Theor Chim Acta (1996) 94: 297–310

Theoretica
Chimica Acta

DFT and MO calculations of atomic and molecular chemisorption energies on surface cluster models

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Received March 11, 1996/Final version received June 10, 1996/Accepted June 18, 1996

Summary. Density functional theory (DFT) (including gradient corrections) and MCPF calculations have been performed for atomic (H, C, N, O) and molecular CH_x ($x = 1$–3) chemisorption on cluster models of different sites of the Cu(1 0 0) surface. The DFT and MCPF results are in good agreement once the important effects of core–valence correlation have been accounted for in the MCPF calculations by including contributions from a core polarization potential (CPP); in the DFT approach the core–valence correlation is obtained directly from the total density using the functional. Very large effects on the four-fold hollow site binding energy from core–valence correlation are found for C, N and CH. Several different DFT functionals were employed and compared in the calculations.

Key words: Metal cluster – Chemisorption – DFT – Core–valence correlation

Introduction

Density functional theory (DFT) has in the recent years emerged as a computational approach of comparable accuracy to the traditional correlated quantum chemical methods (see e.g. [1, 2]). In the DFT formalism exchange and correlation are described by a functional of the density and the computational cost is in principle comparable to a Hartree–Fock calculation. The inclusion of an estimate of the dynamical correlation energy at low cost makes DFT a very attractive alternative to standard correlated calculations. One important area of application is to problems involving chemisorption and reactions on metal surfaces for which the usual cluster models could be extended with respect to the number of atoms while still including the important effects of dynamical correlation.

All computational models which are used today in theoretical studies of chemisorption processes and reactions on solid surfaces have weaknesses, and in order to assess the applicability of the different models it is very important to make comparative studies. An agreement between the molecular orbital (MO)-based method including correlation and the DFT method for small clusters is an essential step to verify both models. Atomic chemisorption on copper clusters and surfaces are processes which are particularly well suited for a comparative study since the essentially closed Cu $3d^{10}$ shell removes uncertainties of $3d$-shell spin couplings;

furthermore some experimentally determined properties of adsorption of hydrogen, nitrogen and oxygen on copper surfaces have been reported in Refs. [3–11].

In particular, hydrogen and oxygen adsorption on the Cu(1 0 0) surface have been extensively studied theoretically using molecular orbital-based cluster models by, e.g., Panas et al. [12, 13], Pettersson et al. [14, 15], Bagus and coworkers [16, 17], and Madhavan et al. [18]. A large number of papers dealing with oxygen chemisorption on Cu(1 0 0), using a five atom cluster to model the surface has also been produced by Illas et al. [19–22]. Both the extent of 3*d* participation in the bonding and the effects of including core (3*d*) correlation has caused substantial debate and, in particular, the importance of 3*d* correlation could still be a cause for concern. Illas et al. [19] report a decreased binding energy of oxygen to a Cu_5 cluster as the result of including core–valence correlation effects modelled by a core-polarization operator, while Pettersson et al. [15] report an increase in the binding energy by 15 kcal/mol; the latter value is in good agreement with large-scale core-correlated calculations [15]. In the present work, we perform a comparative study of H, C, N and O atomic chemisorption at the four-fold hollow site of Cu(1 0 0) using both the approximately size-extensive modified coupled pair functional (MCPF) method and DFT calculations to calculate the correlation energy. In the DFT calculations several different exchange and correlation energy functionals are applied.

Core–valence correlation effects turn out to be extremely important, in particular in the cases of C and N atomic chemisorption; only after including an estimate of these effects in the MCPF calculations are the results brought into agreement with the DFT predictions. The inclusion of core–valence correlation is found to lead to sometimes substantially increased chemisorption energies in agreement with Ref. [15].

CH_x fragments are believed to be important intermediates in several catalytic processes on transition metal surfaces. Three such processes are the Fischer–Tropsch synthesis [23], olefin metathesis [24] and alkane activation [25]. Over the years there have been several theoretical studies of the stabilities of hydrocarbon fragments on transition metal surfaces, in most cases using extended Hückel band structure calculations [26–28] or the semiempirical bond-order conservation model by Shustorovich [29]. *Ab initio* treatments have been reported by Upton [30], Schüle et al. [31], and Siegbahn et al. [32]. In the work of Zheng et al. [26] the bonding of CH_3, CH_2, and CH fragments of Ti(0 0 0 1), Cr(1 1 0), and Co(0 0 0 1) metal surfaces was examined using extended Hückel band structure calculations on two-dimensional slabs of metal and adsorbate. From this study they concluded, in agreement with earlier extended Hückel calculations, that CH_3 prefers the on-top, CH_2 the bridging, and CH the capping geometry. The chemisorption energies for the fragments in their stable sites were found to decrease with increased *d*-band occupation.

In the theoretical study by Schüle et al. [31], molecular orbital calculations including electron correlation were performed for methyl absorbed on cluster models of the Ni(1 1 1) surface. In contradiction to the results of Ref. [26] methyl was found to adsorb at the three-fold hollow site rather than on-top of a Ni atom; the computed chemisorption energy was reported to be in the range of 50–55 kcal/mol. In Ref. [32] Siegbahn et al. describe a theoretical study of CH_x chemisorption on the Ni(1 0 0) and Ni(1 1 1) surfaces. Based on bond-prepared clusters and using large basis sets and multi-reference correlation treatments, they obtained values for adsorption on the Ni(1 0 0) surface of 136, 91 and 49 kcal/mol for CH, CH_2, and CH_3, respectively, with similar stabilities for the Ni(1 1 1) surface.

In the present study we have performed calculations on the stability of CH_x fragments as well as the atoms (H, C, N, O) on cluster models containing up to thirteen metal atoms of the clean Cu(1 0 0) surface in the framework of both the DFT method, using non-local corrections to the energy, and the molecular orbital method. Except for the Cu_{13} and Cu_8 clusters all atoms in the clusters were described at the all-electron level in the MCPF calculations, whereas at DFT only for Cu_{13} cluster the atoms were not described at all-electron level. In the molecular orbital calculations both valence and core–valence correlation were taken into account through a valence correlation treatment combined with a core-polarization potential [33, 34]; in particular, for atomic carbon, nitrogen and for CH adsorption core–valence correlation was found to have dramatic effects on the chemisorption energy and to be necessary to include in the MO-based calculations in order to obtain agreement with the DFT results.

Computational details

Computational model

The Cu(1 0 0) metal surface was modelled by a Cu_5 cluster for the four-fold hollow site and by Cu_2, Cu_6 and Cu_8 clusters for the bridge chemisorption. The bulk bond distance $4.8304a_0$ [35] was used for all clusters and kept fixed during the geometry optimization procedure. The cluster calculations were done using both the DFT method and the conventional molecular orbital (MO) approach. In the DFT calculations we used the linear combination of Gaussian-type orbitals – density functional theory (LCGTO–DFT) program deMon [36, 37] and the DFT facilities included in Gaussian94 [38]. Several different functionals were employed in the DFT calculations. The gradient corrections due to Perdew and Wang for the exchange functional [39], and by Perdew for the correlation [40] (PW86) were used in deMon. The Gaussian94 calculations were performed using the BP86 [38, 41, 40], and the mixed B3P86 [38, 42, 40] and B3LYP [38, 43] functionals; the latter mix in also Hartree–Fock exchange in the exchange functional. The B3LYP functional can be written as

$$F^{\mathrm{B3LYP}} = (1 - A) * F_{\mathrm{x}}^{\mathrm{Slater}} + A * F_{\mathrm{x}}^{\mathrm{HF}} + B * F_{\mathrm{x}}^{\mathrm{Becke}} + C * F_{\mathrm{c}}^{\mathrm{LYP}} + (1 - C) F_{\mathrm{c}}^{\mathrm{VWN}}$$

where $F_{\mathrm{x}}^{\mathrm{Slater}}$ is the Slater exchange, $F_{\mathrm{x}}^{\mathrm{HF}}$ is the Hartree–Fock exchange, $F_{\mathrm{x}}^{\mathrm{Becke}}$ is the gradient part of the exchange functional of Becke [43], $F_{\mathrm{c}}^{\mathrm{LYP}}$ is the correlation functional of Lee, Yang and Parr [44] and $F_{\mathrm{c}}^{\mathrm{VWN}}$ is the correlation functional of Vosko, Wilk and Nusair [45]. A, B and C are the coefficients determined by Becke [43] using a fit to experimental heats of formation for a set of 55 first and second row molecules. However, it should be noted that Becke did not use $F_{\mathrm{c}}^{\mathrm{LYP}}$ in the expression above when the coefficients were determined, but instead the correlation functional of Perdew and Wang [46].

The correlation method chosen in the MO calculations was the modified coupled pair functional (MCPF) method [47], which is an approximately size-extensive, single reference state correlation method. The zeroth-order wave functions were determined at the SCF level. All the valence electrons for first-row atoms and the 4*s* electron for copper were correlated. Core–valence correlation involving excitations from the metal *d*-shell was accounted for through the core-polarization potential (CPP) operator suggested by Müller and Meyer [33]. The method includes two parameters, core polarizability (α_c) and a cut-off distance (ρ_c). Normally, α_c is taken from experiment or from an extended basis set calculation and ρ_c is fitted to reproduce the experimental ionization potential in an SCF calculation on the single-valence electron atom or ion. The ρ_c parameter was reoptimized for the present Cu basis set resulting in $\rho_c = 1.4646a_0$ maintaining the polarizability $\alpha_c = 6.428$. The CPP method applied to transition metal atoms has been described in Ref. [34, 48]. The STOCKHOLM [49] set of programs was used for the correlation treatment and point-by-point optimization of the geometries was performed at the MCPE + CPP level.

When a finite cluster is used to model a metal surface, care must be taken in the evaluation of chemisorption energies. If the ground state of the chemisorbed system does not correspond to the ground state of the "naked" cluster, large oscillations of the chemisorption energies with the cluster size will be obtained if the ground state energy of the "naked" cluster is used in computing the chemisorption energy. This situation can be radically improved if the naked cluster is prepared for bonding according to the principles detailed in Refs. [12] and [50]. This procedure has been applied to the calculation of all chemisorption energies in the present work.

Basis sets

The DFT calculations using the deMon program employ, in addition to the normal (GTO) orbital basis set, two auxiliary bases for the expansion of the Coulumb and exchange-correlation potentials (V_{xc}), respectively. The auxiliary basis for the Coulomb potential reduces the two-electron Coulomb integrals to three-index quantities, while the exchange-correlation auxiliary basis is only used to speed up the numerical integration in each iteration by allowing the use of a smaller grid. The radial grid used to optimize the density consisted of 32 shells with 194 angular points per shell and atom for the fitting of the auxiliary basis coefficients, while the numerical integration for the final energy was done on a much finer grid.

The auxiliary basis used for hydrogen in the DFT calculations was (3,1;3,1) [51] consisting of 3/1 exponents for the inner/outer parts of the Coulomb potential and of V_{xc}, respectively. The inner part uses only *s*-type functions, while for the outer part *s*-, *p*- and *d*-functions having the same exponents are generated. For copper the original (5,5;5,5) basis by Godbout et al. [51] was used, while for carbon and oxygen (5,2;5,2) and (4,4;4,4) sets were used, respectively. The all-electron orbital basis set for Cu was that of Wachters [52] using a [5*s*, 4*p*, 4*d*] contraction with two diffuse *p* functions and one *d* function added. For hydrogen the primitive (5*s*) basis set from Ref. [53] was used, augmented with one *p* function and contracted to [3*s*, 1*p*], while for carbon and oxygen triple-zeta valence polarization (TZVP) [54] was used in a generalized [4*s*, 3*p*] contraction and with one added *d* function.

The basis sets used in the MO (SCF/MCPF) calculations were of double-zeta plus polarization type: for copper Wachters' (14*s*, 11*p*, 6*d*) primitive basis set [52] was used augmented with two diffuse *p* functions and one *d* function, contracted to [5*s*, 4*p*, 2*d*] using the Rafenetti general contraction procedure [55]. For first-row atoms the primitive (9*s*, 5*p*) basis of Huzinaga [53] was used, contracted to [3*s*, 2*p*] and with one *d* function added.

For the Cu_{13} cluster we used a mixed model with the Cu atom directly below the adsorbate described at the all-electron level while one-electron ECP:s were used for the remaining 12 copper atoms. Similarly, the calculations on the Cu_8 cluster were also done using a mixed model with the two copper atoms at the bridge positions described at the all-electron level, while one-electron ECP:s were used for the six remaining Cu atoms. The Cu_8 cluster model was calibrated against all-electron calculations on Cu_6O.

Results and discussion

The core-polarization potential that is employed in the present work is based on the electric fields felt by the cores, but acts only on the valence electrons. This requires a clear separation of the core and valence spaces, making this approximation more rigorous with increasing separation between interacting systems. Since the core in the case of Cu includes the highly polarizable 3*d*-orbitals it becomes particularly important to have reliable reference calculations in cases of short bond distances, such as encountered for C and N chemisorption in the present case. Previous tests have included calculations with explicit 3*d* correlation using large basis sets of Cu_5H and Cu_5O and smaller molecules [15, 48]. In the present case a comparison is done with different DFT approaches as a consistency of both methods. Furthermore, the implementations in deMon and Gaussian94 differ through the use of an auxiliary basis set in deMon for the Coulomb and grid work while Gaussian94 computes all Coulomb integrals using the four-center expressions.

Four-fold hollow site

The question of bond preparing the cluster [50] naturally arises when the chemisorption of several different species are to be compared. Fortunately, in the case of the Cu_5 cluster the $^4A_2$ state, with three open shells in the a_1 and the e symmetries (in C_{4v} notation), is a low-lying state and this cluster state is prepared for bonding for all species in the present study.

For H, C, O and CH chemisorption at the four-fold hollow site the geometries were optimized both at the MCPF + CPP and the DFT levels (using deMon). For the remaining systems the geometry was optimized using deMon and the resulting geometry used also in the MCPF + CPP calculations. The geometries used in the calculations are shown in Table 1 and the contribution of the CPP operator to the chemisorption energies at the given geometry is given in Table 2.

The computed bond distances on the five-atom cluster show a rather large spread between the methods: for hydrogen the computed distance to the surface is $2.26a_0$ at the DFT level compared to $2.34a_0$ for the CPP-corrected MCPF value; the difference from the earlier reported CPP result [48] can be ascribed to the different basis sets used. For the CH chemisorption the difference is larger, $0.25a_0$, while for the C and O adsorbates that approach the surface very closely the difference is about $0.4a_0$. The experimental values for carbon, oxygen and nitrogen are rather uncertain, bond distances between 1.2 and $1.5a_0$ have been reported for oxygen [5, 18], and between 0.40 and $0.70a_0$ for nitrogen [8, 9], while carbon seems to enter or penetrate the surface [32]. Bond distances calculated at the DFT level, except for the value for nitrogen, seem to be long compared with experiment, while

Table 1. Geometries (a_0) optimized at the DFT and MCPF + CPP levels. Experimental values are for oxygen between 1.2 and $1.5a_0$, and for nitrogen between 0.40 and $0.70a_0$

Cluster	DFT		MCPF + CPP	
		Four-fold site		
	Height above surface	Cu–X	Height above surface	Cu–X
Cu_5H	2.26	4.09	2.34	4.14
Cu_5C	0.83	3.51	0.40	3.44
Cu_5N	0.68	3.48	—	—
Cu_5O	1.86	3.89	1.20	3.62
Cu_5CH	1.80	3.86	2.05	3.98
Cu_5CH_2	2.39	4.17	—	—
Cu_5CH_3	4.17	5.39	—	—
		Bridge site		
	Height above surface	Cu–X		
Cu_2O	2.36	3.38		
Cu_5O	2.36	3.38		
Cu_2CH_2	2.65	3.59		
Cu_8CH_2	2.65	3.59		
		On-top site		
Cu_1CH_3		3.61		
$Cu_{13}CH_3$		3.61		

Table 2. Effects of the core-polarization potential on chemisorption energies (in kcal/mol) on Cu(1 0 0). Comparison with DFT values from deMon using the PW86 functional

Cluster	SCF+MCPF	CPP	TOTAL	DFT
		Four-fold site		
Cu_5H	42	1	43	48
Cu_5C	66	93	159	145
Cu_5N	50	73	123	109
Cu_5O	79	32	111	106
Cu_5CH	96	45	141	136
Cu_5CH_2	45	21	66	68
Cu_5CH_3	18	0	18	21
		Bridge site		
Cu_2O	59	16	75	96
Cu_8O	38	24	53	68
Cu_2CH_2	44	28	72	85
Cu_8CH_2	40	35	64	62
		On-top site		
Cu_1CH_3	37	14	49	62
$Cu_{13}CH_3$	—	—	—	56

the MCPF + CPP geometries seem to be more in line with the experimental data. However, the clusters are rather small and the energy surfaces quite flat, so good agreement with experiment on the adsorbate to surface distances is perhaps not to be expected.

The second column in Table 2 shows the CPP effect on the chemisorption energy taken as the difference between the MCPF + CPP and MCPF results at the MCPF + CPP optimized geometry. The effects of the carbon, nitrogen and methyne chemisorption energies are dramatic with energy contributions of 45–93 kcal/mol: for the two former species more than half the chemisorption energy is due to the CPP operator. After inclusion of this effect the comparison with the DFT result is quite favorable: differences of 2–5 kcal/mol for hydrogen, oxygen, and the hydrocarbons, while the differences are 14 kcal/mol for carbon and nitrogen. Comparing with the results using other functionals (see below) it seems likely that the CPP operator in the carbon and nitrogen cases slightly overestimates the effects of core–valence correlation.

No experimental determination of either the carbon or the nitrogen atomic chemisorption energies on copper has to our knowledge been reported in the literature. The chemisorption energy for atomic nitrogen on Ni(1 0 0) has been determined by desorption experiments to 135 kcal/mol [56] assuming no barrier for desorption of N_2. Since N_2 is known to have an activation barrier for dissociation on nickel surfaces, the correct chemisorption energy for atomic nitrogen could be substantially below this value; in Ref. [57] Panas et al. suggested a chemisorption energy for nitrogen on Ni(1 0 0) of about 120 kcal/mol. Experimental chemisorption energies have been published for hydrogen and oxygen on copper. Ertl [58] reports a chemisorption energy of 56 kcal/mol for hydrogen, and values in the range 105–120 kcal/mol have been reported for oxygen [3, 4]. Our calculated binding energies are in good agreement with these results, considering the small cluster used in the investigation. The present results are furthermore in agreement with previously reported theoretical values for hydrogen and oxygen chemisorption with the CPP operator included [15, 34]. The approach used by Illas et al. [19], which results in a decreased chemisorption energy when core–valence correlation effects are included, is in contradiction both with the MCPF + CPP and DFT results as well with earlier explicitly core-correlated results [15].

The four-fold hollow site is the preferred adsorption site for methyne at both the DFT and the molecular orbital levels, while the methyl radical adsorbs at the on-top position; the case of methylene is less clear, but the present calculations give a slight preference for the four-fold hollow site (see below). CH adsorbs with the C–H bond perpendicular to the surface, the carbon pointing downwards. The equilibrium distance between the methylene carbon and the surface, calculated using the DFT method, is $2.39a_0$ at the four-fold hollow site (for methylene and for methyl no separate geometry optimization was carried out using the molecular orbital method). For methyl the distance to the surface at the four-fold position is quite large, $4.2a_0$, and the CPP effect in the molecular orbital picture is accordingly small, less than 1 kcal/mol; the calculated binding energies using the DFT and the molecular orbital method are the same, 21 kcal/mol.

The binding energy of methyne at the MCPF level is 96 kcal/mol. The contribution from the CPP operator is in this case 45 kcal/mol, which is about half of the CPP effect for the carbon atom and 62% of the effect on the iso-valent nitrogen atom. The resulting binding energy is 141 kcal/mol, in quite good agreement with the DFT result. The present results can be compared to the estimate of 136 kcal/mol for the chemisorption of methyne on a nickel surface by Siegbahn and Panas [32].

For methylene the MCPF chemisorption energy is 45 kcal/mol. The CPP effect is 21 kcal/mol, thus increasing the binding energy to 66 kcal/mol. The binding energy obtained from the DFT calculations is 68 kcal/mol, is excellent agreement with the CPP corrected MCPF result. The CPP effect on the methylene binding energy is only about half of the corresponding effect for methyne. It is interesting to note that the CPP effect for methyne decreases from 45 to 38 kcal/mol when the distance between the adsorbate and the surface is increased from 1.80 to $2.39a_0$. Methylene absorbs $2.39a_0$ above the surface with a CPP effect of only 21 kcal/mol. This means that about one-third of the difference in the CPP effect between methyne and methylene can be attributed to the difference in the adsorbate-surface distance, while the remainder is due to the difference in the binding; the number of "covalent" bonds between the surface and the adsorbate is three for methyne and two for methylene.

When the symmetry restriction to four-fold hollow chemisorption is removed in the geometry optimization of methyl on Cu_5 (allowing a complete relaxation of the methyl group), the methyl moves away from the four-fold towards an on-top position. The on-top chemisorption energy was estimated by calculations using a single Cu and a thirteen atom cluster with one all-electron copper atom (directly below the methyl group) surrounded by twelve Cu atoms (8 in the first and 4 in the second layer) described by effective core potentials (ECP) including the $3s$, $3p$ and $4s$ electrons as valence [59]. The binding energy for Cu_1 is about 49 kcal/mol at the MCPF + CPP level and 62 kcal/mol using the DFT method. The effect of adding a surrounding of twelve copper atoms (described at the ECP level) is at the MCPF + CPP level to increase the binding energy by 4 kcal/mol while the binding energy calculated by the DFT method decreases by 6 kcal/mol. The decreased binding energy obtained by the DFT method may be due to some imbalances between the all-electron and the ECP atoms at the DFT level. All calculations agree on a chemisorption energy in the vicinity of 60 kcal/mol, however, and that the chemisorption occurs at an on-top position. It should be noted that for CH_3 on both Ni(1 0 0) and Ni(1 1 1) the hollow position was found to be the most stable [32, 60].

The methyl group is from the point of view of the surface-adsorbate bond iso-electronic with hydrogen. Hydrogen adsorbs at a four-fold hollow position on Cu_5 with a chemisorption energy in the vicinity of 50 kcal/mol, compared to about 20 kcal/mol for CH_3 at the four-fold hollow position. This large difference between the two species can be explained by the directionality of the singly occupied orbital on methyl.

The agreement between the DFT and the molecular orbital results is reasonable after the CPP effect has been added to the MCPF binding energies. This agreement provides strong support for the importance of core–valence correlation effects in describing chemisorption and furthermore shows that both from DFT and the CPP operator very similar values for the contribution of core–valence correlation effects are obtained. In particular, it underlines the importance of including an estimate of these effects in comparing DFT results with MO-based methods and in the evaluation of chemisorption energies.

Bridge site

For the methyne radical it is clear that the hollow position is the preferred chemisorption site. It is also clear that the methyl radical will chemisorb at the on-top position on Cu(1 0 0). The case of methylene is not as easily resolved, however; using the minimal size Cu_2 cluster to represent the bridge position gives a preference for the bridge site. However, the Cu_2 cluster is too small to give reliable predictions and larger cluster models (Cu_6 and Cu_8 in the present work) must be used. Earlier work using extended Hückel theory [26] on Ti(0001), Cr(110) and Co(0001) has suggested a preferred bridge chemisorption in these systems, which, if true also for Cu(100), would make CH_2 rather different from the iso-electronic oxygen atom. The latter chemisorbs in the four-fold hollow position with an experimentally determined barrier to diffusion over the bridge site of the order of 20 kcal/mol.

Even though the two-atom cluster is too small for modelling a surface the results can anyway be of some interest in the comparison of DFT and MO-based approaches and will thus be included below. Since clusters modelling two different chemisorption sites are to be compared, all clusters must be bond-prepared in order to make a meaningful comparison. At short distances the ground state of Cu_2O is $^1A_1$ (in C_{2v} notation) with the valence electron configuration $(1a_1)^2(a2_1)^2(1b_1)^2(1b_2)^2$, and similarly for methylene. The bare Cu_2 system is a closed-shell singlet with the valence electron configuration $(1a_1)^2$. Cu_2 (and Cu_6 and Cu_8) is thus prepared for bonding to both oxygen and methylene according to the principles ("singlet oxygen interaction") in Ref. [61].

The basis set superposition error (BSSE) has been previously studied for Cu_5O by Pettersson et al. [15] when different number of electrons are explicitly correlated. For the large calculation it was only 6 kcal/mol, and 2 kcal/mol when only valence electrons are correlated. In this study we have computed the BSSE for the smallest systems when the d electrons were included in the correlation. It gives 9 kcal/mol for Cu_2O and Cu_2CH_2, and 6 kcal/mol in Cu_1CH_3.

The oxygen binding energy to Cu_2 is 75 kcal/mol at the MCPF + CPP level compared to 72.0 kcal/mol when also the $3d$-orbitals are included in the correlation and the basis set superposition error (BSSE) is accounted for. The corresponding binding energy on Cu_5 is 111 kcal/mol (see Table 2) indicating a barrier to migration of the order of 30–40 kcal/mol, which is almost twice what has been reported in previous molecular orbital results [13]. In the previous work [13] effects of core–valence correlation were not included; these are found to increase the barrier by some 16 kcal/mol in the present work. The corresponding DFT results for the bridge and four-fold hollow positions are 96 and 106 kcal/mol, respectively, and thus a very much lower barrier (10 kcal/mol) is predicted. However, both the molecular orbital and the DFT calculations thus predict the four-fold hollow position to be the preferred chemisorption site with a substantial barrier to surface migration in the former case.

The binding energy of the methylene radical to Cu_2 is 72 kcal/mol and to Cu_5 66 kcal/mol at the MCPF + CPP level; the former value becomes 69.0 kcal/mol when explicit $3d$-orbital correlation and BSSE are included in place of the CPP operator. The corresponding DFT results for bridge and hollow chemisorption are 85 and 68 kcal/mol, respectively. Both calculations thus appear to predict a preferred bridge adsorption site, substantially below the four-fold site (17 kcal/mol) at the DFT level, but only by 6 kcal/mol at the MCPF + CPP level.

Increasing the size of the cluster has quite large effects on the bridge chemisorption energies (Tables 2 and 3): going from Cu_2 to the planar Cu_6 model reduces the computed bridge binding energy of oxygen by 16 and 22 kcal/mol at the MCPF + CPP and DFT levels, respectively. Including two second-layer atoms (all-electron in the DFT calculation, ECP description [59] in the MCPF calculation), completing the four-fold hollow sites surrounding the central bridge position, results in a further decrease of 6 kcal/mol of the binding energy in both treatments. The energy difference between bridge and four-fold hollow has thus become 58 kcal/mol (MCPF + CPP) and 38 kcal/mol (DFT). Although our results seem far from converged with respect to cluster size it is clear that for the oxygen chemisorption, the four-fold hollow position is favored by a substantial amount. In fact, the large values for the energy difference between the hollow and bridge positions would indicate that, e.g., surface phonons should be active in reducing the computed static barrier in the experimental situation.

The situation for CH_2 with respect to increasing the cluster size is similar to that of oxygen, but the effects are smaller. In going from Cu_2 to Cu_8 the binding energy is reduced by 8 kcal/mol at the MCPF + CPP level making the bridge position less stable by 4 kcal/mol compared to the four-fold hollow site. The reduction at the DFT level is by 23 kcal/mol down to a value of 62 kcal/mol in good agreement with the MCPF + CPP result; the resulting extra stabilisation for the hollow site thus becomes 5 kcal/mol. These energy differences are too small to allow a reliable prediction of the preferred chemisorption site from the present small sample of clusters. It is, however, interesting to note the large differences between Cu_2 and the larger cluster models; Cu_2 cannot be used to represent the bridge position in the Cu(1 0 0) surface.

Comparison between functionals

Several different pure and hybrid functionals were used in the present investigation (Table 3). In the calculations using deMon only the gradient corrections due to Perdew and Wang for the exchange functional [39], and by Perdew for the correlation [40] (PW86) were used. In Gaussian94 the calculations were performed

Table 3. Comparison of chemisorption energies (kcal/mol) calculated using MCPF + CPP correction with results using several different DFT functionals (see text)

Cluster	SCF/ MCPF/CPP (Total)	DFT (deMon) (PW86)	DFT (Gaussian94) (BP86)	DFT (Gaussian94) (B3P86)	DFT (Gaussian94) (B3LYP)
Cu_5H	43	48	48	47	45
Cu_5C	159	145	144	134	123
Cu_5N	123	109	105	93	87
Cu_5O	111	106	105	98	95
Cu_5CH	141	136	143	138	130
Cu_5CH_2	68	67	64	67	64
Cu_5CH_3	17	21	14	8	7
			Bridge site		
Cu_2O	75	96	94	81	76
Cu_6O	59	74	69	57	53
Cu_8O	53	68	61	50	45
Cu_2CH_2	72	85	83	80	75
Cu_6CH_2	63.5	62	65	60	55
Cu_8CH_2	64	62	57	58	52
			On-top site		
Cu_1CH_3	49	62	61	56	53

with the BP86 [38, 41, 40], and mixed B3P86 [38, 42, 40] and B3LYP [43] functionals.

As is immediately observed from the table the spread in computed binding energies among the different functionals is quite large, with an average absolute error for the eighteen systems of 13 kcal/mol. The smallest overall deviations are obtained for Cu_5H and Cu_5CH_2 which have a largest deviation of 3 kcal/mol among the different functionals (the MCPF + CPP binding energy results are summarized in the table for ease of comparison). Cu_5C and Cu_5N, which have short distances, give the largest deviations, 22 kcal/mol.

Two classes of functionals are included in the comparison: with and without mixing of Hartree–Fock exchange. Comparing the PW86 and BP86 results, both functionals being of the non-hybrid type, much smaller average (2.7 kcal/mol) and maximum (7 kcal/mol) deviations are obtained. In particular, for the difficult cases of carbon and nitrogen chemisorption in the four-fold hollow site the two functionals agree to within 4 kcal/mol. Similarly, a comparison between the hybrid-type functionals (B3P86 and B3LYP) is much more favorable with a 3.7 kcal/mol average and 8 kcal/mol maximum deviation.

In particular, the B3LYP functional has previously been shown to give results in very good agreement with high-level theoretical treatments or experiment, also for the difficult cases of first-row transition metal complexes. Binding energies of MCH_3^+ and MCH_2^+ have been computed for the first-row transition metals by Holthausen et al. [62, 63] and by Bauschlicher et al. [64], Ricca and Bauschlicher [65, 66] report good agreement for the bond strengths in the $Fe(CO)_5^+$ and the $Fe(CH_4^+)$ systems and similarly Barone reports good results compared to experiment for CuCO [67]. In the present case, however, it is difficult to determine which approach gives the most reliable results.

In the case of Cu_5O we may compare with earlier studies of the core–valence correlation effects on the chemisorption energy [15, 48]. In that study the 3*d*-electrons on the top four Cu atoms in the cluster were explicitly included together with the valence electrons in a CPF calculation of the binding energy. A large, flexible basis set was used to give a total computed chemisorption energy of 102 kcal/mol. Comparison with the results obtained using the CPP operator (with parameters α_c and ρ_c determined to reproduce the atomic ionization potential for Cu with the same basis set and same level of correlation) for the four top-most Cu atoms gave a very good agreement with a computed result of 100 kcal/mol. Inclusion of the second-layer copper atom was found to reduce the binding energy by some three kcal/mol giving a computed value of 97 kcal/mol. In Ref. [48] the CPP was reoptimized to reproduce the experimental ionization potential of Cu atom yielding a chemisorption energy of 108.5 kcal/mol with all five coppers included. The CPP approach when calibrated against experimental IPs could be regarded as a "complete treatment" of core–valence correlation and we believe that the remaining uncertainty for Cu_5O lies in basis set incompleteness and the correlation treatment for the valence. Thus, it is clear that 108 kcal/mol is a lower bound for the oxygen chemisorption energy into the four-fold hollow site of the Cu_5 cluster model and that the hybrid functionals in this case give too low a value for the binding energy.

A detailed comparison with the results for Cu_5N and Cu_5C is more difficult to make. The short distance and very large contribution from the approximate CPP operator make the MCPF + CPP results less reliable and, at the same time, the largest differences (22 kcal/mol) between hybrid and non-hybrid functionals are observed. However, all methods agree that the effects of core–valence correlation, taken as the difference between the valence MCPF results and the total binding energy (MCPF + CPP, DFT) are very large: for Cu_5N 37–43 kcal/mol (hybrid), 55–59 kcal/mol (BP86 and PW86) and 73 kcal/mol using the CPP operator, while for Cu_5C even larger effects are predicted.

From the spread in the results obtained using the different approaches it is clear that more work is needed before a standard procedure to perform DFT cluster calculations can be regarded as established and it is clear that care must be exercised in applying DFT, even with gradient corrections as in the present case, to the calculation of chemisorption energies on cluster models of metal surfaces.

Conclusions

The main finding in the present study is the importance of core–valence correlation effects in the chemisorption of in particular carbon, nitrogen and methyne at the four-fold hollow site of Cu(1 0 0). The core–valence correlation effect was modelled by the CPP operator and the close agreement between the chemisorption energies calculated by the DFT method and at the MCPF + CPP level provide a strong indication that the notion of a very important contribution to the binding from *d*-correlation effects is indeed correct and that this is fairly reliably given by the CPP.

The comparison of results obtained using different functionals shows that the DFT approach is not quite as standardized as one may like to believe. Rather large variations in the computed results are observed for the cluster models studied in the present work, in particular between hybrid and non-hybrid approaches. However, it is clear that the large effects of core–valence correlation are true effects and need to be included in the MCPF calculations in order to obtain agreement with the DFT calculations and experiment.

Acknowledgements. One of the authors (LT) is grateful to the Swedish Institute (SI) for partial support of this work.

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