A theoretical study of dioxymethylene, proposed as intermediate in the oxidation of formaldehyde to formate over copper

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Abstract

The density functional theory-based hybrid method B3LYP was used to study the interaction of the dioxymethylene species with the copper (111) surface. This species has been proposed experimentally as one possible intermediate in the oxidation of methanol catalysed by metal surfaces. The H_2CO_2 species is very unstable, and this makes the experimental study too difficult. As far as we know, there are no direct theoretical or experimental studies of H_2CO_2 adsorption on metal surfaces in the literature. The experimental knowledge is limited to the IR frequencies obtained for adsorption on metal oxides.

In this study, two different clusters and two different adsorption sites have been studied. A two-layer Cu_7 cluster was used to model the H_2CO_2 and $[H_2CO_2]^{2-}$ adsorption on a small copper island, and a large three-layer Cu_{30} cluster was used to model the H_2CO_2 adsorption on a copper (111) surface. These clusters were used to extract information concerning the energetics, geometry and IR frequencies for the dioxymethylene adsorption. When compared with a similar species, formate, dioxymethylene is stabilized more efficiently on the cross-bridge site than on the aligned-bridge site, which is the preferred orientation for formate. However, the oxygen-to-surface distances are similar, and the same is observed for the bonding type, which is mainly ionic. A bridge-bonded conformation is predicted for adsorption on the two sites considered. The comparison of the adsorption energy of the dioxymethylene species and the adsorption energy of atomic oxygen and free formaldehyde yields an interesting result: $H_2CO_{2(ads)}$ is energetically more stable than adsorbed $O_{(ads)}$ and $H_2CO_{(g)}$. The IR frequencies are in good agreement with experimental data obtained for dioxymethylene adsorption on several oxide surfaces. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Chemisorption; Copper; DFT; Dioxymethylene; Heterogeneous catalysis; Metallic surfaces; Methanol oxidation; Vibrations of adsorbed molecules

1. Introduction

The interaction of methanol with transition metal surfaces has been intensively studied in the last two decades [1,2] due to its importance in deoxygenation and in partial oxidation reaction, as both product and reactant. Methanol is the reactant used to obtain formaldehyde in industry, and due to its relatively simple structure, it is a model used to understand reactions in which heavier alcohols participate.

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Numerous studies concerning the methanol interaction with transition metal surfaces can be found in the literature [3–6]. The adsorption on the copper surface has been widely studied since a Cu/ZnO catalyst is used to obtain methanol from syn-gas [7].

The reaction of methanol at an increasing temperature has been followed by means of temperature-programmed desorption (TPD) [8–10] and scanning tunnelling microscopy (STM) [11,12] techniques. Methanol is adsorbed on clean copper (110) at 140 K, and upon heating, it desorbs completely. It seems that O$-$H bond cleavage occurs, but due to the low rate of hydrogen atom recombination on copper and due to the stability of the adsorbed methoxy radical (CH_3O), methanol elimination is preferred over CH_3O decomposition. If oxygen is present on the surface, the hydroxy hydrogen atom reacts with the adsorbed oxygen, and water is eliminated. Since no atomic hydrogen is left on the metallic surface, upon heating, CH_3O decomposition to CO_2 is observed. A large variety of reaction intermediates and products have been detected. Essentially, this mechanism involves the reaction steps shown below.

The adsorption of methanol:

$$CH_3OH_{(g)} \rightarrow CH_3OH_{(ads)}. \qquad (1)$$
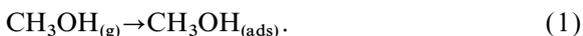
The reaction of methanol (≈ 300 K) with adsorbed oxygen yielding the methoxy radical and water:

$$CH_3OH_{(ads)} + O_{(ads)} \rightarrow CH_3O_{(ads)} + OH_{(ads)} \qquad (2)$$

$$CH_3OH_{(ads)} + OH_{(ads)} \rightarrow CH_3O_{(ads)} + H_2O_{(g)}. \qquad (3)$$

The methoxy species decompose at 350 K to give adsorbed atomic hydrogen and formaldehyde. The latter desorbs from the surface, yielding gaseous formaldehyde, and hydrogen is also desorbed.

$$CH_3O_{(ads)} \rightarrow H_2CO_{(ads)} + H_{ads} \qquad (4)$$

$$H_2CO_{(ads)} \rightarrow H_2CO_{(g)} \qquad (5)$$

$$H_{(ads)} + H_{(ads)} \rightarrow H_{2(g)}. \qquad (6)$$

The desorption of formaldehyde is in competition with the reaction between formaldehyde and co-adsorbed oxygen to yield formate. A possible reaction mechanism for the conversion of formaldehyde into formate is via the dioxymethylene intermediate:

$$H_2CO_{(ads)} + O_{(ads)} \rightarrow H_2COO_{(ads)} \rightarrow HCOO_{(ads)} + H_{(ads)}. \qquad (7)$$

This intermediate has been proposed from TPD studies [8–10] for the formaldehyde oxidation on the (110) surfaces of copper and silver and also from the STM [11,12] studies for the methanol oxidation on the copper (110) surface.

The H_2CO_2 intermediate is formed after reaction of H_2CO with surface oxygen in the mechanism of conversion of formaldehyde to formate. In the case of adsorption on a (110) silver surface [10], the authors have performed the experiments on a pre-oxidized surface with labelled atomic oxygen (^{18}O). The presence of ^{18}O in CO_2 and in desorbed H_2CO shows that formaldehyde interacts with the atomic oxygen present on the surface yielding HCO_2 through the H_2CO_2 intermediate. The low stability of the H_2CO_2 intermediate prevents the experimental verification of its existence.

The presence of the dioxymethylene species in an almost symmetrical form was also found after adsorption of formaldehyde on various metal oxide surfaces [13,14].

This is characterized by some strong absorption bands in the IR region between 1000 and 1200 cm^{-1}. The H_2CO_2 species was also observed in more recent studies concerning the methanol adsorption on Cu/ZnO/Al$_2$O$_3$ [15] and on Cu/SiO$_2$ [16].

The presence of oxygen atoms in all these surfaces (including metal surfaces with pre- or co-adsorbed oxygen) suggests that oxygen has an important role in the $H_2CO_{(ads)} \rightarrow H_2CO_{2(ads)} \rightarrow HCO_{2(ads)}$ reaction.

In this work, we aimed to describe how the experimentally postulated dioxymethylene intermediate adsorbs on the copper (111) surface. Additionally, the computed IR frequencies can help in the interpretation of data. As far as we know, there has been no direct experimental study or theoretical study of H_2CO_2 adsorption on metal surfaces described in the literature.

This paper is organized as follows. Details of the clusters geometry and of the theoretical method

used are described in Section 2. Section 3 presents the numerical results and discussion. The conclusions from the present study are summarized in Section 4.

2. Method

There is no direct experimental evidence for the existence of the H_2CO_2 species adsorbed on metal surfaces. However, this species has been proposed to occur in formate formation catalysed by metal surfaces. Considering that the adsorbed dioxymethylene species is proposed as a precursor of the adsorbed formate species and also due to the proposed symmetry of this species adsorbed on metal oxide surfaces [13], it is only the H_2CO_2 species adsorbed on a bridge-bonded conformation that is studied here. In fact, a bridge-bonded conformation was found experimentally [17] and

theoretically [18] to be preferable for the adsorbed formate species.

In this work, we use the two different copper clusters shown in Fig. 1. A Cu_7 (4,3) cluster (Fig. 1a) was used to model the H_2CO_2 and the $[H_2CO_2]^{2-}$ interaction with the copper (111) surface, simulating a small copper island that could be observed on surfaces of copper deposited on a insulator substrate such as Al_2O_3. A Cu_{30} (14,8,8) (Fig. 1b) was used to model the H_2CO_2 interaction with the infinite copper (111) surface. In the latter case, the adsorption of the anion is not considered since the metal surface plays the role of an electron bath. For adsorption of small species on large surfaces, Olivera et al. [19] observed that charged species behave like neutral species, and only the bonding energy differs. The surface acts as an electron donor or an electron receptor, depending on the adsorbate considered. The two-layer seven atom cluster is a smaller section of the three-layer

a)

top view   side view

b)

top view   side view
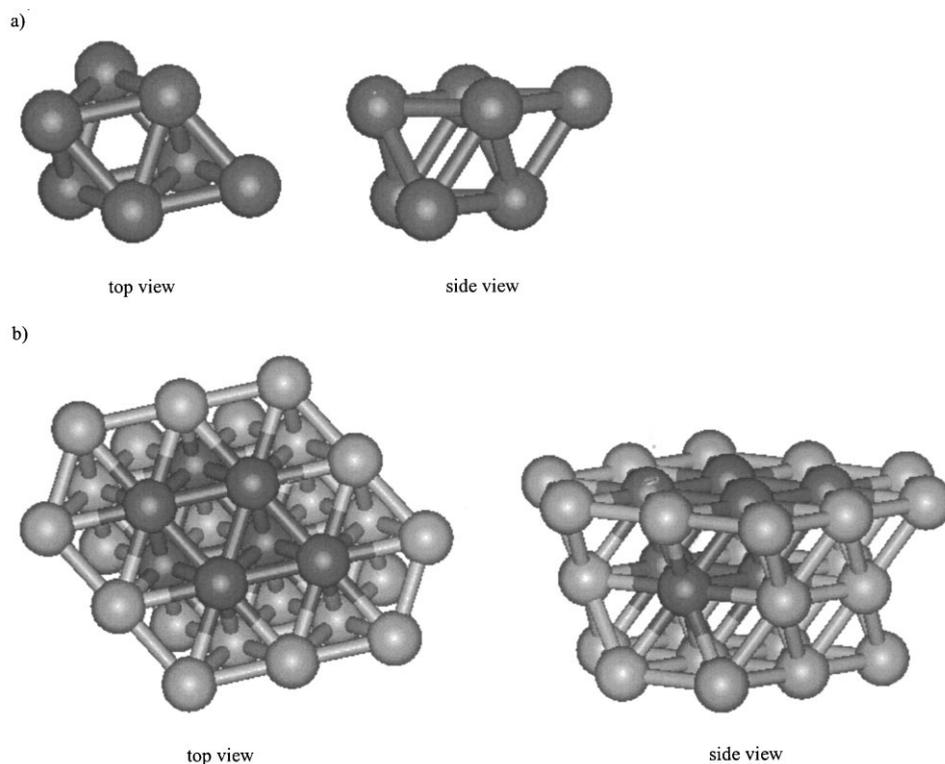
Fig. 1. Metal clusters used to simulate the (111) copper surface. (a) Top and side views of the Cu_7 (4,3) cluster. (b) Top and side views of the Cu_{30} (14,8,8) cluster.

30-atom metal cluster, and both are sections of the ideal Cu (111) surface. The Cu–Cu nearest-neighbour distance is taken from the bulk as 2.551 Å. Small clusters were previously found to give a reasonable description of the copper (111) surface, providing reliable geometries and IR frequencies [18,20–22]. Although it is usually more difficult to obtain accurate binding energies [20,22], we have previously obtained virtually identical geometric and energetic parameters for the HCO_2/Cu system using either a Cu_8 cluster or a Cu_{18} cluster [18].

Two different orientations of the H_2CO_2 species were considered; the cross-bridge shown in Fig. 2a and the aligned-bridge shown in Fig. 2b. In the cross-bridge orientation (also called long-bridge), the oxygen atoms of the dioxymethylene species are placed above the longer bridge site present in Cu (111) with one oxygen atom located at the fcc hollow site and the other oxygen atom at the hcp hollow site. The hcp hollow site is the hollow site that has one copper atom of the second layer directly underneath it, while in the case of the fcc hollow site, there is one copper atom directly underneath it only in the third layer. In the aligned bridge orientation (also called short-bridge), the oxygen atoms of the dioxymethylene species are both located along the short bridge present in the Cu (111) surface. The oxygen atoms are free to move along the adsorption sites considered.

The geometry of the adsorbed H_2CO_2 and

$[H_2CO_2]^{2-}$ species was optimized in the calculations. Only one restriction was imposed during these optimizations, the conservation of the mirror plane that contains the carbon, the oxygen and the copper atoms that define the long or the short bridges. In both cases, the calculations were made with a starting geometry for the H_2CO_2 and $[H_2CO_2]^{2-}$ species with the same surface-to-oxygen distance for both oxygen atoms.

The density functional theory (DFT) was used to obtain the geometry, energy and IR frequencies for the dioxymethylene species adsorbed on the copper (111) surface in the two orientations described above. The B3LYP hybrid method proposed by Becke [23] included in the Gaussian 94 [24] package was used. This method includes a mixture of Hartree–Fock (HF) and DFT exchange terms associated with the gradient corrected correlation functional of Lee et al. [25].

The seven metal atoms of the Cu_7 cluster are treated with the LANL2DZ basis set, which treats the outer 19 electrons of copper atoms with a double zeta basis set and the inner 1s, 2s and 2p electrons with the effective core potential of Hay and Wadt [26]. The Cu_{30} metal cluster was treated with two basis sets. The region closest to the adsorbate, composed of four atoms of the first layer and three atoms of the second layer (shown in dark grey in Fig. 1b) were treated with the LANL2DZ basis set. In the other 23 copper atoms of the outer region, only the 4s electron is treated
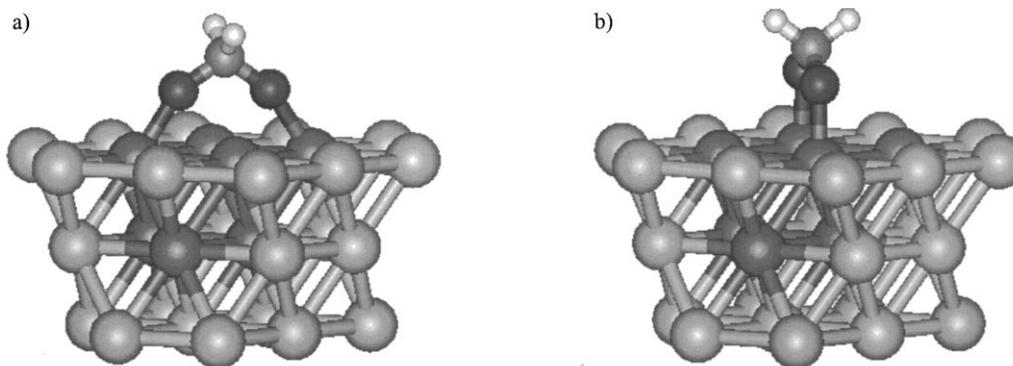
Fig. 2. Side view of the dioxymethylene species adsorbed on the Cu_{30} (14,8,8) cluster shown in Fig. 1b. (a) Dioxymethylene species adsorbed on the cross-bridge site where the two oxygen atoms are located above two adjacent fcc and hcp hollow sites. (b) Dioxymethylene species adsorbed on the aligned-bridge site where the two oxygen atoms are positioned above the short-bridge site present in the Cu (111) surface.

explicitly, while their inner electrons are included in the effective core potential of Bagus et al. [27]. The non-metallic atoms (O, C and H) are described by the 6-31G** basis set of double zeta quality with p polarization functions in hydrogen atoms and d polarization functions in carbon and oxygen atoms. Calculations were made for the lowest possible spin multiplicity systems.

IR frequencies were obtained by calculation of the analytic second derivatives, and an infinite mass was used for the copper atoms.

3. Results

Table 1 summarizes the computed geometry results of the free H_2CO_2 and $[H_2CO_2]^{2-}$ in the gaseous state. Three different states have been studied for the H_2CO_2 species, two of them belonging to the C_{2v} symmetric type, $^3A_2$ and $^3B_1$, and the $^3A'$ state belonging to the C_s symmetric type. As expected, a distorted tetrahedral like geometry is found. The total energy and the geometric results for the $^3A'$ (two different C—H bond lengths) state are not shown in Table 1 since they are very close to those obtained for the $^3B_1$ electronic state. The differences in the geometric parameters for the two $^3A_2$ and $^3B_1$ states are large. When compared to the $^3A_2$ state, the C—O bond length, the OCO and HCH angles are higher in the $^3B_1$ state. The C—H bond length and the OCH angle are smaller. The two extra electrons in $[H_2CO_2]^{2-}$ destabilize this molecule by approximately 380 kJ mol^{-1} when compared with the H_2CO_2 species. The larger repulsion between the two

oxygen atoms in $[H_2CO_2]^{2-}$ causes the increase in the OCO angle and the subsequent increase in the C—H bond length and decrease in the HCH angle. When compared with the results obtained for free HCO_2 and HCO_2^- [18], it can be seen that the CO and C—H bond lengths are larger for the H_2CO_2 and $[H_2CO_2]^{2-}$ species. The OCO angle is smaller.

Table 2 lists the calculated IR frequencies for free H_2CO_2 and $[H_2CO_2]^{2-}$. The low CH_2 stretch frequencies obtained show that the C—H bond is weaker than the typical C—H bond in similar compounds. Usually, the C—H stretching frequencies are found to lie in the 2800–3100 cm^{-1} interval. The C—O stretch frequencies are lower than those obtained for the formyloxy (HCO_2) species [18]. This was to be expected since the C—O bond order in HCO_2 is higher than that in H_2CO_2 and $[H_2CO_2]^{2-}$. The weaker bond in the latter species is in good agreement with the lower IR frequencies observed for single-bond C—O stretching.

For the adsorbed species, Table 3, two distinct conformations were found for the radical and the anion. The H_2CO_2 species is adsorbed on the aligned-bridge site with the two oxygen atoms placed almost above the two copper atoms of the short-bridge, and the nearest-neighbour distance is 1.857 Å. The oxygen-to-surface distance is 1.856 Å, and the OCO plane of the H_2CO_2 species is normal to the surface. The O–Surf distance is close to the experimental value found for the

Table 1
Geometry and energy of the optimized free H_2CO_2 and $[H_2CO_2]^{2-}$ species

	H_2CO_2		$[H_2CO_2]^{2-}$
	$^3A_2$	$^3B_1$	$^1A_1$
Energy (a.u.)	−189.585	−189.575	−189.443
Distance (CO) (Å)	1.331	1.315	1.324
Distance (CH) (Å)	1.130	1.153	1.322
Angle (OCO) (°)	107.3	134.1	123.4
Angle (HCH) (°)	101.9	104.5	93.6
Angle (OCH) (°)	111.9	103.8	108.9

Table 2
IR wavenumbers (cm^{-1}) for free H_2CO_2 and $[H_2CO_2]^{2-}$ species[a]

	H_2CO_2		H_2CO_2
	$^3A_2$	$^3B_1$	$^1A_1$
$\upsilon_s(CH_2)$	2693	2439	2693
$\upsilon_{as}(CH_2)$	2646	2405	2646
$w(CH_2)$	1280	1426	1280
$\delta(CH_2)$	1257	1355	1257
$\upsilon_s(CO_2)$	1141	1191	1141
$\upsilon_{as}(CO_2)$	1104	990	1104
$\tau(CH_2)$	1038	846	1038
$\rho(CH_2)$	572	762	572
$\delta(CO_2)$	559	606	559

[a] υ: stretch; w: wag; δ: bend; τ: twist; ρ: rock.

Table 3
Energy, geometry and total NPA and Mulliken charges for the H_2CO_2 and $[H_2CO_2]^{2-}$ species adsorbed on the aligned-bridge and cross-bridge sites of the Cu_7 (111) surface[a]

	H_2CO_2 adsorbed on Cu_7 (4,3)		$[H_2CO_2]^{2-}$ adsorbed on Cu_7 (4,3)	
	Aligned bridge	Cross bridge	Aligned bridge	Cross bridge
Adsorption energy (kJ mol^{-1})	−366.8	−404.2	−818.7	−804.5
Distance (surf–O_1) (Å)	1.856	1.661	1.912	1.730
Distance (surf–O_2) (Å)	1.856	1.618	1.912	1.716
Distance (CuO_1) (Å)	1.857	2.391	1.913	2.440
Distance (CuO_2) (Å)	1.857	2.362	1.913	2.431
Distance (CO_1) (Å)	1.400	1.394	1.392	1.391
Distance (CO_2) (Å)	1.400	1.406	1.392	1.390
Distance (CH) (Å)	1.110	1.105	1.124	1.120
Angle (OCO) (°)	117.8	111.1	118.4	112.3
Angle (HCH) (°)	107.7	109.0	105.6	106.5
Angle (O_1CH) (°)	107.7	108.8	108.0	109.3
Angle (O_2CH) (°)	107.7	109.5	108.0	109.6
q (NPA) (a.u.)	−1.24	−1.37	−1.42	−1.53
q (Mulliken) (a.u.)	−0.71	−0.66	−0.84	−0.79

[a] Negative values for the adsorption energy are exothermic. For adsorption on the cross-bridge site, the labels 1 and 2 in the oxygen atoms refer to the oxygen atom located above one hcp hollow site and one fcc hollow site, respectively.

adsorbed formate species, which is 1.98 ± 0.04 Å [17]. The C−O bond length is 1.400 Å, and this bond is weakened after adsorption when compared with the CO bond in the free species. The bond length is also longer than that observed experimentally [28] for the adsorbed formate species, 1.27 ± 0.04 Å, and for other free species with a C−O bond [29]. The same trend is observed for the C−H bond length, with this being slightly higher than the C−H bond length calculated for the adsorbed formate and methoxy species [18,20]. The 117.8° value calculated for the OCO angle is smaller than the $127 \pm 7°$ angle obtained for the adsorbed formate species [28], and this is due to the steric effects caused by the extra hydrogen atom.

The total charge on the adsorbate has been calculated by Mulliken population analysis and by natural population analysis (NPA) [30]. The charge values are −0.71 and −1.24 a.u., as obtained by the Mulliken and NPA methods, respectively. The smaller charge on the adsorbate calculated with the Mulliken analysis is in agreement with previous calculations [18], where it is observed that charges obtained by a Mulliken analysis give an underestimation of total charges.

On the cross-bridge site, H_2CO_2 is adsorbed with the oxygen atoms located at two different oxygen–surface distances. The oxygen–surface distance is smaller for the oxygen atom adsorbed on the fcc site. The oxygen–surface distances are, respectively, 1.661 and 1.618 Å for the oxygen atom placed above the hcp hollow site or above the fcc hollow site. The oxygen–copper nearest bond length is ~ 2.4 Å, considerably higher than the computed value for adsorption on the aligned-bridge site. The C−O bond lengths are close to 1.4 Å, as found for the H_2CO_2 adsorption on the aligned-bridge site. The OCO angle is smaller for adsorption on this site and equal to 111.1°.

The total charge on the adsorbate is −1.37 a.u. and −0.66 a.u. calculated, respectively, with NPA and Mulliken atomic charges. Surprisingly, the NPA total charge is more negative than that calculated for adsorption on the aligned-bridge site, and the opposite variation is observed for the Mulliken total charge.

For the $[H_2CO_2]^{2-}$ anion adsorption on the Cu_7 cluster (right-hand side of Table 3), the similarity with the calculated values for the radical adsorption can be easily observed. The differences in the bond distances are smaller than 0.1 Å, and

in bond angles, the differences are about 3°. The same is observed for total charges on the adsorbate. The values are nevertheless slightly more negative. This is expected for a large surface since the metal surface is an electron charge store and can give a charge to the adsorbate, as occurs with the radical, and accept a charge from the adsorbate, as occurs with the anion. This was previously found by Olivera et al. [19] for a large variety of charged species adsorbed on large clusters.

Calculated IR wavenumbers for H_2CO_2 and $[H_2CO_2]^{2-}$ adsorbed on the Cu_7 cluster are listed in Table 4. Although there are no experimental data on the same systems for comparison purposes, FT-IR experimental parameters for dioxymethylene adsorption on zirconia (ZrO_2), thoria (ThO_2) and titania (TiO_2) [13] are close to those obtained in this study. The agreement between the vibrational frequencies obtained for the radical and the anion consolidates the observation that even on small clusters, the adsorbed species are the same. It is shown that the O–surface stretching frequencies are higher for adsorption on the aligned-bridge site due to the direct interaction with metal atoms of the surface. When compared with calculated IR wavenumbers for the gaseous forms, the smaller C—O stretching frequencies found for the adsorbed species show that there is an weakening in the C—O bonds due to the strong interaction of oxygen with the surface. The large

difference in the C—H stretching frequencies between the gas forms of the radical and the anion is no longer observed in the adsorbed species. The calculated frequencies for the adsorbate are more similar to those obtained for the free H_2CO_2 species than to the anion. Despite the negative charge on the adsorbate, the structure of the adsorbed species agrees better with the geometry of the free H_2CO_2 species.

The adsorption of one oxygen atom adsorbed on the fcc hollow site of this Cu_7 cluster was studied. This site is the one that stabilizes the oxygen atom more strongly on the surface. Our aim was to compare the energetics of the adsorbed dioxymethylene species with the energetics of free formaldehyde and atomic oxygen adsorbed on a fcc hollow site. The difference in the total energies obtained shows that the adsorbed dioxymethylene species is more stable: $[E_{tot}(H_2CO_2-Cu_7)] > [E_{tot}(H_2CO)+E_{tot}(O-Cu_7)]$.

The H_2CO_2 species adsorbed on the aligned-bridge site is 77.2 kJ mol^{-1} more stable than $H_2CO_{(g)}+O_{(ads)}$, and for the cross-bridge site, the radical is stabilized by an extra $114.6 \text{ kJ mol}^{-1}$. The main conclusion is that, thermodynamically, the reaction of formaldehyde with atomic oxygen is favoured on the Cu (111) surface, and this proposed intermediate may appear in the following reaction step: $H_2CO_{(ads)}+O_{(ads)} \rightarrow H_2COO_{(ads)} \rightarrow HCOO_{(ads)}+H_{(ads)}$.

Table 4
IR wavenumbers (cm^{-1}) for H_2CO_2 and $[H_2CO_2]^{2-}$ adsorbed on the Cu_7 (111) surface[a]

	H_2CO_2 adsorbed on Cu_7 (4,3)		$[H_2CO_2]^{2-}$ adsorbed on Cu_7 (4,3)	
	Aligned bridge	Cross bridge	Aligned bridge	Cross bridge
$\upsilon_{as}(CH_2)$	2877	2955	2663	2724
$\upsilon_s(CH_2)$	2871	2929	2710	2752
$\delta(CH_2)$	1525	1521	1513	1522
$w(CH_2)$	1391	1366	1398	1380
$\tau(CH_2)$	1158	1205	1227	1203
$\rho(CH_2)$	1094	1109	1113	1133
$\upsilon_s(CO_2)$	1056	1082	1076	1090
$\upsilon_{as}(CO_2)$	1003	962	1016	984
$\delta(CO_2)$	611	592	603	585
$\upsilon_{as}(O–Surf)$	428	329	368	218
$\upsilon_s(O–Surf)$	400	366	344	268

[a] υ: stretch; w: wag; δ: bend; τ: twist; ρ: rock.

The differences in the total energies obtained from $[E_{tot}(HCO_2-Cu_7)+E_{tot}(H-Cu_7)-E_{tot}(Cu_7)]-[E_{tot}(H_2CO)+E_{tot}(O-Cu_7)]$ are -287.4 kJ mol^{-1} for the formate species adsorbed on the aligned-bridge site and -247.0 kJ mol^{-1} for the formate species adsorbed on the cross-bridge site. The hydrogen atom is adsorbed on the fcc hollow site. From a thermodynamic point of view, the conversion of formaldehyde to formate is favourable.

The calculated results for the adsorption of H_2CO_2 on the Cu_{30} cluster are shown in Tables 5 and 6. On this cluster, it is observed again that the cross-bridge site stabilizes the H_2CO_2 species more strongly. The geometric results presented in Table 5 are in good agreement with the results obtained for the H_2CO_2 adsorption on the Cu_7 cluster (see Table 3). The deviations are smaller than 0.06 Å and 2° for distances and angles, respectively. These results show again that it is possible to study this kind of system with small clusters. The oxygen-to-surface distance obtained for adsorption on the aligned-bridge site is slightly longer, and the oxygen-to-carbon distance is slightly shorter. The H_2CO_2 internal angles are practically the same. The charge transfer is slightly smaller. Using

Table 5

Energy, geometry and total Mulliken charge for the H_2CO_2 species adsorbed on the aligned-bridge and cross-bridge sites of the Cu_{30} (111) surface[a]

H_2CO_2/Cu_{30} (14,8,8)	Aligned bridge	Cross bridge
Adsorption energy (kJ mol^{-1})	-342.9	-415.3
Distance (surf–O_1) (Å)	1.915	1.640
Distance (surf–O_2) (Å)	1.915	1.653
Distance (CuO_1) (Å)	1.917	2.374
Distance (CuO_2) (Å)	1.917	2.383
Distance (CO_1) (Å)	1.393	1.397
Distance (CO_2) (Å)	1.393	1.396
Distance (CH) (Å)	1.111	1.107
Angle (OCO) (°)	116.5	110.6
Angle (HCH) (°)	106.7	108.5
Angle (O_1CH) (°)	108.3	109.5
Angle (O_2CH) (°)	108.3	109.3
q (adsorbate) (a.u.)	-0.65	-0.64

[a] Negative values for the adsorption energy are exothermic. For adsorption on the cross-bridge site, the labels 1 and 2 in the oxygen atoms refer to the oxygen atom located above one hcp hollow site and one fcc hollow site, respectively.

Table 6

IR wavenumbers (cm^{-1}) for H_2CO_2 adsorbed on the Cu_{30} (111) surface[a]

	H_2CO_2 adsorbed on Cu_{30} (14,8,8)	
	Aligned bridge	Cross bridge
$\upsilon_{as}(CH_2)$	2851	2922
$\upsilon_s(CH_2)$	2859	2905
$\delta(CH_2)$	1503	1522
$w(CH_2)$	1379	1380
$\tau(CH_2)$	1221	1210
$\rho(CH_2)$	1090	1118
$\upsilon_s(CO_2)$	1054	1104
$\upsilon_{as}(CO_2)$	1023	975
$\delta(CO_2)$	614	592
$\upsilon_s(O–Surf)$	410	309
$\upsilon_{as}(O–Surf)$	400	277

[a] υ: stretch; w: wag; δ: bend; τ: twist; ρ: rock.

Mulliken atomic charges, a 0.65 a.u. charge transfer from the metal surface to the adsorbate is predicted. For adsorption on the cross-bridge site (right-hand side in Table 5), a H_2CO_2 geometry with two different oxygen-to-surface distances is predicted. In this cluster, it is verified that the shorter oxygen-to-surface distance is smaller for the oxygen atom placed above the hcp hollow site. Also, the difference between the two oxygen-to-surface bond lengths is smaller for adsorption on this cluster. The two oxygen-to-surface distances are practically the same, and a bridge-bonded conformation is predicted. For adsorption on the cross-bridge site, the charge transfer from the metal surface to the H_2CO_2 is 0.64 a.u.

IR wavenumbers obtained for H_2CO_2 adsorption on the Cu_{30} cluster are presented in Table 6. The results are in good agreement with those obtained for adsorption on the smaller cluster except the oxygen-surface stretching frequencies due to the differences in the oxygen-to-surface distances, as explained above.

The variation of the adsorption energy with the tilting of the OCO plane is shown in Fig. 3 for H_2CO_2 and $[H_2CO_2]^{2-}$ adsorbed on the Cu_7 cluster and for H_2CO_2 adsorbed on the Cu_{30} cluster. The results show that the OCO conformation normal to the surface stabilizes both the radical and the anion adsorbed on the cross-bridge site of
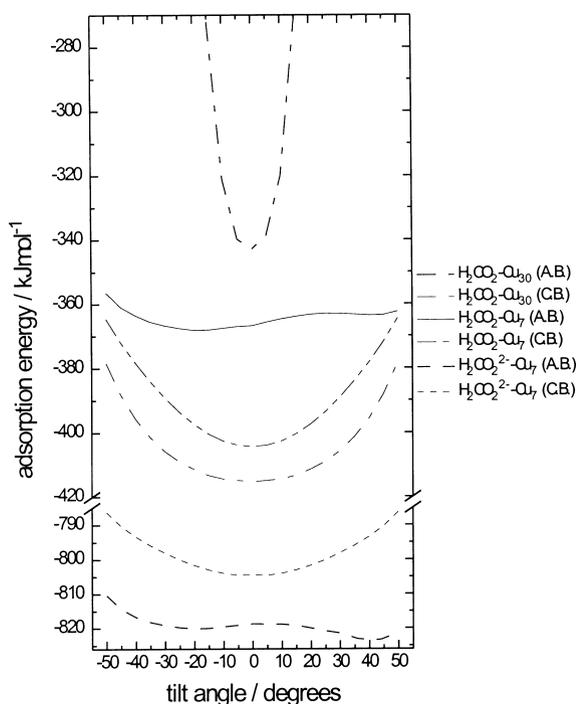
Fig. 3. Adsorption energy variation with tilting of the OCO plane of the H_2CO_2 and $[H_2CO_2]^{2-}$ molecules from the surface normal for the aligned-bridge and cross-bridge sites of the copper (111) surface. For adsorption on the aligned-bridge site, negative tilting angles mean tilting of the OCO plane of the adsorbed species with one hydrogen atom approaching the fcc hollow site, while positive tilting angles mean tilting of the OCO plane of the adsorbed species with one hydrogen atom approaching the hcp hollow site.

the Cu_7 and Cu_{30} metal clusters more efficiently. The minima are observed exactly for a zero degree tilt angle. The variation in adsorption energy is very similar for adsorption of the radical on both metal clusters where only the absolute adsorption energy does not match. These curves are also similar to that obtained for the tilting of the OCO plane of the anion. A different behaviour is observed for adsorption on the aligned-bridge site. The conformation with the OCO axis normal to the surface is the most favourable adsorption energy only for H_2CO_2 adsorbed on the larger cluster. This is expected since, in this way, the interaction of atomic orbitals of the oxygen atoms with the short-bridge containing copper atoms is greater. For adsorption on the cluster with seven

copper atoms, this is not observed. A tilted geometry for both the radical and the anion is predicted. The only explanation is the small charge delocalization due to the limited size of the cluster. Hence, the dioxymethylene chemisorption should be different on a small metal island from that observed on the large surface. The most favourable adsorption site is the cross-bridge site for the radical and the aligned-bridge site for the anion.

In Fig. 4, the component of the dipole moment normal to the surface is plotted against the distance of the substrate to the metal surface. This method was proposed by Bagus and co-workers [31–33]. The linear behaviour observed is a sign that the bonding has a predominantly ionic character. The slope of the curves is indicated in the graph and gives an idea of the charge on the adsorbate.
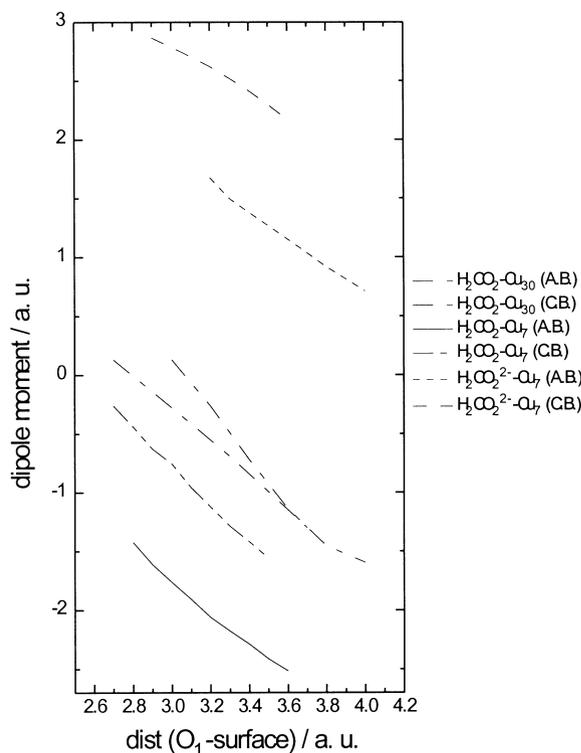
Fig. 4. Variation of the dipole moment component normal to the surface with the distance from the surface of the H_2CO_2 species at the aligned-bridge site and at the cross-bridge site. The slopes from top to bottom are: -1.68, -1.42, -1.35, -1.63, -1.18 and -1.06.

4. Conclusions

In this work, we have used the DFT hybrid method B3LYP to investigate the adsorption of dioxymethylene on the copper (111) surface. For that purpose, two different clusters have been employed. A Cu_7 metal cluster was used to model a small metal island, and a Cu_{30} metal cluster was used to model the infinite surface. Two adsorption sites have been considered, and it was concluded that the cross-bridge conformation is that which stabilizes the dioxymethylene species more strongly. A bridge-bonded conformation is predicted for both sites. It was observed that even for adsorption on the smaller cluster, the radical (H_2CO_2) and anionic ($[H_2CO_2]^{2-}$) forms behave similarly upon adsorption. The adsorbed forms are very different from the free molecules. The geometric differences between the adsorption on the Cu_7 and the Cu_{30} cluster are very small, indicating that small clusters are a good choice for studying this type of system. It was also found that these species are adsorbed with the OCO plane normal to the metal surface. Tilting the OCO plane of H_2CO_2 adsorbed on the aligned-bridge site causes a large destabilization effect. The same is not observed for H_2CO_2 adsorption on the cross-bridge site, where only a small decrease in adsorption energy is observed. The border effect is observed for two aligned-bridge site of the Cu_7 cluster. There is a stabilization of adsorption energy due to the interaction of the hydrogen atom's slightly positive charge with the hollow sites being slightly negatively charged. On the larger cluster, this has not been verified due to the larger dispersion of the charges.

The energy difference between the free molecules is 380 kJ mol^{-1}, the radical being more stable. The energy gap should be close to the difference between those of adsorbed H_2CO_2 and $[H_2CO_2]^{2-}$, since both species have the same geometry after adsorption on the Cu (111) surface. This was verified after our computations since the adsorption energy difference between the radical and the anion is ~ 450 and ~ 400 kJ mol^{-1} for adsorption on the aligned-bridge site and cross-bridge site, respectively. The adsorption energy for the H_2CO_2 species on the cross-bridge site is large

(~ 400 kJ mol^{-1}). This is a strong indication of the possible presence of this intermediate in the methanol oxidation reaction. The formaldehyde reaction with atomic oxygen present on the surface yielding the dioxymethylene species is predicted to be thermodynamically favourable. Compared with the free formaldehyde and adsorbed atomic oxygen atom, the adsorbed dioxymethylene species is stabilized by ~ 115 kJ mol^{-1}. The decomposition of this species to adsorbed formate and adsorbed atomic hydrogen is also favoured. The differences in energy are 210.2 kJ mol^{-1} for adsorption on the aligned-bridge site and 132.4 kJ mol^{-1} for adsorption on the cross-bridge site.

The total charges found for the adsorbed H_2CO_2 and $[H_2CO_2]^{2-}$ molecules are similar for adsorption on the two sites considered despite the method used to calculate the atomic charges. There is an estimated charge donation from the metal surface to the adsorbed species by approximately $0.7e$ if Mulliken charges are used, and a larger value is found when the NPA populations are used. The charge transfer predicted with this method is in agreement with the values predicted by the dipole moment variation with the distance of the adsorbate to the metal. Also, from these results, it was found that the bonding type of the species considered in both adsorption sites of the copper (111) surface is predominantly ionic.

For the equilibrium geometries of H_2CO_2 adsorbed on the two metal clusters and of $[H_2CO_2]^{2-}$ adsorbed on the smaller cluster, a study of the IR frequencies was carried out, and the results obtained are in good agreement with the available experimental data.

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