a Pd centre, makes the bonding of C_2H_2 molecule to the intermediate $Pd(C_4H_4)$ stronger. However, a substantial activation of this acetylene molecule was found only for electron-enriched Pd atoms [140]. Thus, increase of the electron density on Pd appears to be a mechanism to enhance the reactivity of the metal.

The activation of C_2H_2 is more efficient on Pd located on the MgO(1 0 0) surface compared to an isolated Pd atom. The distortion of C_2H_2 adsorbed on Pd changes as follows: corner > edge > terrace > free atom. The amount of the electron density transferred from C_2H_2 to Pd or to Pd_1/MgO is similar in all systems studied. It is notably smaller than the opposite charge transfer, to C_2H_2. The donor ability (basic character) of deposited Pd increases depending on the site on MgO it occupies, from terrace to edge and to corner, in accord with the calculated deformation of the adsorbed C_2H_2 molecule. Thus, the substrate directly modifies the properties of supported Pd atoms, and low-coordinated sites are more active than regular ones on terraces.

The catalytic activity of a deposited Pd atom could be promoted by various surface irregularities on MgO, e.g., morphological defects, mono-vacancies or di-vacancies, impurity atoms. To examine which defects are important for the acetylene trimerization, the structure and stability of Pd atoms as well as $Pd(C_2H_2)$, $Pd(C_2H_2)_2$, $Pd(C_4H_4)$ and $Pd(C_2H_2)(C_4H_4)$ complexes on regular and defect sites at the MgO surface were calculated [141]. In particular, complexes on O^{2-} sites as well as on neutral (F_s) and charged (F_s^+) surface oxygen vacancies were addressed. A Pd atom bound at terrace O_{5c} sites is found to be able to attach and activate one or two acetylene molecules and to form a stable $Pd(C_4H_4)$/complex, whereas (similarly to an isolated Pd atom) a third acetylene molecule is not activated. Neither low-coordinated O anions appear to increase the catalytic activity of supported Pd_1. At variance, Pd atoms on variously located F_s and F_s^+ vacancies not only form a stable $Pd(C_4H_4)$ complex but also notably stabilize (activate) a third acetylene molecule; its bond to the supported $Pd(C_4H_4)$ complex reaches 200 kJ mol^{-1} for F_s centres formed by a missing O_{3c} atom. It is, thus, concluded, that F_s centres are able to promote the catalytic activity of the deposited Pd atoms [141].

The studies of the acetylene cyclization to benzene on Pd atoms supported on MgO showed that only in the presence of surface defects can a single Pd atom become catalytically active. Oxide supports may act very similarly to a polydentate ligand in coordination chemistry [144]. The MgO support is seemingly not inert and reinforces donation of electron density to the hydrocarbon adsorbed on Pd. However, Lewis basicity of O anions on the MgO(0 0 1) surface is apparently too weak to notably increase the electron density on the metal, and thus, to significantly change the catalytic activity of supported Pd. Differently, the oxygen vacancies are good basic sites due to the electron density left in them by the missing atom. They promote the activity of a deposited Pd atom to catalyse the acetylene trimerization.

6.2. Propyne coupling on Cu(1 1 1)

In principle, one would expect that the cyclotrimerization process of acetylene occurring on Pd, and possibly on other metallic surfaces, will also occur in a similar fashion for other alkynes of increasing complexity. Hence, the catalytic coupling of propyne on Pd and Cu surfaces was studied using surface science techniques [138]. Dimerization to benzene is observed for Cu(1 1 1), whereas, cyclotrimeriza-

tion to trimethylbenzene is found to happen on Pd(1 1 1). To shed light on the reasons of different chemistry exhibited by these two metal surfaces, the mechanism of coupling of propyne on Cu(1 1 1) has been studied with the help of DF cluster [145,146] and slab-model [146] calculations.

The cluster model used in both works was too small to reach a quantitative description of the adsorption energy and geometry of propyne on Cu(1 1 1) [145,146]. Yet, these cluster model calculations served to illustrate how the gas phase reaction helps to understand the key features of the surface catalysed process. According to the DF calculations, the gas phase dimerization is highly disfavoured because of the energy required to promote propyne to the triplet state; otherwise the reaction cannot take place. The promoted propyne has to undergo a subsequent isomerisation process to vinylcarbene to allow head-to-tail or head-to-head coupling resulting in 1,4- and 1,3-cyclohexadiene intermediates, respectively. The DF calculations show that on the Cu surface propyne is adsorbed in a geometry very close to that of gas phase propyne in the triplet state (Fig. 3), notice that gas phase propyne exhibits in the ground state a linear C–C–C skeleton. Therefore, the activation of the reacting molecules does not require any extra energy expense. In addition, vinylcarbene biradicals may form at the surface because the isomerisation does also proceed (thermodynamically) with no further energy cost. Both head-to-tail and head-to-head interactions suggested by experiments [138] are possible, leading to cyclohexadiene (1,4-cyclohexadiene and 1,3-cyclohexadiene), which can undergo dehydrogenation to yield benzene and H_2 at moderate energy cost.

This example shows that a simple model – not free from computational and physical approximations – can provide very useful information regarding the key molecular steps of a complex chemical reaction catalysed by a metal surface. Improving the level of calculation may lead to some variations in the energy profile but it is most unlikely that the qualitative picture will be changed. Of course, a complete description of the reaction requires determination of *all* involved isomers and transition state structures, as well as the energy barriers between the different intermediates. The recent improvement of DF computational codes and hardware will surely make such wide-scale calculations almost routine in the near future.

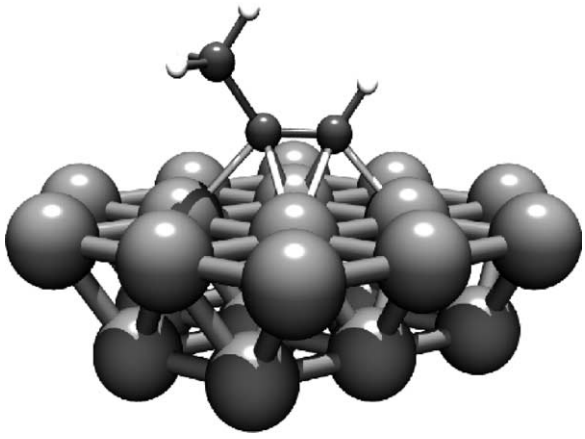

Fig. 3. Structure of propyne molecule adsorbed on Cu(1 1 1) surface as obtained from periodic DF calculations. Note, that the C atoms attached to the surface exhibit a sp^2-like hybridisation.

7. Conclusions and outlook

Above, we presented a brief account of the research opportunities offered by modern high-level DF electronic structure methods to address a variety of problems pertinent to heterogeneous catalysis. As examples, we selected recent and older DF case studies related to such diverse issues as: (i) description of the structure, bonding and vibrations of adsorption complexes on metal surfaces, including electrochemical environment, (ii) accuracy of calculated energies characterizing adsorbate–substrate interactions, (iii) transition metal nanosize clusters as models of both single crystal surfaces and supported catalysts, (iv) central role of defect sites in catalytic transformations, exemplified by very important process of N_2 activation, (v) cyclotrimerization of alkynes on model metal catalysts ranging from single supported Pd atoms to single crystal Cu(1 1 1) surface.

As one could see, the dynamics of developing DF studies undertaken during the past decade is really amazing. Simple cluster models treated at LDA level and not at all pretending to quantify energetic aspects have been substituted by sophisticated periodic slab- and size-converged cluster models capable, due to GGA and hybrid exchange–correlation functionals employed, to accurately represent not only adsorption (and reaction) energies, but also those of transition states (and reaction barriers) under scrutiny. Furthermore, a striking progress has been reached lately in increasing complexity of the systems addressed—from monoatomic and diatomic adsorbates interacting presumably with regular sites of idealised substrates to molecular species of 10 atoms or more formed on catalysts comprised of more than one component and emerging distinct defects.

Thus, not only has the application scope of DF calculations been recently extended dramatically but also their precision has been significantly improved. However, speaking on the latter issue, one has to confess that the accuracy of contemporary DF results is still not always sufficient. There are (fortunately, well-identified by now) application areas, where alternative methods – usually much more computationally extensive – remain unavoidable. Just to mention few of such problematic cases, one can note that significantly improved GGA energetics over the LDA ones does not necessarily mean also more accurate structural and vibrational parameters, often vice versa, especially when interactions with TM systems are inspected; a ‘‘universal’’ exchange–correlation functional that furnishes equally high accuracy for the whole set of calculated observables of the latter systems is still to be provided [147]. Moreover, the limitations of DF approaches to adequately describe weakly

interacting systems, selected magnetic systems and adsorption complexes with a ''normal'' strength of bonds but on the substrates where a forbidden gap is significantly underestimated in DF studies (which is often the case) should also be reiterated here. More difficult cases and limitations are considered above.

So far, we only very briefly touched (see Section 4.1) an important problem of drastic rearrangements of the structure and stoichiometry of catalysts possible at reaction conditions typical for industrial processes. The latter commonly require high pressure and elevated temperature at variance with model surface science measurements, performed at ultra-high vacuum and liquid nitrogen temperatures, and with DF calculations corresponding to 0 K. Not until very recently has it been possible to address effects of catalysts rearrangement in great detail. Oxidation of TM catalysts is probably a process most thoroughly studied to date both experimentally, e.g. [148–150], and by means of DF calculations (see, Refs. [150–152] and references therein).

Notwithstanding the remaining problems, DF methods are certainly established as very useful computational tools. In particular, they deliver such information on catalytically relevant systems that is essentially inaccessible to experiment and allow to rationalise measured data as well as to examine models and hypotheses based on the latter. No doubt, the present DF studies are harbingers of even more fascinating calculations of reactions on various model catalysts, closer and closer approaching the complexity of real catalytic systems.

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