First-principles study of the adsorption of formaldehyde on the clean and atomic oxygen covered Cu(1 1 1) surface

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Abstract

The interaction of formaldehyde with the clean and atomic oxygen-covered Cu(1 1 1) surfaces has been studied by means of cluster model density functional calculations in which $Cu_{22}(14,8)$ is used to represent the perfect Cu(1 1 1) surface. The calculations point towards a η^1-H_2CO–O orientation with the oxygen atom almost on top of a copper surface atom. The formaldehyde adsorption energy is of ~22–25 kJ/mol and the internal geometry of adsorbed formaldehyde is almost identical to that of the molecule in the gas-phase. The C–O bond is almost parallel to the surface and the conformation with the molecular plane normal to the surface is slightly preferred to the conformation with the molecular plane nearly parallel to the surface. A Cu_{22}–O model where atomic oxygen is adsorbed on a fcc hollow site was used to study the co-adsorption and reaction of formaldehyde with atomic oxygen. Oxygen co-adsorption has a dramatic effect on the formaldehyde adsorption energy which is increased by ~50%. The calculated energy barrier for the formation of the dioxymethylene intermediate species through the $H_2CO + O \rightarrow H_2CO_2$ reaction is of ~36 kJ/mol. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The interaction of formaldehyde with transition metal surfaces is of considerable interest since H_2CO is the main product originated in the industrial partial oxidation of methanol on silver surfaces and it is an important intermediate in the industrial synthesis of methanol on supported copper surfaces [1,2]. From the extensive available literature concerning the methanol oxidation on transition metal surfaces [3–19], it appears that the low-index copper surfaces are the most studied transition metal catalysts [3–17].

In these copper surfaces, formaldehyde is produced by the decomposition of adsorbed methoxy species, CH_3O, which is a very stable intermediate on copper surfaces [14,15]. Adsorbed methoxy is decomposed to H_2CO at temperatures higher than 350 K and it is known that this reaction is favored by the presence of atomic oxygen on the surface as well as co-adsorbed hydroxy species [11,16].

However, once formaldehyde is formed at the surface its desorption to yield the desired gas-phase product is in competition with the reaction between H_2CO and co-adsorbed oxygen to yield adsorbed formate species. As a matter of fact, several recent experimental works show that the oxidation of methanol to formate is the preferred reaction route on copper surfaces [3–10]. The formation of formate species from

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methanol oxidation has also been observed on when the reaction is catalyzed by silver surfaces [18], the industrial catalyst used nowadays in the production of formaldehyde from methanol. However, it is worth pointing out that this route is in disagreement with the conclusions reached by previous works based on different experimental techniques. In fact, from temperature programmed desorption (TPD) studies [12,13], albeit in a rather limited range of experimental conditions, formaldehyde was observed as the major product of the methanol oxidation and, hence it was assumed that the formate formation pathway was unfavorable on copper surfaces. Similarly, Barnes et al. [17] performed a molecular beam study and concluded that no significant amounts of formate were produced.

The understanding of the mechanisms of methanol oxidation catalyzed by metal surfaces requires a detailed knowledge of the adsorption and reaction modes of the different species involved in the reaction. In this paper, we present a theoretical study of one of the elementary steps involving methanol oxidation catalyzed by metals. This includes the adsorption mode and adsorption energy of formaldehyde on a clean and oxygen covered copper surface. This work follows a previous research in the same overall catalytic process that was devoted primarily to the study of the methoxy to formaldehyde reaction [16].

This work is organized as follows: details of cluster models and theoretical method employed to perform the present study are given in Section 2. The geometric parameters and vibrational frequencies of free and adsorbed formaldehyde are discussed in Section 3. Section 4 shows the pathway for the reaction between adsorbed formaldehyde and co-adsorbed atomic oxygen on the Cu(1 1 1) surface to yield the adsorbed dioxymethylene species (H_2CO_2). Also, in Section 4, details about the transition state for the $H_2CO + O \rightarrow H_2CO_2$ surface reaction are presented. Finally, in Section 5, the most important conclusions of the present work are summarized.

2. Computational details

The present work is devoted to the study of the interaction of formaldehyde with the Cu(1 1 1) surface. For that purpose, the B3LYP density functional theory, DFT, based three-parameter hybrid method pro-
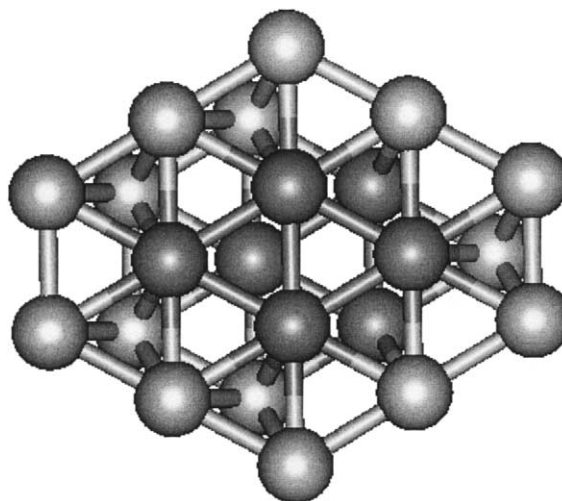

Fig. 1. Top view of the $Cu_{22}(14,8)$ cluster used to model the Cu(1 1 1) surface. Dark and light grey atoms belong to the inner and outer regions, respectively.

posed by Becke was used. This method comprises an exchange functional that mixes the non-local Fock exchange with gradient corrected form of Becke [20] and adds the functional correlation proposed by Lee et al. [21] based in the previous work of Colle and Salvetti [22,23]. The Cu(1 1 1) metal surface was modeled by the $Cu_{22}(14,8)$ cluster shown in Fig. 1. This metal cluster is a section of the ideal (1 1 1) copper surface with a Cu–Cu nearest-neighbor distance of 2.551 Å taken from the bulk. The cluster metal–metal distances have been kept frozen during calculations.

Depending on the orientation of the formaldehyde molecular plane with respect to the metal surface, the different adsorption conformations that have been explicitly studied can be divided in two groups. In the first group, the molecular plane is normal to the surface and the three-conformations studied are shown in the left-hand side of Fig. 2. These are the η^1-H_2CO conformations with the formaldehyde carbon (A) or oxygen (B) atoms directly above one surface copper atom, and that where the formaldehyde oxygen atom is placed above a fcc three-fold site (C). In the second group, the formaldehyde molecular plane is parallel to the copper surface and the conformations considered in this study are shown in the right-hand side of Fig. 2. Two η^2-H_2CO conformations with the carbon and oxygen atoms placed above the surface and along
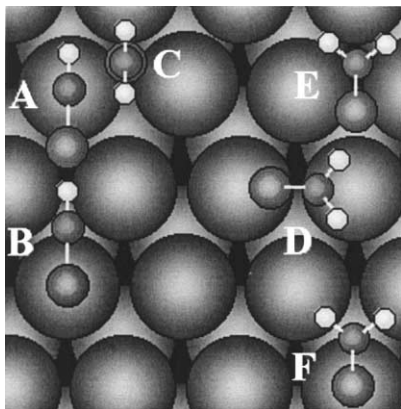
Fig. 2. Top view of the initial positions for formaldehyde adsorbed on Cu(1 1 1) with the molecular plane normal (structures A, B and C) or parallel (structures D, E and F) to the metallic surface: (A) η^1-H$_2$CO–C on a top site; (B) η^1-H$_2$CO–O on a top site; (C) η^1-H$_2$CO–O on a fcc hollow site; (D) η^2-H$_2$CO on a short-bridge site; (E) η^2-H$_2$CO on a cross-bridge site; (F) η^1-H$_2$CO–O on a top site.

the short-bridge (D) or the long-bridge (E) sites were studied and a η^1-H$_2$CO conformation with the oxygen atom on top of a copper atom (F). Nevertheless, the purpose of the above discussion is to provide reasonable starting geometries. The final stable structures have always been obtained from a full geometry optimization process of the adsorbate coordinates using analytical gradients and always maintaining a symmetry plane perpendicular to the surface. In one special case, a search for the reaction transition state has been carried out, vide infra.

The B3LYP calculations have been carried out in the LCAO framework with the Kohn-Sham orbitals expressed in terms of Gaussian-type orbitals (GTO). For the non-metallic atoms all electrons are explicitly included and the standard 6-31G** GTO basis set is used. The surface cluster model is divided in local and outer regions. The atoms in the local region are those directly interacting with the adsorbed species whereas the rest of cluster atoms define the outer region, cf. Fig. 1. Two different basis sets are used for the metal atoms depending on whether they belong or not to the local region. For the atoms in the local region, the $1s^2 2s^2 2p^6$ core electrons are included in the relativistic small core LANL2 effective core potential, ECP, proposed by Hay and Wadt [24], whereas the remain-

ing electrons are described by the LANL2DZ basis which is of double-ζ quality. For the copper atoms that belong to the outer region, the same small core ECP is used, but the valence electrons are described by means of the smaller LANL2MB basis set. All calculations were carried out by means of the Gaussian 98 package [25].

3. Adsorption of formaldehyde on Cu(1 1 1)

The final formaldehyde adsorption conformations obtained by performing total geometry optimization starting from the initial structures in Fig. 2, are depicted in Figs. 3 and 4. From the possible conformations with the formaldehyde molecular plane perpendicular to the surface that have been described in the previous section, a unique final perpendicular conformation appears. In fact, starting the geometry optimization procedure from A, B or C leads always to the same final conformation, structure G in Fig. 3. On the other hand, two different conformations are predicted with the molecular plane nearly parallel to the surface. These structures are labeled as H and I in Fig. 3, structure H is obtained from the D initial structure, whereas I appears to be the final optimized geometry starting from either E or F. Side views of structures G, H and I are presented in Fig. 4. A common feature to adsorption structures G, H and I is that formaldehyde prefers an adsorption mode where the oxygen atom is
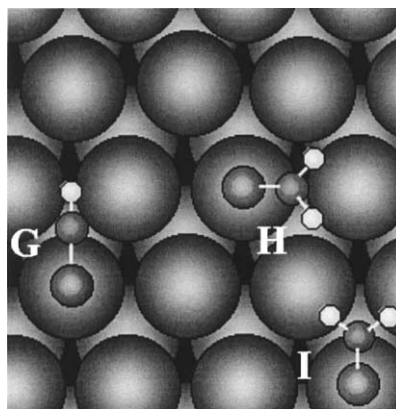

Fig. 3. Top view of the optimized geometries — G, H and I — for formaldehyde adsorbed on the Cu(1 1 1) surface. Starting structures in Fig. 2 lead to the G, H and I final geometries (see text).
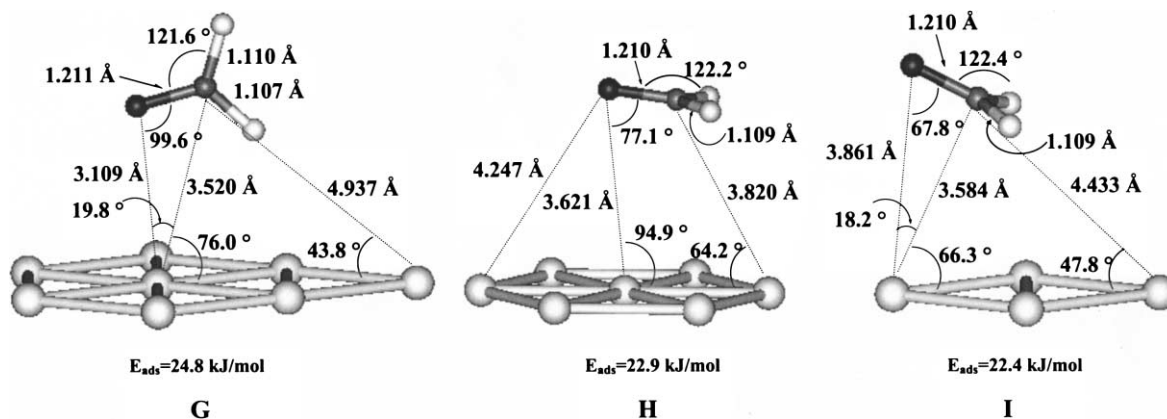
Fig. 4. Optimized geometries for formaldehyde adsorbed on the Cu(1 1 1) surface. Labels G, H and I stand for the structures depicted also in Fig. 3. Only a few surface atoms are displayed.

located directly above a surface copper atom. In any of these situations, the optimized geometry of adsorbed formaldehyde is very close to that corresponding to the gas-phase molecule, and accordingly, formaldehyde is weakly adsorbed, $E_{ads} \sim$ 22–25 kJ/mol. The larger adsorption energy corresponds to the G final structure, $E_{ads} \sim$ 24.8 kJ/mol, although this figure is very close to the values computed for structures H and I, $E_{ads} \sim$ 22.9 and 22.4 kJ/mol, respectively. As stated above, the internal geometric parameters of the adsorbed formaldehyde molecule are identical to those computed for the gas-phase molecule. This is due to the weak interaction of formaldehyde with the Cu(1 1 1) surface also indicated by the fairly large perpendicular distance from H_2CO to the surface. The almost negligible geometry change with respect to the gas-phase values and the weak interaction energy are consistent with a strong tilting of the C–O bond of formaldehyde away from the surface normal, in all cases. For a strong chemisorption bond dominated by a backdonation mechanism as for CO on metal surfaces [26–29], there is a large energy costs to tilt the molecule [30]. The energy required to tilt the molecule is much smaller, when the bond is not directional. In this case, the Pauli repulsion and the electrostatic interaction govern the magnitude of the tilting. The large tilting angle calculated for adsorbed formaldehyde is in agreement with the findings of Bowker et al. [31] for adsorption of formaldehyde on Cu(1 1 0). From the photoelectron spectra, these authors conclude that

formaldehyde interacts with the surface by the in plane O 2p orbital and in a conformation with the molecular plane parallel to the surface close to the calculated structure H. Likewise, the tilting angle for the most stable structure, G is approximately 75°, is in nice agreement with the experimental conformation proposed for formaldehyde on the Ag(1 1 1) surface [32]. These authors, found a tilting angle of 57° ± 6° and predict a conformation rather reminiscent of structure, G, where the formaldehyde molecular plane is quasi-perpendicular to the surface.

Finally, we remark that since the internal geometry of adsorbed formaldehyde is identical to the geometry of the molecule in the gas-phase, similar IR spectra for the adsorbed and gas-phase forms are to be expected from the transferability of the normal modes [33]. This is indeed confirmed by proximity of the vibrational frequencies obtained from experimental data for both formaldehyde adsorption on copper [34] and on silver [35] surfaces, and for the gas-phase molecule [36,37].

4. Co-adsorption of formaldehyde and atomic oxygen on Cu(1 1 1)

In order to study the influence of co-adsorbed oxygen on the geometry and adsorption energy of formaldehyde, cluster models with co-adsorbed oxygen and formaldehyde have also been employed. The changes in both geometry and adsorption energy of
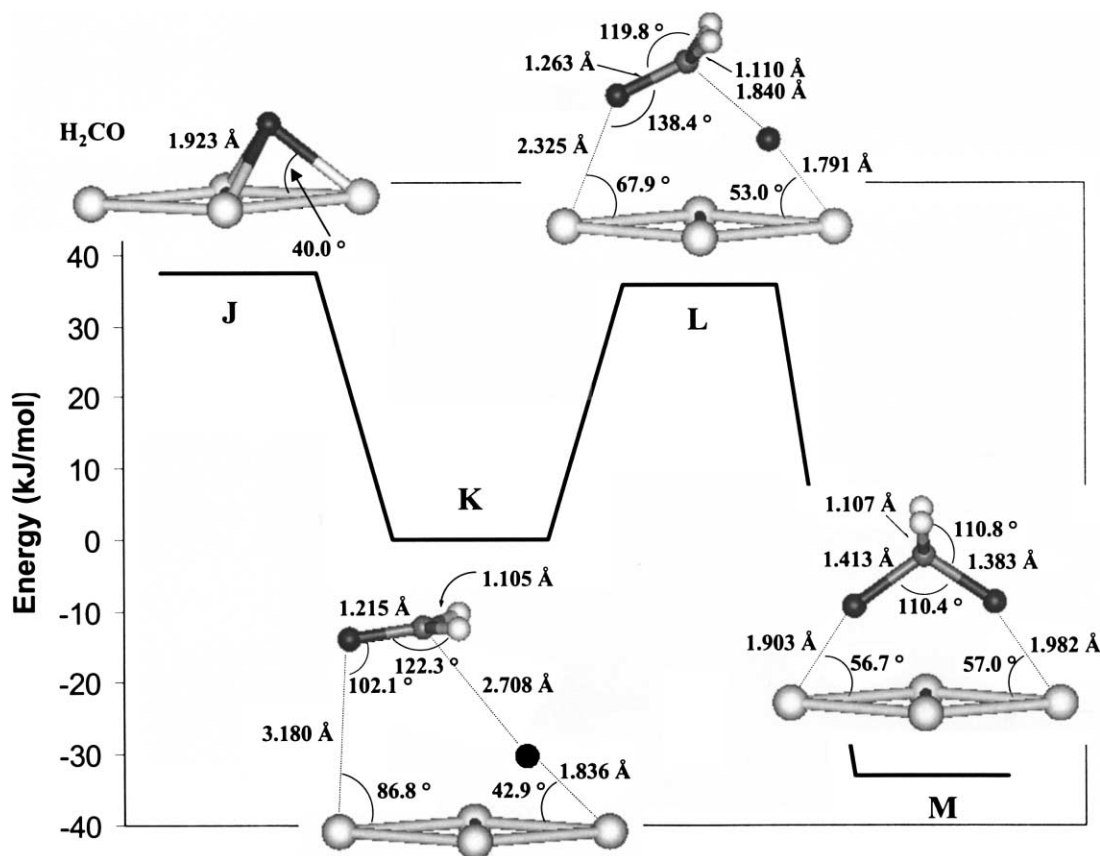
Fig. 5. Geometric and energetic variation during the co-adsorption and reaction of formaldehyde with atomic oxygen on the Cu(1 1 1) surface. J corresponds to the reactants — $H_2CO_{(g)} + O_{(ads)}$, K represents the $H_2CO_{(ads)} + O_{(ads)}$ co-adsorbed species and is taken as the zero reference energy, L stands for the approximate $H_2CO\cdots O_{(ads)}$ transition state structure and, finally, M represents the $H_2CO_{2(ads)}$ reaction product. Only a few surface atoms are displayed.

adsorbed formaldehyde in the I structure originated by this co-adsorption are displayed in Fig. 5. The choice of this I structure follows from the fact that this structure is possibly the most adequate starting structure for the search of the transition state of the $H_2CO + O \rightarrow H_2CO_2$ reaction. This is in agreement with the fact that H_2CO_2 was previously found to adsorb preferentially on the long-bridge site [38]. Due to the increase of computational effort in the search of the transition state structure, the copper atoms in the outer region were described as one-electron pseudoatoms and the 4s electron described by a contracted double-ζ basis set. The ECP and basis set parameters for the Cu one-electron atoms are those reported by

Bagus et al. [39] and used very recently to study the mechanism of propyne catalytic coupling on Cu(1 1 1) [40]. Nevertheless, once the transition state structure is located, the total energy is computed using the LANL2 ECP and the corresponding basis sets for the local and outer regions as described above. It is worth pointing out that the full optimization of the adsorbed dioxymethylene species, M using this more approximate description yields results that are identical to those from reference [38]. In the co-adsorption studies, the oxygen atom is placed above an fcc hollow site which was previously assigned as the one that stabilizes more efficiently atomic oxygen on single metal surfaces [41]. The comparison of the internal geo-

metry of formaldehyde I and K structures shows that the C–O bond is slightly longer, when atomic oxygen is co-adsorbed, while the internal angles remain unchanged. Moreover, oxygen co-adsorption causes a decrease in the formaldehyde oxygen atom distance to the surface and an increase in the atomic co-adsorbed oxygen to the surface distance. The interaction energy of adsorbed formaldehyde in presence of co-adsorbed oxygen can be calculated as the difference between the total energy of $H_2CO + O$ adsorbed on Cu(1 1 1) and the total energy of separate H_2CO and O–Cu(1 1 1) fragments. From the value, thus, computed it follows that the interaction of both adsorbed species on the copper surface increases the adsorption energy of formaldehyde by 56%. Another consequence of oxygen co-adsorption is that when oxygen is present, the molecular plane of formaldehyde is less tilted away from the parallel to the surface. Following previous work [16], the transition state for the reaction between co-adsorbed H_2CO and atomic oxygen structures to yield dioxymethylene was approximated by performing a scan of the formaldehyde carbon atom to the co-adsorbed oxygen distance, but with a full optimization of the rest of coordinates of the adsorbed species. The transition state structure, thus, computed is displayed in Fig. 5-L and the energy barrier for this reaction is 35.7 kJ/mol. This low calculated value is in agreement with the experimental fact that the reaction between formaldehyde and adsorbed oxygen on the Cu(1 1 0) surface occurs readily below 300 K [31]. In the transition state structure the C–O bond is weaker than in structure K as can be seen from the corresponding interatomic distance that is 0.05 Å longer. In the transition state, the distance corresponding to the bond that is being formed between formaldehyde and co-adsorbed oxygen, C⋯O, is 1.840 Å, much shorter than the value in structure K, 2.708 Å. The approach of the formaldehyde molecule towards the co-adsorbed oxygen atom is accompanied by a weakening of the bond between this atomic oxygen and the copper surface. The low energy barrier calculated for this reaction is an indication that dioxymethylene may be the intermediate between formaldehyde and formate species in the methanol oxidation reaction path. The fact that dioxymethylene is not observed in the experimental studies could be attributed to the high reactivity of this species. This is in agreement with results reported in a previous work that for the overall

$H_2CO + O \rightarrow H_2CO_2 \rightarrow HCO_2$ reaction, estimates the exothermicity in more than 200 kJ/mol [38].

5. Conclusions

The DF results reported in this work, for formaldehyde adsorption on the Cu(1 1 1) surface predict that, in any of the sites considered, this species is only weakly adsorbed. Six starting geometries were considered and, after optimization, three different conformations have been reached. These conformations are rather similar since the oxygen atom of formaldehyde sits above one copper atom of the surface in a η^1-H_2CO–O coordination. The three optimized geometries have close total energies and the internal geometry is almost indistinguishable from that corresponding to the gas-phase molecule. The C–O axis of formaldehyde is rather tilted with respect to the surface, the C–O bond being almost parallel to the surface plane. These results are in agreement with experimental data obtained for formaldehyde adsorbed on copper and silver surfaces. From the three stable structures, the conformation with the molecular plane normal to the surface is slightly preferred to those with the molecular plane nearly parallel to the surface. The weak interaction with the surface and the almost unchanged internal structure with respect to the gas-phase geometry leads to vibrational frequencies for the adsorbed molecule that are expected to be very close to gas-phase values, this is confirmed by key calculations.

The co-adsorption of formaldehyde and atomic oxygen on the Cu(1 1 1) surface has also been studied. The co-adsorption of oxygen and H_2CO was studied with the aldehyde molecule adsorbed above one copper atom of a long-bridge site with the co-adsorbed oxygen above a fcc site. It is found that the presence of atomic oxygen on the surface stabilizes formaldehyde by 15 kJ/mol. Moreover, a transition structure for the $H_2CO + O \rightarrow H_2CO_2$ reaction has been proposed. An important feature of the transition state structure is that the formaldehyde molecule is no longer planar. The geometry of the adsorbed dioxymethylene, which is the reaction product species, is in good agreement with that calculated previously using a slightly different cluster model [38]. The predicted energy barrier for the $H_2CO + O \rightarrow H_2CO_2$ reaction is 36 kJ/mol

and the final product is 33 kJ/mol more stable than the co-adsorbed species. The low energy barrier calculated for this reaction is an indication that dioxymethylene may be the intermediate between formaldehyde and formate species in the methanol oxidation reaction path. These findings explain why some authors [4] claim that formaldehyde desorption is in competition with the reaction between formaldehyde and pre-adsorbed oxygen leading to formate.

Acknowledgements

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