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LETTER TO THE EDITOR

First-principles study of CO adsorption on ZnO surfaces

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Abstract
Using density-functional theory we have calculated the equilibrium geometries and binding energies of a CO monolayer adsorbed on the nonpolar $(10\bar{1}0)$ and the polar (0001)-Zn and $(000\bar{1})$-O surfaces of ZnO. Different adsorption sites and CO orientations were considered, and for the polar surfaces the influence of a hydrogen coverage upon CO adsorption was studied. For the clean surfaces we find that CO exclusively binds to Zn ions with a binding energy of 0.24 and 0.37 eV for the nonpolar $(10\bar{1}0)$ and the polar (0001)-Zn surface, respectively. A purely repulsive interaction of CO with surface oxygen ions is obtained. On the other hand, if the polar surfaces are hydrogen saturated, we predict a weak chemisorption of CO to the OH-terminated $(000\bar{1})$ surface with a binding energy of 0.20 eV but no CO adsorption for the ZnH-terminated (0001) face.

Zinc oxide is a very important material for various catalytic processes. $Cu/ZnO/Al_2O_3$ mixtures are widely employed in the commercial synthesis of methanol via the hydrogenation of CO and in the water-gas shift reaction. CO is a basic component of the feed gas in both processes. However, the adsorption of CO on clean ZnO surfaces is not well understood. The most stable surfaces of ZnO are the two nonpolar $(10\bar{1}0)$ and $(11\bar{2}0)$ faces consisting of an equal number of Zn and O ions and the two polar (0001)-Zn and $(000\bar{1})$-O basal planes containing only Zn and O atoms, respectively. Although the chemical composition of these surfaces is very different, Gay *et al* [1] found essentially the same CO adsorption energy of $(12 - 7\Theta)$ kcal mol^{-1}, depending on the CO coverage Θ, for all four surfaces with ultraviolet photoelectron spectroscopy (UPS). This observation was recently confirmed in a study of CO adsorption probabilities by Becker *et al* [2], where the same CO binding energy on the two polar surfaces was obtained, although a slightly lower adsorption energy of $(7 - 2\Theta)$ kcal mol^{-1} was found at low coverages.

This is a very surprising result and completely inconsistent with existing theoretical studies. Several semiempirical cluster calculations [3–7] as well as a detailed *ab initio* study of CO adsorption on Zn_4O_4 clusters [8] predict a modest chemisorption of CO to Zn sites but essentially no binding to O ions. Only one periodic slab calculation exists in which Jaffe and Hess [9] confirm for the nonpolar $(10\bar{1}0)$ surface using Hartree–Fock (HF) theory

that CO binds to Zn atoms but not to O ions. In view of these results, the experimentally observed CO adsorption on the O-terminated $(000\bar{1})$ surface is very puzzling. Already very early on it was speculated [1] that on the $(000\bar{1})$-O surface CO is mainly bound to Zn ions on step edges and other defects. However, such an assumption does not explain the observation in several experiments using temperature programmed desorption (TPD) [10], x-ray photoelectron spectroscopy (XPS) [11] and near-edge x-ray adsorption fine structure (NEXAFS) measurements [12] where, even at room temperature, adsorbed CO was found on the $(000\bar{1})$-O surface. The signature from XPS and NEXAFS suggests that the CO is bound in the form of carbonate species and, at higher temperatures, desorption of CO_2 was observed.

Altogether, the experimental results are severely hampered by the fact that they only obtain data integrated over the whole surface area and that they cannot distinguish between CO adsorbed on ordered surface areas or defect sites. However, for the polar ZnO surfaces it is well known that they are very inhomogeneous [2]—typically only 0.1% of the surface area consists of flat terraces with diameters exceeding 50 Å. In such a situation, theoretical calculations of adsorption energies and geometries are very helpful for the interpretation of experimental results and the understanding of the catalytic activity of such complex surfaces.

Another important aspect concerning the CO adsorption on the polar ZnO surfaces was recently discovered in He–atom scattering (HAS) experiments [13]. It was observed that O-terminated $(000\bar{1})$ surfaces with a (1×1) diffraction pattern are always hydrogen covered. Such a hydrogen termination of the $(000\bar{1})$-O surface has not been considered yet in theoretical studies and may play a crucial role in the understanding of CO adsorption on the O-terminated polar ZnO surfaces.

In the present letter we have studied the adsorption of CO on different ideal, defect-free, ZnO surfaces. For the nonpolar $(10\bar{1}0)$ surface we compare monolayer versus half-monolayer coverage and CO adsorption geometries with the C-atom ('C-down') and the O-atom ('O-down') coordinated to the surface. For the two polar surfaces, different adsorption sites are considered and we study the influence of a hydrogen coverage of the surface.

Technical details

Density-functional theory (DFT) within the PBE [14] generalized-gradient approximation was used to calculate the CO adsorption geometries and energies. Norm-conserving pseudopotentials were employed together with a mixed-basis set of plane waves and a few localized non-overlapping orbitals [15]. Very good convergence was achieved with a plane-wave cut-off energy of 20 Ryd. All surfaces were represented by periodically repeated slabs. The construction of the appropriate supercells, details on convergence parameters, k-point sampling, Brillouin-zone integration and corrections due to the electrostatic dipole moment of the slabs as well as the calculated bulk and clean surface structures of ZnO are given in [16].

Validation of the method

Some caution has to be taken when applying DFT in situations where rather weak interactions occur, like in the case of CO adsorbed on a metal oxide surface. To test the reliability of our DFT results, we have calculated the equilibrium distances and adsorption energies of CO on an isolated Zn_4O_4 cluster which we can compare with recently published results based on a particular multi-configuration coupled-cluster method ('MC-CEPA') [8]. The wurtzite-like geometry of the Zn_4O_4 cluster with H atoms bound on-top of the three-fold coordinated Zn and O atoms is shown in figure 1(a). In total we have considered eight different CO–cluster interactions: the CO molecule bound linearly with either the C or the O side to the top and

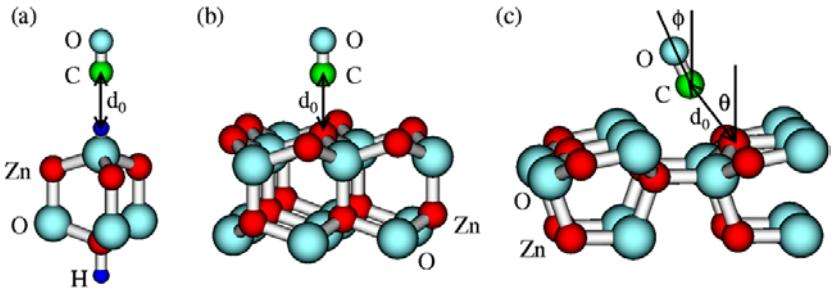

Figure 1. 'C-down' adsorption geometries of CO on (a) the Zn_4O_4 cluster with adsorbed H atoms, (b) the Zn-terminated polar (0001) surface and (c) the nonpolar $(10\bar{1}0)$ surface.

(This figure is in colour only in the electronic version)

Table 1. Equilibrium distances d_0 and binding energies E_{ad} of CO to the Zn_4O_4 cluster for different adsorption configurations. For the O–CO, O–OC, ZnH–CO and ZnH–OC geometries purely repulsive potential energy curves are found in DFT as well as at the HF level. The MC-CEPA values are taken from [8].

	PBE		MC–CEPA	
Site	d_0 (Å)	E_{ad} (eV)	d_0 (Å)	E_{ad} (eV)
Zn–CO	2.08	0.53	2.27	0.33
Zn–OC	2.51	0.10	2.46	0.08
OH–CO	2.17	0.14	2.43	0.12
OH–OC	2.28	0.05	2.30	0.08

bottom Zn and O atom of the cluster, respectively, with and without an attached hydrogen atom. The results in table 1 show that DFT reproduces very well the quantum-chemical calculations. The same trends for the different cluster terminations and orientations of the CO molecule are found with a pure repulsive interaction for the O and ZnH termination and a significantly stronger bond of the 'C-down' than the 'O-down' configuration in the other two cases. Only the strength of the Zn–C bond is slightly overestimated. But overall these results demonstrate that DFT is well suited for the study of CO adsorption on ZnO surfaces.

Nonpolar $(10\bar{1}0)$ *surface*

For the study of the CO monolayer coverage, slabs with a (1×1) surface unit cell and a thickness of six ZnO layers (thus consisting of 12 atoms) were used. For the half-monolayer coverage, the surface unit cell was doubled in the *a* direction. In the first set of calculations the atomic positions in the slab were kept fixed and were set equal to the positions of the first six layers of a fully relaxed 20-layer ZnO slab (see [16]).

We began our investigation by performing two-dimensional scans of the $(10\bar{1}0)$ surface unit cell. The CO molecule was held perpendicular to the surface, and for a mesh of 30 equally spaced positions the binding energy at the vertical equilibrium distance was determined. For both the 'C-down' and the 'O-down' orientation, we find that the surface area in the vicinity of the topmost O ion is purely repulsive and only one energy minimum close to the Zn position could be detected.

In the next step, the CO molecule was allowed to freely orientate, but the CO distance and the atomic positions in the slab were not allowed to relax (denoted as 'rigid' in table 2).

Table 2. Calculated adsorption geometries and energies E_{ad} for CO on the nonpolar $(10\bar{1}0)$ surface, compared to HF results and experimental values. '1×1' and '2×1' refer to a full and a half monolayer coverage of CO, respectively. The structural parameters d_0, θ and ϕ are defined in figure 1.

Orient.	Method	Cover.	Relax.	d_0 (Å)	θ (deg)	ϕ (deg)	E_{ad} (eV)
'C-down'	PBE	1×1	Rigid	2.51	29	26	0.16
			Full	2.24	37	25	0.24
	HF [9]		Rigid	2.71	32.5	39.5	0.17
	Exp [1]				≈30	≈30	0.22
	PBE	2×1	Rigid	2.47	28	26	0.21
			Full	2.17	36	26	0.32
	Exp [1]				≈30	≈30	0.36
'O-down'	PBE	1×1	Rigid	3.07	23	58	0.06
	HF [9]		Rigid	2.56	27	49	0.22

The CO molecule rotates in the direction of the unsaturated Zn dangling bond so that almost linear Zn–C–O and Zn–O–C configurations are formed (see figure 1(c)). The molecule stays confined in the mirror plane perpendicular to the surface and containing the surface ZnO dimer. The 'C-down' orientation of the CO molecule is found to be the most stable one, in agreement with experimental observation [1]. In contrast, HF predicts a stronger bond for the 'O-down' configuration. This is a well-known deficiency of the HF method and is mainly related to inaccuracies in the description of the CO multipole moments in HF theory [17].

In the third step, the CO molecule and the first three ZnO layers of the slab were fully relaxed (see 'full relaxation' in table 2). The main effect of the relaxation is that the Zn atom coordinated to the CO molecule moves out of the surface, back towards a more truncated-bulk-like position. At the clean surface, the ZnO dimers are tilted by 10° with the Zn ion lying below the oxygen (see [16]). Upon CO adsorption this tilt reduces to 4.4° and 2.3° for the full and half-monolayer coverage, respectively. The relaxation of the surface atoms almost does not influence the orientation of the CO molecule. The CO adsorption geometry is found to be independent of the coverage and agrees very well with previous HF calculations and with experimental results from angular resolved UPS measurements [18]. The increase in the CO binding energy for lower coverages is only partially due to the reduction of the CO repulsion. A large contribution is related to the fact that, for lower coverages, more degrees of freedom per CO molecule can relax and thereby lower the total energy of the system. Overall, the relaxation of the surface atoms is not negligible—the relaxation energy contributes 1/3 to the CO binding energy. The coverage dependence of the CO adsorption energy is well reproduced compared to experiment [1] with calculated values of 0.24 and 0.32 eV for the full and half-monolayer coverage, respectively, and experimental results of 0.22 and 0.36 eV. Finally, we find a small contraction of the CO bond length which is also observed in experiment [1]. This is a rather unusual behaviour, since on metal surfaces usually an expansion and a weakening of the CO bond is found. This may be the crucial difference which makes ZnO a very selective catalyst for methanol synthesis.

Polar surfaces

Three different high-symmetry adsorption sites with a three-fold symmetry are present at the polar surfaces: an on-top position, a hollow-site position above atoms in the second surface layer and a hollow-site with no atoms beneath. The polar surfaces were represented by slabs

Table 3. Equilibrium distances d_0 and binding energies E_{ad} of CO at different adsorption sites of the clean and hydrogen-covered polar ZnO surfaces for a monolayer CO coverage and fixed slab geometry.

	Clean surface		With H coverage	
Adsorption site	d_0 (Å)	E_{ad} (eV)	d_0 (Å)	E_{ad} (eV)
(0001)-Zn surface:				
On top:	2.20	0.30	Repulsive	
Hollow (O):	Repulsive		3.35	<0.02
Hollow (vac):	2.18	0.06	3.41	<0.02
$(000\bar{1})$-O surface:				
On top:	Repulsive		2.05	0.19
Hollow (Zn):	3.29	<0.02	2.01	0.12
Hollow (vac):	3.74	<0.02	2.03	0.11

consisting of eight ZnO double layers with a (1×1) surface unit cell. Since partially occupied bands are present at the polar surfaces [16], a rather dense $(6\times6\times1)$ k-point mesh has to be used for Brillouin-zone integrations. The CO molecules were oriented perpendicular to the surfaces with the C-atom coordinated towards the surface. This is the experimentally observed adsorption geometry [19], but by tilting the CO molecule out of the direction of the surface normal we also checked for a few configurations that the perpendicular orientation is indeed a local energy minimum.

We start with a the fully relaxed slab geometry (see [16]) and do not move the surface atoms upon the adsorption of a full CO monolayer. Table 3 summarizes the results for the CO equilibrium distances and the adsorption energies for the four different surface terminations and the three adsorption sites. In the cases denoted as '<0.02 eV' in table 3, a very shallow energy minimum is found in the potential energy curve when we approach the CO monolayer to the surface. However, this energy minimum is smaller than the repulsion energy between the CO molecules in the monolayer of 0.067 eV so that only a very weak physisorption of CO at low coverages may occur. Only two configurations with a significant binding energy for CO are found: the on-top position on the Zn-terminated (0001) surface and the on-top position on the H-covered $(000\bar{1})$-O face. CO does not chemisorb on the clean O-terminated $(000\bar{1})$ and H-saturated (0001)-Zn surface. In particular, the experimentally observed CO adsorption on the $(000\bar{1})$-O surface cannot be explained by a binding of the CO molecules to hollow sites with Zn ions in the second surface layer, and the formation of carbonate species at the clean O-terminated surface as suggested in [11] can be ruled out.

Finally, we performed a full relaxation of the configurations with CO bound on top of the Zn ions and OH groups of the (0001)-Zn and the hydrogen-covered $(000\bar{1})$-O surface, respectively. In table 4 the results are compared with new experimental data [20] obtained with a special technique, which is only sensitive to ordered areas of the surfaces. The agreement is very reasonable, in particular, if it is taken into account that DFT slightly overestimates the Zn–C bond, as has been shown in the cluster benchmark (see table 1).

In summary, we find that CO only binds to Zn ions present at the nonpolar $(10\bar{1}0)$ and the polar (0001)-Zn surface and to the OH groups of the hydrogen saturated $(000\bar{1})$-O surface. In all cases, the 'C-down' adsorption geometry is more stable than the 'O-down' configuration. The relaxation of the surfaces is a significant effect and the contribution to the adsorption energy is not negligible. No binding of CO to surface oxygen ions is found. Therefore, in the experiments where a chemisorption of CO on the $(000\bar{1})$-O surface was observed, CO was

Table 4. As in table 3, but after a full relaxation of the slab. The results are compared to experimental values from [20].

	PBE		Exp
On-top adsorption site	d_0 (Å)	E_{ad} (eV)	E_{ad} (eV)
Clean (0001)-Zn surface:	2.10	0.37	0.28
H-saturated (000$\bar{1}$)-O surface:	2.00	0.20	0.20

either bound to defects sites and step edges or the surface was hydrogen-covered, as has been speculated in [13]. Altogether, pronounced differences in the adsorption properties of CO are found for the four polar surface terminations. This opens up the possibility of employing CO as a probe molecule to identify surface terminations, and by comparing theoretical and experimental results, to validate microscopic models of the complex, inhomogeneous polar ZnO surfaces [20].

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