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A DFT study of the methanol oxidation catalyzed by a copper surface

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Abstract

The energy variation in the overall catalytic oxidation of methanol to carbon dioxide on a copper surface is analyzed using the density functional theory. Adsorption energies, geometries and charges for methanol and the various intermediates were computed from geometry optimized calculations on a large cluster containing 22 copper atoms used to model the Cu(1 1 1) surface. The calculated parameters are reported for the most stable adsorption modes of the various species considered: CH_3OH, CH_3O, H_2CO, H_2CO_2, HCO_2, H and O. The results obtained are in good agreement with available experimental data. The adsorption energies obtained were then used to plot the energy variation along the decomposition of methanol. The energy profile shows that the several reaction steps are lower in energy than the initial state: $CH_3OH_{(g)} + O_{(ads)}$. It is also shown that the stability of the adsorbed formaldehyde species is responsible for getting H_2CO or CO_2 as the final oxidation products. The decomposition of formaldehyde to formate is highly exothermic and this is the main reason for the high reactivity of the dioxymethylene intermediate. This prevents, therefore, the experimental verification of its existence. The total energy of the final products is 210 kJ/mol lower than that of the initial state. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the last two decades, there has been considerable interest in the chemistry of methanol on transition metal surfaces, inspired in part by the use of copper as a catalyst in methanol synthesis [1–4]. Adsorbed methoxy, formaldehyde, formate and dioxymethylene are important intermediates for the metal catalyzed synthesis of oxygenate products from carbon monoxide and molecular hydrogen or for the reverse reaction, that is, the decomposition of methanol on a metal surface. The knowledge of the mode of coordination of these species is therefore an essential piece of information for a better understanding of the mechanism and selectivity in these reactions. In addition, the fact that some of these intermediates are stable on a large variety of metallic surfaces makes these reactions attractive to study by several surface techniques.

All oxygen containing species mentioned above are bonded to metal surfaces through their oxygen

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atom(s) except for CO which is bonded, on the metallic surfaces studied, through its carbon atom. In general, the bonding of these species involves the electron donation from the HOMO orbital of the adsorbate to the neighbor metallic atoms followed by a back-donation from the p and d metal orbitals to the LUMO of the adsorbate. This results in a strong surface–adsorbate bond and in a decrease of the CO bond order in the adsorbed species.

The adsorption and decomposition of methanol have been investigated on a variety of metal surfaces, for example, Cr(1 1 0) [5], Ni(1 0 0) [6], Ni(1 1 0) [7], Ni(1 1 1) [8], Cu(1 0 0) [9–11], Cu(1 1 0) [3,12–15], Cu(1 1 1) [16–19], Ag(1 1 0) [20,21], Ag(1 1 1) [22], Au(1 1 0) [23], Pd(1 1 0) [24], Pd(1 1 1) [25], Pt(1 0 0) [26], Pt(1 1 0) [27], Pt(1 1 1) [4], Mo(1 0 0) [28], Mo(1 1 0) [29] and Al(1 1 1) [30]. In all these surfaces, methoxy radical, CH_3O, is the dominant surface intermediate at temperatures below 350 K, and it is easily formed by cleavage of the methanol O–H bond. The product distribution observed during the thermal decomposition varies with the nature of the surface and with the existence or not of pre-adsorbed oxygen. This is due to the great dependence of the methoxy fragment reactivity on the surface orientation of the metal.
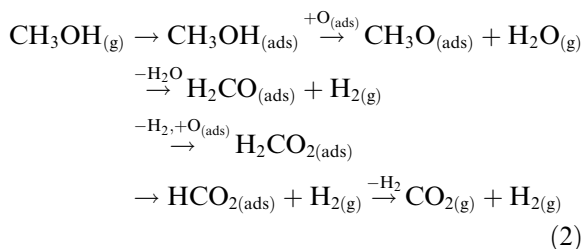
For copper surfaces, methanol is molecularly adsorbed at $\sim$90 K on the clean surface and desorbs without reaction at 210 K [31]. If pre-adsorbed atomic oxygen is present on the surface, formation of methoxy radical and water (187–350 K) take place by the following deprotonation reaction of methanol:

$$2CH_3OH_{(g)} + O_{(ads)} \xrightarrow{Cu} 2CH_3O_{(ads)} + H_2O_{(g)} \qquad (1)$$

Bowker and Madix [32] have observed the formation of methoxy species on a clean Cu(1 1 0) surface at 270 K but it recombines with the coadsorbed hydrogen and desorbs as intact methanol. Adsorbed methoxy radical is a stable intermediate and was the object of extensive experimental and theoretical studies. On Cu(1 1 1), it was concluded that CH_3O is adsorbed by the oxygen atom on a fcc hollow site with its CO axis normal to the metal surface. With the increase of temperature ($>$350 K) [31], methoxy radical is

decomposed to formaldehyde. Depending on the experimental conditions, formaldehyde is the major product of methanol oxidation on copper surfaces and it is desorbed on Cu(1 1 1) [31] and on Cu(1 1 0) [32,33] at $\sim$370 K. From the experimental results it seems that this dehydrogenation occurs directly to the metallic surface but as atomic oxygen exists on the surface it is possible that the hydrogen atom jumps from the carbon atom to a neighboring O atom or OH radical coadsorbed on the surface. In this case, water would be produced as it happens in reaction (1). We have previously compared both reactions [34], decomposition of CH_3O on the clean copper surface and on the copper surface with coadsorbed OH species. We have concluded that both reaction schemes are possible since the energy required is similar. Formaldehyde is weakly adsorbed on these surfaces and without the presence of oxygen it is desorbed from the surface without further reaction. On Cu(1 1 0) formaldehyde is adsorbed in two different forms [33]: (i) Molecularly, with the C–O axis tilted away from the normal to the surface. This leads to overlap not only with the oxygen lone pair orbital but also with the C–O π-bonding orbital. (ii) In a polymeric form (para-formaldehyde), where there are only C–O single bonds, $-(CH_2O)_n-$. This polymeric form was also found for H_2CO adsorption on Ag(1 1 0) and Ag(1 1 1) [35,36]. In the presence of oxygen, formaldehyde undergoes oxidation to formate via the formation of a dioxymethylene intermediate, H_2CO_2 [32,37–41]. Recent experimental studies propose the methanol oxidation to formate as the preferred reaction route on copper surfaces [42–45]. At 470–490 K, formate is decomposed to hydrogen and carbon dioxide [31,34,41].

A possible mechanism for the global methanol oxidation process can be summarized as follows:

$$CH_3OH_{(g)} \rightarrow CH_3OH_{(ads)} \xrightarrow{+O_{(ads)}} CH_3O_{(ads)} + H_2O_{(g)}$$
$$\xrightarrow{-H_2O} H_2CO_{(ads)} + H_{2(g)}$$
$$\xrightarrow{-H_2, +O_{(ads)}} H_2CO_{2(ads)}$$
$$\rightarrow HCO_{2(ads)} + H_{2(g)} \xrightarrow{-H_2} CO_{2(g)} + H_{2(g)}$$
$$\qquad (2)$$

The majority of experimental work, concerning the adsorption of the species considered in this paper, was done for Cu(1 0 0) and Cu(1 1 0). We cannot find in the literature but a few works for the adsorption on the Cu(1 1 1) surface. This is rather surprising since it has been reported that copper atoms in the structure of the ZnO catalyst used in methanol synthesis adopt a (1 1 1) arrangement [46].

In this work we report a series of density functional theory (DFT) quantum calculations for the interaction of CH_3OH, CH_3O, H_2CO, H_2CO_2 and HCO_2 with the Cu(1 1 1) surface. From them, important results concerning adsorption properties and an energetics profile in the course of the total methanol oxidation reaction (Eq. (2)) were obtained. Also, from a theoretical point of view, the interaction of these small molecules with the copper surface is interesting because they are the smallest CO containing molecular species and therefore could serve as a model for the O-surface interactions of larger alcohols and their oxidation products.

This paper is organized as follows. In Section 2, details of the cluster geometry and the theoretical method are given. Section 3 presents the numerical results and their discussion, while in Section 4 the most important conclusions are summarized.

2. Computational methodology

A Cu_{22} substrate cluster (Fig. 1) with 14 copper atoms in the first layer and eight in the second layer was used to model the Cu(1 1 1) surface in interaction with the CH_3OH, CH_3O, H_2CO, H_2CO_2 and HCO_2 species. This substrate of C_s symmetry forms a compact section of the ideal Cu(1 1 1) surface with a Cu–Cu distance taken from the bulk. Small clusters were previously found to give a reliable description of the metal surface for different adsorbate systems such as methoxy [47–50], dioxymethylene [51,52], formate [53], ethylene [54], carbon dioxide [55], etc.

The interaction of the different species with the Cu(1 1 1) surface is described by a $Cu_{22}A$ aggregate with A = CH_3OH, CH_3O, H_2CO, H_2CO_2 and HCO_2. The Cu–Cu distances are kept fixed in all
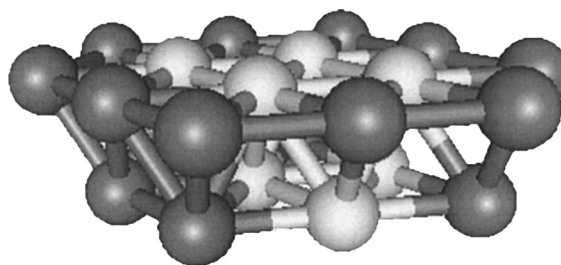

Fig. 1. Side view of the Cu_{22} (14,8) cluster used to simulate the Cu(1 1 1) surface. The four metal atoms of the first layer and the three atoms of the second layer (shown in light grey) were treated with the LANL2DZ basis set while the other atoms (shown in dark grey) were treated with the LANL2MB basis set.

the calculations performed while the internal geometry of the adsorbate was fully optimized.

Earlier on, we have studied, by means of the DFT based B3LYP method and the cluster approach, the adsorption of the methoxy [49,50], dioxymethylene [51,52] and formate [53] species. The methoxy radical was found to be preferentially adsorbed on the fcc hollow site of the Cu(1 1 1) surface with the CO axis nearly perpendicular to the surface. Dioxymethylene is adsorbed more efficiently with the oxygen atoms aligned on a cross-bridge site, i.e., one oxygen atom located almost above a fcc hollow site and the other almost above a hcp hollow site. The site that stabilizes more efficiently the formate species is the short-bridge site where the oxygen atoms are placed above two copper atoms, which define the short bridge. Dioxymethylene and formate are adsorbed on the Cu(1 1 1) surface with the OCO plane normal to the surface.

A key point of the present work concerns the thermodynamic profile of the methanol oxidation reaction on Cu(1 1 1). To obtain a reasonable description of this reaction profile it is necessary to describe the different sites and adsorption species at the same level of theory. Therefore, the corresponding adsorption energies described in our preliminary studies [49–53] have been calculated again by performing a full optimization of the internal parameters of the adsorbate but using a single cluster model and same basis sets.

In this work, the three parameter hybrid method proposed by Becke [56] with the gradient

corrected functional of Lee et al. [57] was used to determine the geometry, adsorption energy and charges of the several species proposed to be involved in the methanol oxidation reaction catalyzed by the Cu(1 1 1) surface. The central seven copper atoms (four from the first layer and three from the second layer) were treated with the LANL2DZ basis set while for the other fifteen copper atoms the LANL2MB basis set was used. Both basis sets describe the 10 inner electrons of the copper atoms by the effective core potential of Hay and Wadt [58]. The 19 valence electrons are described by a double zeta basis set (LANL2DZ) or by a minimal basis set (LANL2MB). The non-metallic atoms, oxygen, carbon and hydrogen, were treated by the 6-31G** basis set of double zeta quality plus p polarization functions in hydrogen atoms and d functions in oxygen and in carbon atoms. The calculation method used as well as the basis sets are included in the GAUSSIAN 98 package [59].

3. Results and discussion

In this work, the DFT is employed to obtain information about the energetics of the methanol oxidation. For that purpose, the adsorption energy of the various adsorbed intermediates has been obtained and this required the full optimization of the geometry of the adsorbates. Since we have previously studied the adsorption properties of some of these intermediates, the results reported below concern only the adsorption on the most favorable sites. To avoid any source of misunderstanding, the discussion of the results concerning the adsorption properties of the different intermediates is divided in different subsections.

3.1. Methanol

The computed results for free and adsorbed methanol are presented in Table 1. The geometric parameters obtained for the free molecule are in good agreement with available experimental data [60]. As far as we know, only the very recent work of Sun et al. [61] concerns a theoretical treatment of the adsorption of methanol on single transition

Table 1
Energy and geometry for the methanol molecule free and adsorbed on the Cu(1 1 1) surface[a]

Methanol	Free molecule	Adsorbed on Cu(1 1 1)
E_{tot} (a.u.)	−115.722	–
E_{ads} (kJ/mol)	–	−34.7
dist (CH$_a$) (Å)	1.093	1.093
dist (CH$_b$) (Å)	1.101	1.101
dist (CH$_c$) (Å)	1.101	1.099
dist (CO) (Å)	1.417	1.422
dist (OH$_d$) (Å)	0.965	0.970
dist (Osurf.) (Å)[b]	–	3.397
dist (Csurf.) (Å)[b]	–	4.064
dist (H$_d$surf.) (Å)[b]	–	2.449
dist (CuO) (Å)[c]	–	3.563
dist (CuC) (Å)[c]	–	4.201
dist (CuH$_d$) (Å)[c]	–	2.679
ang (H$_a$CO) (°)	106.9	107.3
ang (H$_b$CO) (°)	112.9	112.4
ang (H$_c$CO) (°)	112.9	112.1
ang (COH$_d$) (°)	107.9	107.5
ang (COsurf.) (°)[d]	–	28.0
died (H$_a$COH$_b$) (°)	118.5	118.3
died (H$_a$COH$_c$) (°)	118.4	118.9
died (H$_b$COH$_c$) (°)	123.1	122.8
$q_{adsorbate}$ (a.u.)	–	0.08

[a] The total Mulliken charge on the adsorbate is also given.
[b] Distance to the metal surface.
[c] Distance to the nearest copper atom on the surface.
[d] Angle between methanol C–O axis and the parallel to the metal surface.

metal surfaces. The authors have studied the adsorption of methanol on the clean and on the atomic oxygen covered Ag(1 1 0) surface. From our results it is concluded that this alcohol is weakly adsorbed on the Cu(1 1 1) surface with its C–O axis highly bent and the internal geometry almost unchanged when compared with the free species. The adsorption energy is ca. 35 kJ/mol and we have not observed a specific adsorption site for methanol, as it happens for instance with CH$_3$O. The C–O axis is weakly deviated from the line that connects the two copper atoms which defines the cross-bridge site. The distances from the carbon and oxygen atoms to the surface are 4.07 and 3.40 Å, respectively, while the distances of the same atoms to the nearest copper atom on the surface are 4.20 and 3.56 Å, respectively. The hydrogen of the alcohol group is the atom closest to the surface, Fig. 2a. This finding is consistent with the
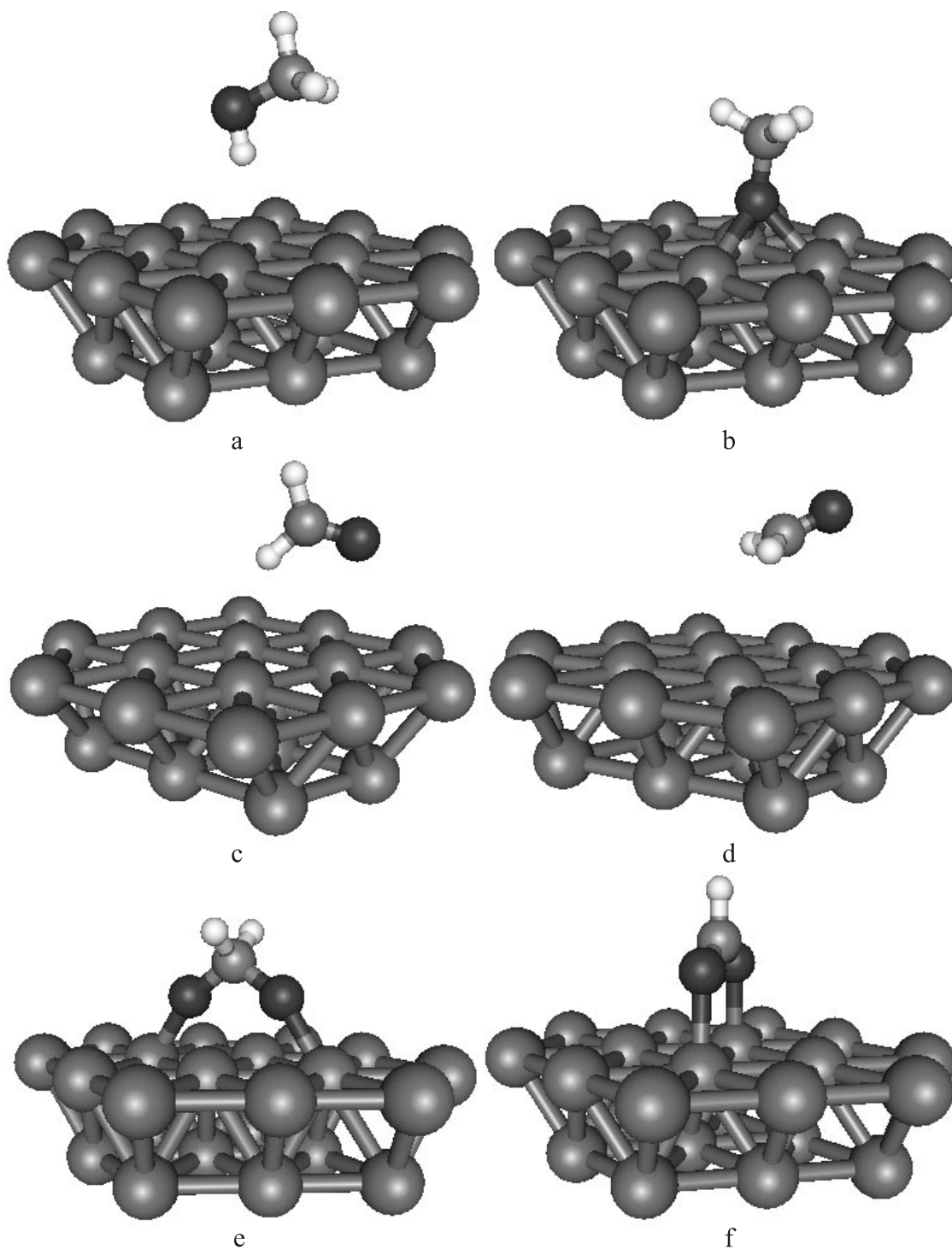
Fig. 2. Optimized structures for (a) methanol, (b) methoxy, (c) and (d) geometries I and II of formaldehyde, (e) dioxymethylene and (f) formate adsorbed on the clean Cu(1 1 1) surface.

results of Bowker et al. [32] and Sexton [62] where it was observed that methanol adsorbs on the clean surface as coadsorbed methoxy and hydrogen. The optimized structure is a precursor of the co-adsorbed species since the hydrogen atom of the alcohol group could be activated more efficiently by the surface and then the OH bond breaking would take place. Upon adsorption, the total charge in methanol is 0.08 e, which means that there is charge transfer from methanol to the metal surface. The weak interaction of this molecule with the metal surface – low adsorption energy and large distance to the surface – is a strong evidence for a physisorbed species.

3.2. Methoxy

On transition metal surfaces, methoxy is adsorbed preferentially on hollow sites [18]. On the Cu(1 1 1) surface, CH_3O is preferentially adsorbed on the fcc hollow site. Table 2 and Fig. 2b summarize the computed results for the methoxy species adsorbed on the Cu(1 1 1) surface.

The methoxy species is adsorbed with its C–O axis almost normal to the metal surface with a tilting angle close to 7° which is in excellent agreement with the recent work of Amemiya et al. [63]. This small tilting angle should be responsible for the conflicting assignments reported in the literature. A tilted orientation for the molecular axis of the CH_3O radical was found for adsorption on Cu(1 1 0) [64,65]. The same was proposed for adsorption on Cu(1 0 0) by the near-edge X-ray absorption fine structure (NEXAFS) study of Outka et al. [66] and by the infrared spectroscopy [67,68] studies of Ryberg. Outka and coworkers [66] report that the CO axis is tilted by 20–40° from the Cu(1 0 0) surface normal. However, Camplin and McCash [11] using the reflection absorption infrared spectroscopy (RAIRS) technique, found the methoxy radical C–O bond to be perpendicular to the Cu(1 0 0) surface. A later study of Lindner et al. [69] with a combined NEXAFS and photoelectron research concluded that the C–O axis is perpendicular to the surface and that a low symmetry adsorption site between the bridge and the fourfold hollow site is occupied. X-ray photoelec-

Table 2
Energy, geometry and total Mulliken charge for the methoxy, dioxymethylene and formate species adsorbed respectively on the fcc hollow, cross-bridge and short-bridge sites of the Cu(1 1 1) surface

Cu(1 1 1)	Methoxy	Dioxymethylene	Formate
E_{ads} (kJ/mol)	−154.4	−284.8	−228.6
dist (CH_a) (Å)	1.099	1.105	1.106
dist (CH_b) (Å)	1.099	1.105	–
dist (CH_c) (Å)	1.098	–	–
dist (CO_a) (Å)	1.416	1.403	1.264
dist (CO_b) (Å)	–	1.388	1.264
dist $(O_a surf.)$ (Å)[a]	1.450	1.598	2.012
dist $(O_b surf.)$ (Å)[a]	–	1.660	2.012
dist (CuO_a) (Å)[b]	2.067	1.918	2.017
dist (CuO_b) (Å)[b]	–	1.970	2.017
ang $(H_a CO_a)$ (°)	110.1	109.7	116.1
ang $(H_b CO_a)$ (°)	110.9	109.7	–
ang $(H_c CO_a)$ (°)	110.9	–	–
ang $(H_a CO_b)$ (°)	–	108.6	116.1
ang $(H_a CH_b)$ (°)	108.4	109.5	–
ang $(O_a CO_b)$ (°)	–	110.8	127.8
ang (COsurf.) (°)[c]	7.0	–	–
died $(H_a COH_b)$ (°)	120.0	–	–
$q_{adsorbate}$ (a.u.)	−0.27	−0.56	−0.32

[a] Distance to the metal surface.
[b] Distance to the nearest copper atoms on the surface.
[c] Angle between methoxy C–O axis and the normal to the metal surface.

tron diffraction (XPD) [18] studies for adsorption on Cu(1 1 1) and RAIRS [22] for adsorption on Ag(1 1 1) showed that the CO bond axis is normal to the surface plane.

The calculated C–O bond length, 1.416 Å, for the adsorbed species is in good agreement with the experimental results of Hofmann et al. [16], 1.42 Å (−0.03/ + 0.10) and of Amemiya et al. [63], 1.46 ± 0.05 Å. As predicted in previous theoretical works [48–50], the computed distance from oxygen to nearest surface copper atom is higher than the experimental values reported in the literature [16,63]. However, the calculated value, 2.067 Å, is very close to the XPD result [16], 1.98 ± 0.03 Å, and to the SEXAFS result [63], 2.00 ± 0.03 Å.

Due to the small C–O axis tilting angle, the methyl group internal symmetry is almost unchanged and the dihedral angles are still close to 120°. The H–C–O angles are 110.9° for the two

hydrogen atoms closest to the surface and 110.1°
for the third hydrogen atom. The calculated ad-
sorption energy is of about 154 kJ/mol.

3.3. Formaldehyde

Table 3 presents the results obtained for the free
and adsorbed formaldehyde molecule. As it hap-
pens with methanol, formaldehyde is weakly ad-
sorbed on the Cu(1 1 1) surface and the adsorption
energy is close to 20 kJ/mol.

Two different optimized structures were found
(see Fig. 2c and d) but both are similar in terms of
adsorption energy. The calculated internal pa-
rameters for the adsorbed formaldehyde molecule
are reported in Table 3. They are very similar to
the calculated values for the free species and also
to the experimental values [60]. The C–O and C–H
bond lengths are 1.210 and 1.109 Å, respectively.
For the structure labeled I (Fig. 2c) the computed
internal angles are 122.2° and 115.6° for the OCH
and HCH angles, respectively. In structure II (Fig.

2d) the OCH angle is 122.4° and the HCH angle is
115.2°. Like methanol, formaldehyde is adsorbed
at a large distance from the metal surface but in
this case it seems that formaldehyde is preferen-
tially adsorbed with the oxygen atom almost above
one copper atom. In structure I, the oxygen and
the carbon atoms are placed at 3.621 and 3.551 Å
from the nearest copper atom on the surface, while
in structure II the oxygen and the carbon atoms
are placed at 3.861 and 2.551 Å from the nearest
neighbor copper atom. However, despite the dif-
ferences between the optimized structures con-
cerning the geometry of formaldehyde above the
metal surface, the adsorption energy differs by
only 0.5 kJ/mol. The almost unchanged internal
structure of adsorbed formaldehyde when com-
pared with this molecule in the gas phase results in
the calculated low interaction energy for formal-
dehyde on the Cu(1 1 1) surface. This weak ad-
sorption is in agreement with experimental results
where it is observed that formaldehyde is the ma-
jor product of methanol oxidation catalyzed by
copper surfaces. Only a small amount of this ad-
sorbed formaldehyde is decomposed to formate on
clean copper surfaces.

3.4. Dioxymethylene

The dioxymethylene species has been proposed
as the reaction intermediate in the formaldehyde
oxidation to formate [31,37–41]. The H_2CO_2 in-
termediate is formed after reaction of H_2CO with
surface oxygen. Barteau et al. [40] performed an
experiment where H_2CO was adsorbed on a
Cu(1 1 0) surface with pre-adsorbed labeled atomic
oxygen (^{18}O). The authors noticed the presence of
[18]O on desorbed H_2CO which means that form-
aldehyde interacts with the atomic oxygen present
on the surface. A similar result was obtained for
[18]O adsorption on Cu(1 1 1) [31]. Despite the great
interest on this adsorbed species only recently the
adsorption of dioxymethylene on copper surfaces
was studied [51,52]. The low stability of the di-
oxymethylene intermediate prevents the experi-
mental observation of its existence.

Dioxymethylene is preferentially adsorbed on
the cross-bridge site of the Cu(1 1 1) surface. The

Table 3
Energy and geometry for the formaldehyde molecule free and
adsorbed on the Cu(1 1 1) surface[a]

Formaldehyde	Free molecule	Structure I on Cu(1 1 1)	Structure II on Cu(1 1 1)
E_{tot} (a.u.)	−114.501	–	–
E_{ads} (kJ/mol)	–	−22.9	−22.4
dist (CH_a) (Å)	1.111	1.109	1.109
dist (CH_b) (Å)	1.111	1.109	1.109
dist (CO) (Å)	1.207	1.210	1.210
dist (Osurf.) (Å)[b]	–	3.608	3.844
dist (Csurf.) (Å)[b]	–	3.418	3.386
dist (CuO) (Å)[c]	–	3.621	3.861
dist (CuC) (Å)[c]	–	3.551	3.584
ang (H_aCO) (°)	122.4	122.2	122.4
ang (H_bCO) (°)	122.4	122.2	122.4
ang (HCH) (°)	115.2	115.6	115.2
ang (COsurf.) (°)[d]	–	9.0	22.2
$q_{adsorabate}$ (a.u.)	–	0.07	0.06

[a] The total Mulliken charge on the adsorbate is also given.
[b] Distance to the metal surface.
[c] Distance to the nearest copper atom on the surface.
[d] Angle between formaldehyde C–O axis and the parallel to
the metal surface.

results obtained for the optimal conformation on this adsorption site are presented in Table 2 and also in Fig. 2e. The dioxymethylene oxygen atoms are located at two different distances from the metallic surface, being closer to the surface the oxygen atom that is placed above one hcp hollow site. The difference between the oxygen to surface distances have little effect in the internal geometry of the adsorbed H_2CO_2 species. The C–O bond lengths are 1.403 and 1.388 Å for the oxygen atom adsorbed on the hcp hollow and the fcc hollow sites, respectively. The C–H bond length is 1.105 Å and the HCH, OCH and OCO angles are close to 110°. The calculated adsorption energy is 285 kJ/mol obtained as the difference between the total energy of the H_2CO_2–cluster aggregate and the total energy of the two H_2CO_2 and metal cluster fragments. This result cannot be used as a measure of the stability of the adsorbed dioxymethylene species since H_2CO_2 is unstable in the gas phase, it dissociates to H_2 and CO_2. However, the adsorbed species is more stable than adsorbed formaldehyde and atomic oxygen by 47 kJ/mol.

3.5. Formate

The adsorption of the formate species on Cu-(1 0 0) and Cu(1 1 0) has been extensively studied by several experimental techniques [33,38,41,70–73]. Recently, we have studied the adsorption of HCO_2 on Cu(1 0 0), Cu(1 1 0) and Cu(1 1 1) [53]. It was concluded that the HCO_2 adsorption is similar on the three surfaces considered, with the oxygen atoms aligned on the short-bridge site.

The results obtained for formate adsorption on the Cu_{22} cluster used in this work are shown in Table 2 and Fig. 2f. Formate is bonded to the Cu(1 1 1) by an adsorption energy close to 229 kJ/mol. The oxygen atoms are placed almost atop the oxygen atoms that define the short-bridge site as can be seen by the small difference between the oxygen to surface distance and oxygen to nearest copper atom on the surface distance. The C–H and C–O bond lengths are 1.106 and 1.264 Å, respectively. The computed C–O and O-surface distances and the O–C–O angle are in good agreement with

Table 4
Energy, geometry and total Mulliken charge for atomic hydrogen and atomic oxygen adsorbed on the fcc hollow site of the Cu(1 1 1) surface

Cu(1 1 1)	Hydrogen	Oxygen
E_{ads} (kJ/mol)	−168.8	−285.8
dist (Asurf.) (Å)[a]	0.984	1.237
dist (CuA) (Å)[b]	1.796	1.946
$q_{adsorbate}$ (a.u.)	0.03	−0.60

[a] Distance to the metal surface.
[b] Distance to the nearest copper atoms on the surface.

the experimental photoelectron and NEXAFS studies [45,46].

3.6. Hydrogen and oxygen

In order to obtain full information about the energy variation in the total oxidation of methanol, parameters about atomic hydrogen and atomic oxygen adsorption on the Cu_{22} are also necessary. Hydrogen and oxygen are known to be preferentially adsorbed on the fcc hollow site [34,74,75]. The results obtained for adsorption on the Cu(1 1 1) fcc hollow site are reported in Table 4.

Hydrogen is adsorbed on the copper surface at a 0.984 Å and with an adsorption energy of 168.8 kJ/mol while oxygen is placed at 1.237 Å from the surface with an adsorption energy of 285.8 kJ/mol. When compared with the methoxy species, the oxygen atom is placed closer to the metallic surface and the charge transferred from the metal surface is larger. However, the charge in the methoxy oxygen atom is −0.58 a.u. (result not shown) which is almost the same charge that is present in the adsorbed oxygen atom. This is due to charge transfer from the methyl hydrogens to the oxygen in the methoxy radical.

3.7. Total energy variation

The energy diagram for the total methanol oxidation to carbon dioxide catalyzed by the Cu-(1 1 1) surface is illustrated in Fig. 3. The diagram is plotted for the reaction beginning with two molecules of methanol reacting on a surface with pre-adsorbed atomic oxygen. As referred above, the
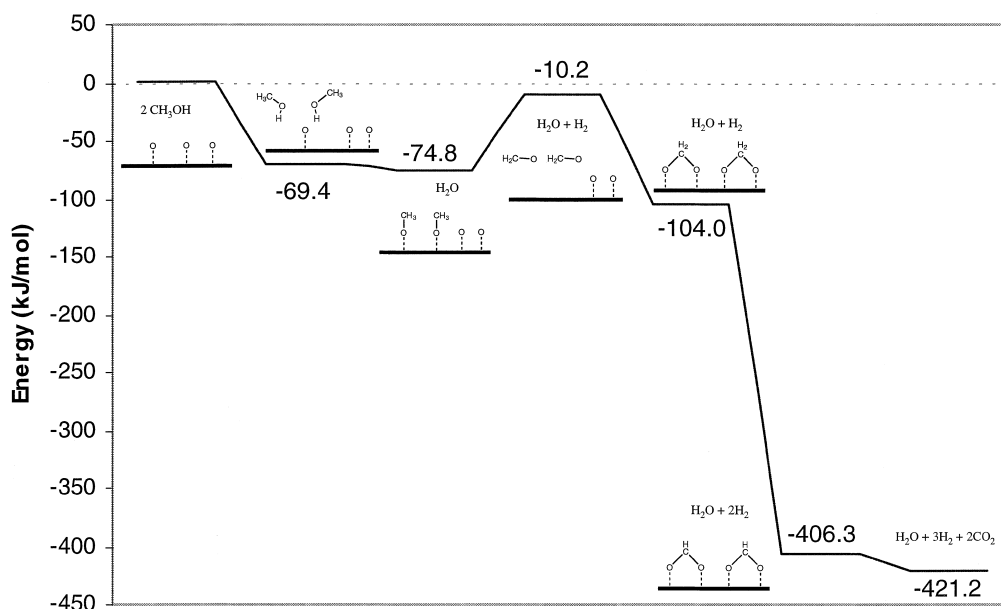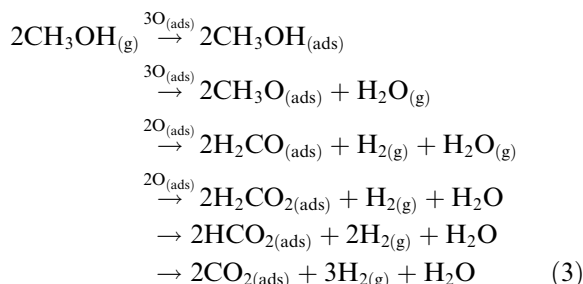
Fig. 3. Energy diagram for the CH_3OH oxidation over a Cu(1 1 1) surface. The zero in energy is considered for the system composed by two free methanol molecules plus adsorbed atomic oxygen.

existence of pre-adsorbed oxygen is essential to occur methanol dissociation in methoxy and water.

$$2CH_3OH_{(g)} \overset{3O_{(ads)}}{\rightarrow} 2CH_3OH_{(ads)}$$
$$\overset{3O_{(ads)}}{\rightarrow} 2CH_3O_{(ads)} + H_2O_{(g)}$$
$$\overset{2O_{(ads)}}{\rightarrow} 2H_2CO_{(ads)} + H_{2(g)} + H_2O_{(g)}$$
$$\overset{2O_{(ads)}}{\rightarrow} 2H_2CO_{2(ads)} + H_{2(g)} + H_2O$$
$$\rightarrow 2HCO_{2(ads)} + 2H_{2(g)} + H_2O$$
$$\rightarrow 2CO_{2(ads)} + 3H_{2(g)} + H_2O \qquad (3)$$

The zero in energy is considered for the copper surface with adsorbed atomic oxygen and with methanol in the gas phase. The adsorption of one methanol molecule lowers the energy by 35 kJ. Note that in this energy diagram, coadsorption effects are not included as well as reaction barriers. The methanol decomposition to adsorbed methoxy and desorbed water is energetically favorable. This is due to the fact that the methoxy radical is strongly stabilized on transition metal surfaces. The energy stabilization on the Cu(1 1 1) surface is

higher than the energy required for desorption of one water molecule from the catalyst. The same is not verified in the reaction where the methoxy species produces adsorbed formaldehyde and molecular hydrogen in the gas phase. In this case, some energy is consumed. However, the energy step shown in the diagram is still lower than the total energy of the methanol in the gas phase plus the copper surface covered with atomic oxygen. In the absence of atomic oxygen on the catalyst, formaldehyde will desorb from the surface. Using the calculated adsorption energy for formaldehyde, ~23 kJ/mol, the total cost in the production of H_2CO from CH_3OH will be ~18 kJ/mol. The reaction of formaldehyde with adsorbed oxygen yielding the dioxymethylene species is highly favorable. The gain in energy is 47 kJ/mol, approximately. Then, dioxymethylene is decomposed to adsorbed formate species and to molecular hydrogen, which is desorbed from the metal surface. This reaction step is extremely exothermic. The final energy represents a gain of 203 kJ/mol when compared with the initial step. The large exothermicity in the $H_2CO_{(ads)} + O_{(ads)} \rightarrow H_2CO_{2(ads)}$

and in the $H_2CO_{2(ads)} \rightarrow HCO_{2(ads)} + \frac{1}{2}H_{(g)}$ reaction paths as well as in the global $H_2CO_{(ads)} + O_{(ads)} \rightarrow H_2CO_{2(ads)} \rightarrow HCO_{2(ads)} + \frac{1}{2}H_{(g)}$ reaction scheme should be responsible for the high reactivity of the dioxymethylene species. Dioxymethylene seems to be the intermediate in the decomposition of formaldehyde to formate. The large exothermicity of the global reaction causes problems in the detection of this intermediate species in experimental works. In the final reaction, also favorable, formate is decomposed to gas phase carbon dioxide and molecular hydrogen. In a catalytic system, the overall reaction of methanol oxidation should be governed by the way how formaldehyde interacts with the catalyst.

4. Conclusions

Using the DFT and the cluster model approach, we have studied the energy variation in the methanol oxidation on a copper catalyst. The results agree with the proposed model for the reaction catalyzed by transition metal surfaces.

For that purpose we have started to calculate the adsorption properties of all intermediates in this specific reaction. The results obtained for methoxy and formate species are in good agreement with experimental data. Both intermediates are strongly attached to the metal surface by the oxygen atom(s) and at an oxygen-nearest copper atom in the surface distance of ≈ 2.1 Å. The plane containing the carbon and oxygen atoms of the formate species is predicted to be normal to the surface and the C–O axis in the methoxy radical is quasi-perpendicular to the metal surface. The geometries of adsorbed methanol and formaldehyde are similar to the gas phase molecules and the low adsorption energy found is also in agreement with experimental data. These two molecules do not have a specific adsorption site and the distance to the metal surface is high. It is concluded that these molecules interact weakly with the Cu(1 1 1) surface, possibly in a physisorbed state. The adsorption geometry of the dioxymethylene intermediate is in agreement with our previous results where the cross-bridge was predicted to stabilize more efficiently this species.

The oxygen atoms are located at two different distances from the catalyst and the OCO plane is normal to the metal surface.

Using the calculated adsorption energies for the species specified above and also the adsorption energies of atomic oxygen and atomic hydrogen the variation in energy along the methanol to carbon dioxide reaction was obtained. The results show that the total energy of the different reaction stages is always below the total energy of the initial state. The initial state refers to the copper surface covered with atomic oxygen and methanol in the gas phase. In each reaction step, the total energy is more negative than the energy in the previous stage except in methoxy decomposition to formaldehyde and molecular hydrogen. The final stage, with water, hydrogen and carbon dioxide as products, is 421.2 kJ/mol lower in energy than the initial step where two methanol molecules interact with the metal surface.

Previously, using the same level of theory during all calculations, it was predicted that formate adsorbed with practically the same adsorption energy on the Cu(1 0 0), Cu(1 1 0) and Cu(1 1 1) surfaces [53]. Hence, a similar behavior is predicted for the other reaction intermediates present in the oxidation of methanol. Thus, an identical energy profile to that displayed in Fig. 3 is to be expected for the global methanol oxidation mechanisms on Cu(1 0 0) and Cu(1 1 0). The adsorption energy of an adsorbate decreases from copper to gold [50,75]. Therefore, when compared with the Cu(1 1 1) surface, lower energy differences between the several reaction steps in Fig. 3 are predicted for methanol oxidation on silver and gold surfaces. However, due to different distances between the preferred adsorption sites for the different species on distinct metal surfaces, a suitable prediction of what will happen with energy barriers in the various decomposition steps along the oxidation mechanism of methanol is not possible.

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