Methoxy radical reaction to formaldehyde on clean and hydroxy radical-covered copper (111) surfaces: a density functional theory study

J.R.B. Gomes [a, b], J.A.N.F. Gomes [a,*], F. Illas [b]

[a] *CEQUP/Dept. de Química, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal*
[b] *Departament de Química Física i Centre de Recerca en Química Teórica, Universitat de Barcelona, C/ Martí i Franquès 1, E-08028 Barcelona, Spain*

Abstract

The ab initio cluster approach has been used to investigate the decomposition reaction of methoxy radical to formaldehyde catalysed by a copper (111) surface and also to study the influence of co-adsorbed hydroxy species on the same reaction. Previous experimental studies indicate that the former reaction occurs with C−H bond cleavage without the interference of other co-adsorbed species on the metal surface. However, it has been observed in theoretical works that tilting of the methoxy C−O axis has a marked destabilization effect on the methoxy adsorption energy. This tilting of the methoxy C−O axis is important in the decomposition reaction since it allows one of the methyl hydrogens to approach the surface. From the results reported in the present paper, we can predict a lower energy barrier for this reaction when hydroxy species are adsorbed on the surface. These findings also indicate that defects such as steps on the surface near to adsorbed methoxy islands should lower the energy barrier since the tilting of the methoxy C−O axis should be smaller. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalysis; Chemisorption; Clusters; Copper; Density functional calculations; Radicals; Single crystal surfaces; Surface chemical reaction

1. Introduction

The understanding of the reactivity of surface intermediates provides useful information in the study of surface reactions and of heterogeneous catalysis. Because of the important role of methanol in industry, this alcohol and its reaction intermediates/products have been widely studied in the past two decades [1]. In the heterogeneous catalysis of methanol oxidation on several transition metals, various surface intermediates have been detected. The selective partial oxidation of CH_3OH to H_2CO has long been carried out over silver catalysts [2,3]. On copper and silver surfaces, the methanol oxidation yields essentially H_2CO [1,2]. The more active transition metals (Ni, Pd and Pt) oxidize methanol to CO and CO_2 [4]. On Fe and Mo surfaces some CH_4 was also found. Methanol is adsorbed molecularly on clean copper surfaces via the oxygen lone pairs of electrons and upon heating it desorbs intact, the conversion to formaldehyde being negligible [2,5,6]. It has been shown by UV photoemission [2,7] that OH bond

* Corresponding author. Fax: +351 2 6082959.
E-mail address: jfgomes@fc.up.pt (J.A.N.F. Gomes)

cleavage occurs on the surface producing methoxy species. Upon heating, the high stability of the methoxy species (greater than 150 kJ mol^{-1} [8]) and the low rate of hydrogen atom recombination on copper leads to the recombination of adsorbed CH_3O and H instead of CH_3O decomposition. If oxygen atoms are present on the surface, the reactivity of methanol is higher owing to the removal of the alcohol hydrogen by the adsorbed oxygen to form water. Water is eliminated at a temperature lower than that required for the recombination of CH_3O and H on the clean surface [4,6]. The absence of atomic hydrogen on the surface leads to decomposition of CH_3O to H_2CO. On silver and gold surfaces, the methoxy species is observed only when oxygen is pre-adsorbed on the metal surface. The decomposition of the methoxy species to formaldehyde and hydrogen is experimentally observed.

It has been identified by theoretical [8–11] as well as experimental [12–14] work that CH_3O binds to the surface via its oxygen atom with the CO axis normal to the surface. Theoretical work concerning the adsorption of the methoxy species on metal surfaces [8–11] shows that tilting of the methoxy CO axis has a marked destabilization effect on the adsorption energy. For a tilting of 30°, the destabilization in energy is approximately 30 kJ mol^{-1}. On the copper (111) surface, the methoxy hydrogen atom closest to the surface is placed at a distance of 3.3 Å if the CO axis is perpendicular to the surface, and at a distance of 2.5 Å if the CH_3O species is tilted by 30°. Since typical R—H bond lengths lie in the interval 0.9–1.6 Å [15], it can be inferred that the interaction of the hydrogen atom with the surface is negligible. Thus, the hydrogen atom would interact with the surface only if the C—O axis is significantly tilted from the surface normal and this would result in a very marked destabilization in the CH_3O adsorption energy. The activation energy for the C—H bond scission should be lower if the CO axis of CH_3O is kept quasi-perpendicular to the surface and this is possible if another adsorbed species interacts and captures one of the hydrogen atoms of CH_3O. In this case, the distance from the methyl hydrogen atom to the co-adsorbed species is much smaller than the hydrogen to surface distance and

a stronger interaction should occur. This is corroborated by experimental findings on copper [16] and palladium [17] surfaces where the production of H_2CO is favoured in the presence of oxygen.

In this work, the study of methoxy co-adsorption (adsorbed on the fcc hollow site of the copper (111) surface) with OH (adsorbed on top, hcp and fcc sites) is presented. Theoretical calculations were performed for the reaction of the methoxy species yielding formaldehyde, and a comparison with the results obtained for the clean surface is made.

2. Theoretical details

In the present work, the interaction of the isolated methoxy radical, isolated hydroxy radical and both co-adsorbed species with the copper (111) surface is studied. For that purpose, the density functional theory (DFT) hybrid method B3LYP [18] was used. The B3LYP method comprises the three-parameter functional of Becke (mixture of DFT and HF terms) using the correlation functional of Lee et al. [19]. Four different metal clusters belonging to the C_s point symmetry group were used and are shown in Fig. 1. These two-layer clusters are a section of the ideal Cu (111) surface with a Cu—Cu nearest neighbour distance taken from the bulk and equal to 2.551 Å. The methoxy radical is known, from theoretical [8–11,20] and experimental [12–14] results, to adsorb preferentially on the fcc hollow site. The same is verified for the hydroxy species [21]. As stated above, the aim of this work was to study the co-adsorption of the two radicals on the copper surface. For that purpose we carried out calculations for the interaction of the methoxy species adsorbed on the fcc hollow site with the hydroxy radical adsorbed on four different neighbouring sites (top, short-hcp, long-hcp and fcc). When compared with the hydroxy radical, the methoxy radical is less mobile on the metal surface and that is one of the reasons for fixing the adsorption site of the former species. Another reason for keeping the methoxy radical on top of an fcc site is that we aim to compare the adsorption of an isolated methoxy species on the clean copper surface and
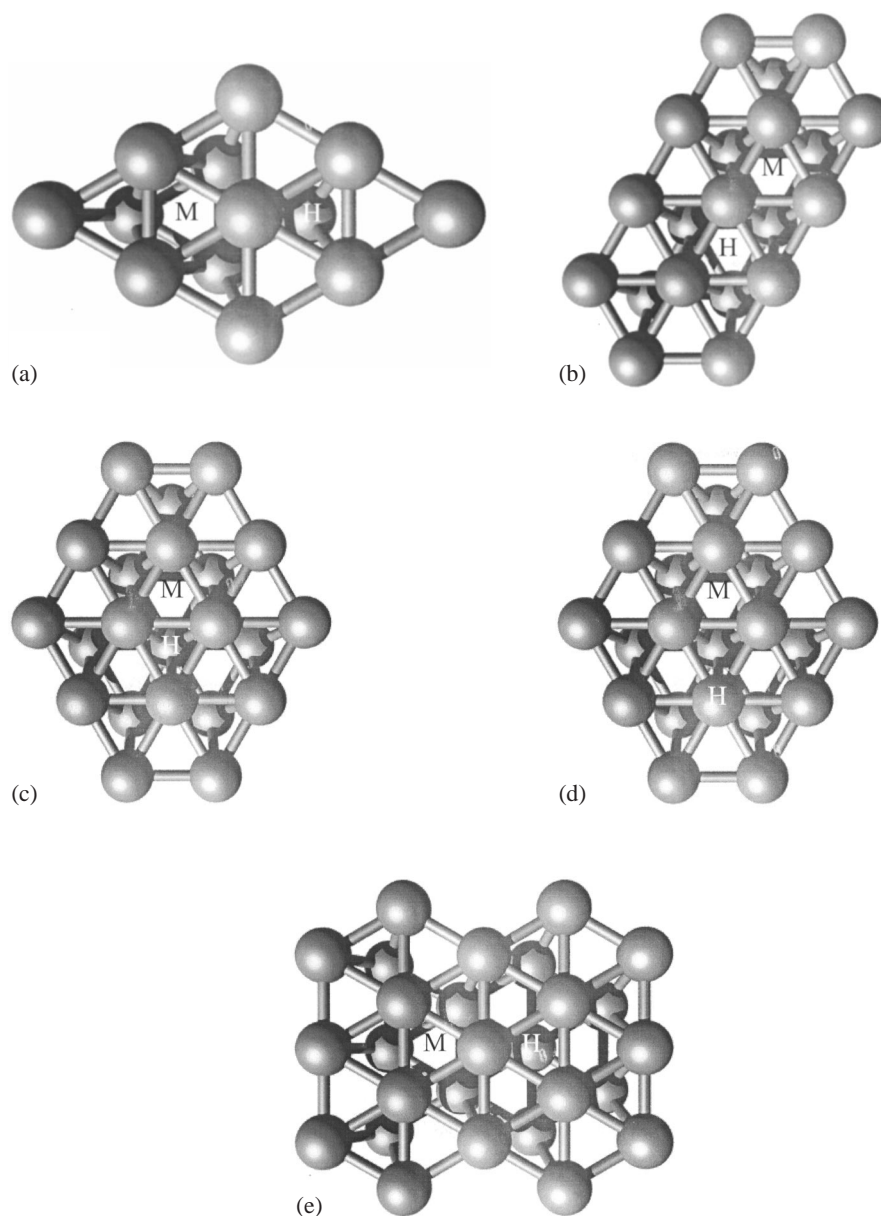
Fig. 1. Top views of the different clusters used to model the (111) copper surface. M labels the sites where methoxy is adsorbed and stands for the sites of adsorbed H after the reaction without and with co-adsorbed OH. (a) Cu_{13} (9,4) cluster with H meaning adsorption on the long-hcp site. (b) Cu_{20} (13,7) cluster with H meaning adsorption on the fcc site. (c) Cu_{22} (9,4) cluster with H meaning adsorption on the short-hcp site. (d) Cu_{22} (13,7) cluster with H meaning adsorption on the top site. (e) Cu_{27} (9,4) cluster with H meaning adsorption on the long-hcp site.

on the copper surface with co-adsorbed hydroxy species. Four different conformations for the two co-adsorbed species are shown in Fig. 1 where the methoxy radical is adsorbed on a fcc hollow site. These conformations are set-up with the help of three different cluster models. Those are the Cu_{13}

(9,4) cluster, shown in Fig. 1a, which was used to model the interaction of the methoxy species with the hydroxy radical adsorbed on the hcp hollow site that connects the fcc site via a copper atom; the Cu_{20} (13,7) cluster, shown in Fig. 1b, which was used to model the interaction of the methoxy species with the hydroxy radical adsorbed on a fcc hollow site and these two fcc hollow sites are connected by a hcp hollow site; the Cu_{22} (14,8) cluster which was used to model the interaction of the methoxy radical with the hydroxy species adsorbed on the nearest hcp hollow site, Fig. 1c, and with the hydroxy species adsorbed on a top site located on the farther edge of the cross-bridge site, Fig. 1d. These clusters were used also for the study of the CH_3O decomposition except the Cu_{13} cluster which was replaced in this case by a larger Cu_{27} (17,10), Fig. 1e.

The metal atoms were described differently depending on where these atoms are located in terms of the adsorption sites studied. If the metal atoms are in a local region (metal atoms involved directly with the adsorbate), these atoms are described with a basis set where the inner 1s, 2s and 2p electrons are treated with the effective core potential of Hay and Wadt [22] and where the outer electrons are treated with a basis set of double zeta quality. If the metal atoms do not interact directly with the adsorbate, a larger core is used, i.e. only one electron is treated explicitly and the inner 28 electrons are included in an electron core potential [23]. These 'different' regions are shown in Fig. 1 where the atoms near the M and H sites belong to the local region and the others to the outer region. In all clusters, seven metal atoms have been considered with small core except for the Cu_{20} cluster where only five copper atoms are treated with the small core basis set. The non-metal atoms were treated with the 6-31G** basis set of Pople et al. of double zeta quality with d polarization functions on carbon and oxygen atoms and p polarization function on hydrogen.

In the present work full geometry optimization is carried out for all atoms of the adsorbed species. Geometry constraints were applied to the cluster model atoms. The constraints ensure that the model represents an extended surface rather than a gas phase cluster. It is necessary to propound some logical reaction path that takes into account the experimental information. The reaction path used in this work assumes that the processes, methoxy reaction on the clean surface and on an OH-covered surface, take place following the $C \cdots H \cdots$ metal and the $C \cdots H \cdots O-H$ reaction coordinates. These were monitored by performing a scan of the $H \cdots$ metal and $H \cdots O-H$ distances for CH_3O adsorption on the clean surface and on the surface with co-adsorbed OH, respectively. All internal parameters of the adsorbates were fully optimized at each point of the reaction coordinate. The only exception is the $O-H$ bond length in the study of the CH_3O and OH interaction since the $O-H$ bond length in OH radical and water are very similar.

In all cases, the lowest possible spin multiplicity was considered and the C_s symmetry was used when possible. All calculations were carried out using the Gaussian 94 package [24].

3. Results

To facilitate the discussion of the results concerning the reaction of the methoxy radical in the clean and OH-covered surface and to separate clearly the methoxy decomposition from the reaction with OH we present the results in four different subsections. In Subsection 3.1, the adsorption of the different free species on Cu (111) is discussed, then Subsection 3.2 is devoted to the co-adsorption of CH_3O and OH on Cu (111), next, in Subsection 3.3, the CH_3O decomposition to $H_2CO + H$ is presented and, finally, Subsection 3.4 presents the reaction of CH_3O with OH yielding H_2CO and H_2O.

3.1. Free species adsorption on Cu (111)

In order to proceed with the study of the reaction path described in Section 2, it is necessary to start with the study of the interaction of the isolated species with the metal surface. The results for the optimized geometry of adsorbed H, OH, H_2CO and CH_3O on the Cu_{22} cluster (Fig. 1c and d) are shown in Table 1. Only the adsorption of

Table 1
Adsorbate binding energies and optimized geometric parameters for the adsorption of H, OH, H_2CO and CH_3O on the copper (111) surface

Parameter	Values for the following isolated species							
	H_{top}	H_{hcp}	H_{fcc}	OH_{top}	OH_{hcp}	OH_{fcc}	H_2CO_{top}	CH_3O_{fcc}
Ads. energy (kJ mol^{-1})	−75.7	−155.1	−165.4	−162.4	−222.2	−223.6	−19.9	−160.5
d (O−Surf.) (Å)	–	–	–	1.962	1.437	1.492	3.755	1.458
d (O−Cu) (Å)	–	–	–	1.962	2.097	2.097	3.762	2.073
d (H−Surf.) (Å)	1.511	1.052	1.026	–	–	–	–	–
d (H−Cu) (Å)	1.511	1.442	1.478	–	–	–	–	–
d (C−O) (Å)	–	–	–	–	–	–	1.212	1.412
d (C−H) (Å)	–	–	–	–	–	–	1.108	1.100
d (O−H) (Å)	–	–	–	0.967	0.967	0.967	–	–
Tilting (C−O) (°)	–	–	–	–	–	–	119.4	8.1
Tilting (O−H) (°)	–	–	–	27.9	12.6	8.0	–	–
Angle (O−C−H) (°)	–	–	–	–	–	–	122.4	110.8
Angle (H−C−H) (°)	–	–	–	–	–	–	115.2	108.2

the isolated species on the sites that are used in the study of the methoxy species decomposition is considered. The results obtained are similar to those obtained on the three other cluster models. Atomic hydrogen and the methoxy and hydroxy radicals adsorb preferentially on the fcc hollow site while formaldehyde is weakly adsorbed on the surface and without a specific coordination mode. Atomic hydrogen is located above the hcp and fcc hollow sites at a similar distance. The hydrogen distance to surface is 1.511 Å for adsorption on the top site, 1.052 Å on the hcp site and 1.026 Å

on the fcc site. The hydroxy species is adsorbed on the top and fcc sites with the O−H axis tilted away from the surface normal by 28 and 8°, respectively, the distance from the oxygen to the surface is 1.962 Å above the top site and 1.492 Å when adsorbed the fcc hollow site. The results for formaldehyde adsorption correspond to a highly bent species, i.e. the oxygen atom is placed above one copper atom at a distance of ∼3.8 Å and the carbon atom distance to the surface is rather smaller. In any case, the distance from O to the nearest surface Cu atom is 3.75 Å whereas that of

Table 2
Equilibrium distances for the co-adsorption of the methoxy (fcc hollow site) and hydroxy (top, hcp and fcc sites) radicals on the copper (111) surface

Species adsorbed on Cu (111)	Parameter	Values for the following co-adsorbed species		
		fcc + top	fcc + long-hcp	Fcc + fcc
$CH_3O + OH$	Ads. energy (kJ mol^{-1})	−345.9	−482.5	−429.0
CH_3O	d (O−Surf.) (Å)	1.429	1.535	1.479
CH_3O	d (O−Cu) (Å)	2.052	2.127	2.087
CH_3O	d (C−O) (Å)	1.423	1.414	1.402
CH_3O	d (C−H) (Å)	1.096	1.101	1.102
CH_3O	ang (O−C−H) (°)	109.7	111.7	111.3
CH_3O	tilting (C−O) (°)	0.8	12.4	3.6
OH	d (O−Surf.) (Å)	1.886	1.502	1.493
OH	d (O−Cu) (Å)	1.886	2.104	1.945
OH	d (O−H) (Å)	0.966	0.967	0.965
OH	tilting (O−H) (°)	20.8	41.9	9.3

C to its nearest surface atoms is of 3.65 Å; this geometry results in a Cu—O—C tilting angle of 119.4°. The carbon atom is placed above one hollow site with the two hydrogen atoms pointing towards the surface. The internal geometry of this adsorbed species is very similar to that corresponding to the gas phase molecule [15]. This is in agreement with the low adsorption energy found (~ 20 kJ mol^{-1}), which is characteristic of a physisorbed state. A different structure, with the oxygen atom above one hollow site and with the C—O axis less tilted, was also obtained in the minimization procedure. In this second structure, there is only one hydrogen atom pointing towards the surface, the tilting angle was $\sim 60°$ and the adsorption energy was ~ 20 kJ mol^{-1}. In Table 1 is shown only the geometrical parameters for CH$_3$O adsorbed on the fcc hollow site. This site is known, from both theoretical [8,9,11,20] and experimental [12,13] data, to be the one that stabilizes more efficiently the methoxy species. From a previous study [9], CH$_3$O adsorption on the fcc hollow site is more stable by ~ 30 kJ mol^{-1} than that on the hcp hollow site, ~ 40 kJ mol^{-1} than that on the bridge site and ~ 65 kJ mol^{-1} than that on the top site. The methoxy species is markedly destabilized by CO axis tilting. For a tilt of 45° the calculated adsorption energy for CH$_3$O adsorbed on the fcc site is lowered by ~ 60 kJ mol^{-1}. The calculated structure for the adsorbed methoxy species (see Table 1) is in agreement with previous theoretical [8,9,11,20] and experimental [12,13] findings. As in the case of the O—H adsorption on the fcc hollow site, a small tilting angle from the surface normal is predicted for the methoxy C—O axis. The optimum geometrical parameters for adsorbed methoxy are also reported in Table 1.
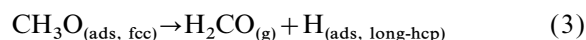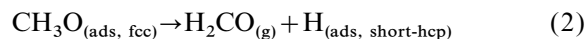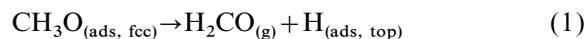
3.2. Co-adsorption of CH$_3$O and OH on Cu (111)

The results corresponding to the optimum geometry of methoxy, adsorbed on the fcc hollow site of Cu(111), having a co-adsorbed hydroxy radical on a top, hcp and fcc site are shown in Table 2. Let us first consider the situation where

the OH radical is adsorbed on the top site, see Fig. 1d. In this case, the methoxy C—O axis is almost normal to the surface in contrast to the adsorption of this radical on the clean surface. When compared with CH$_3$O adsorbed on the clean surface, the oxygen to surface distance is smaller by only ~ 0.03 Å and the C—O bond is increased by ~ 0.01 Å. The C—H distance is 1.096 Å and the O—C—H angle is 109.7°. The hydroxy radical is also less tilted and the oxygen to surface distance is decreased by ~ 0.08 Å. For the hydroxy radical adsorbed on the hcp hollow site, see Fig. 1a, the equilibrium geometry differences between the adsorption of the isolated and the co-adsorbed species are also small. In this situation, the C—O and O—H axes of, respectively, the methoxy and hydroxy radicals are more tilted. The internal parameters are practically unchanged. The differences are even smaller for co-adsorption of both species on fcc sites, see Fig. 1b, which are the preferred adsorption sites for the isolated species. The oxygen to surface distances are very similar between the two co-adsorbed species indicating that the hydrogen atoms in the methoxy radical interact weakly with the metal surface and the steric effects on the geometries of the adsorbates are minor. From the adsorption energies presented in Table 2 it is shown that co-adsorption is more favourable with both species adsorbed on hollow sites.

3.3. The energetics of the CH$_2$O to H$_2$CO plus H decomposition

The energy variation corresponding to the decomposition reaction of adsorbed CH$_3$O yielding gaseous formaldehyde and adsorbed atomic hydrogen is shown in Fig. 2. Four different reaction schemes were studied depending on the site where the generated hydrogen atom was adsorbed. These possibilities are as follows:

$$CH_3O_{(ads, fcc)} \rightarrow H_2CO_{(g)} + H_{(ads, top)} \qquad (1)$$

$$CH_3O_{(ads, fcc)} \rightarrow H_2CO_{(g)} + H_{(ads, short\text{-}hcp)} \qquad (2)$$

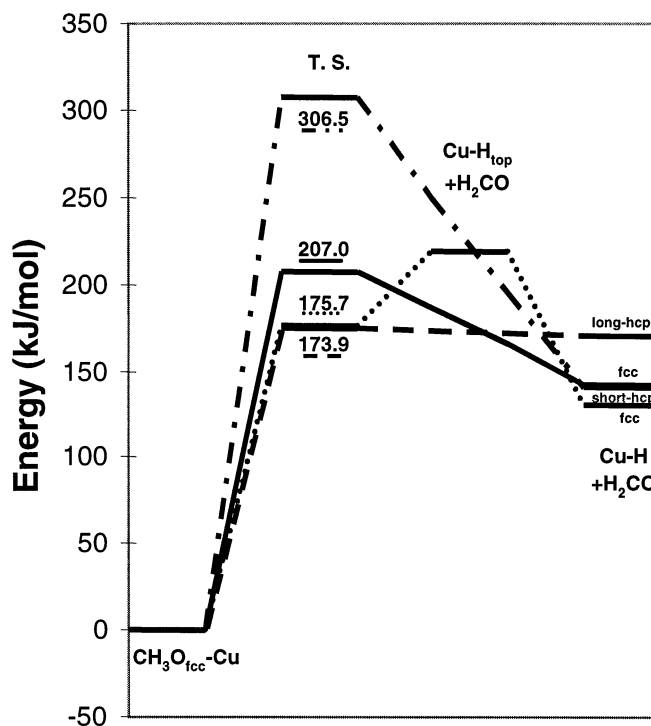$$CH_3O_{(ads, fcc)} \rightarrow H_2CO_{(g)} + H_{(ads, long\text{-}hcp)} \qquad (3)$$

Fig. 2. Energy diagram for the decomposition reaction of the methoxy species to formaldehyde and atomic hydrogen catalysed by copper. The solid line shows the results for methoxy C—O axis tilting towards a fcc hollow site, the dotted line that for the tilting towards a top site, the dot-dashed line that for the tilting towards a short-hcp hollow site and the dashed line that for the tilting towards a long-hcp hollow site. The hydrogen atom is adsorbed on these sites while formaldehyde is desorbed from the surface yielding gaseous H₂CO.

$$CH_3O_{(ads, fcc)} \rightarrow H_2CO_{(g)} + H_{(ads, fcc)}. \qquad (4)$$
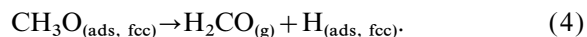
For each of these possibilities a reaction coordinate was defined as explained in a previous section and all geometrical parameters were optimized along the reaction path. The geometry where the energy reaches a maximum value is assumed to be the transition state. In principle, one should characterize this stationary point by a full frequency calculation. However, this is not a convenient strategy because of the use of a rather large surface cluster model with fixed geometry. Instead, we discuss the energy barriers corresponding to the four reaction schemes described above.

The calculated results for these four possibilities show that the decomposition reaction is more favourable when the methyl group tilts towards the long-hcp hollow site, reaction scheme (3). In this situation, the energy barrier is found to be

174 kJ mol^{-1}. The energy barrier for the methoxy decomposition with the hydrogen atom falling on the top site lowers its value when the hydrogen atom is allowed to move to the contiguous fcc site; in this case the energy barrier is 176 kJ mol^{-1}. However, the energy of the system reaches its higher value precisely when the hydrogen atom is placed at the on-top site. Therefore, the resulting energy barrier is higher than that obtained when the hydrogen atom could move freely on the surface. For the two other situations, with hydrogen being adsorbed on the short-bridge and fcc sites, the energy barrier is much higher. In the former case, this is due to the marked tilting of the C—O axis needed for one hydrogen atom of the methoxy methyl group to approach the surface. The Pauli repulsion or steric effects are very large and the adsorption barrier increases to 306 kJ mol^{-1}. This is almost twice the barrier

corresponding to the movement of the hydrogen atom towards the top and long-hcp sites. In the latter situation, H on the fcc site, the energy barrier is 207 kJ mol^{-1} and this is also due to the large C—O axis tilting angle needed to reach a good approximation of the methyl group to the fcc site. As for adsorption on the short-bridge site, the steric effects cause an increase in the energy barrier.

The geometric parameters obtained for the transition state structures are reported in Table 3. The lowest energy barriers are correlated with the larger hydrogen to surface distances and the lowest C—O axis tilting angles. The oxygen to surface distance is much larger than that observed for the optimal geometry (Table 2). This denotes the weakening of adsorbate binding to the surface. This effect was expected because, as shown in Table 2, the formaldehyde species is weakly adsorbed on the copper surface. The decrease in the C—O bond length is also a sign of the stronger C—O bond in formaldehyde. However, the C—O distances found in the transition state for these four situations are still much larger than the characteristic bond length for a C—O double bond. The C—H distance for the cleaving bond varies from 1.33 to 1.44 Å and this is related to the distance between the methoxy adsorption site and the site where the hydrogen atom is adsorbed. Another factor that can induce a higher energy barrier is the low O—C⋯H angle value ($\sim 99°$)

observed for decomposition to the short-hcp site when compared with the $\sim 110°$ angle observed in the other three situations. The geometrical parameters corresponding to the transition state structures for the remaining, less favourable, decomposition schemes are given in Table 3.

3.4. The reaction of CH$_3$O with OH yielding H$_2$CO and H$_2$O

The calculated energy profile for the reaction between the methoxy and the hydroxy species co-adsorbed on the copper (111) surface are shown in Fig. 3. The reaction of CH$_3$O, adsorbed on the fcc site, with OH has been studied for OH adsorbed on four different adsorption sites:

$$CH_3O_{(ads,\ fcc)} + OH_{(ads,\ top)} \rightarrow H_2CO_{(g)} + H_2O_{(g)} \tag{5}$$

$$CH_3O_{(ads,\ fcc)} + OH_{(ads,\ short\text{-}hcp)} \rightarrow H_2CO_{(g)} + H_2O_{(g)} \tag{6}$$

$$CH_3O_{(ads,\ fcc)} + OH_{(ads,\ long\text{-}hcp)} \rightarrow H_2CO_{(g)} + H_2O_{(g)} \tag{7}$$

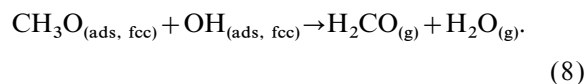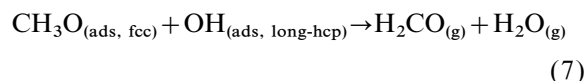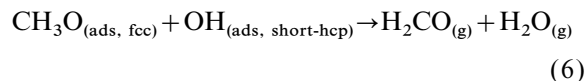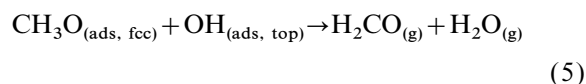$$CH_3O_{(ads,\ fcc)} + OH_{(ads,\ fcc)} \rightarrow H_2CO_{(g)} + H_2O_{(g)}. \tag{8}$$

Table 3
Transition structures for the methoxy decomposition reactions (1)–(4) yielding gaseous formaldehyde and atomic hydrogen adsorbed on top, short-hcp, long-hcp and fcc sites

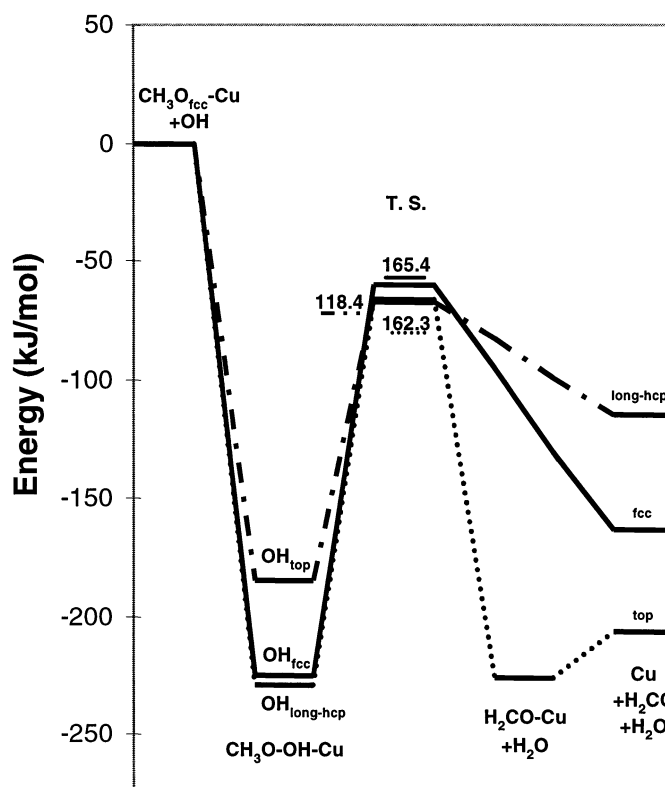| Parameter	Values for the following sites			
	H$_{top}$	H$_{short\text{-}hcp}$	H$_{long\text{-}hcp}$	H$_{fcc}$
d (O—Surf.) (Å)	1.700	1.896	1.748	1.952
d (O—Cu) (Å)	2.249	2.401	2.285	2.240
d (C—O) (Å)	1.385	1.346	1.400	1.356
d (C—H) (Å)	1.099	1.106	1.098	1.104
d (C⋯H) (Å)	1.326	1.355	1.438	1.382
d (H⋯ads. site) (Å)	1.450	0.800	1.350	0.900
d (H⋯Cu) (Å)	1.450	1.452	1.518	1.587
tilt (C—O) (Å)	68.6	82.0	71.4	79.4
ang (O—C—H) (°)	113.8	117.3	113.3	116.6
ang (O—C⋯H) (°)	112.3	98.8	110.6	107.7
ang (H—C—O—H) (°)	130.1	135.2	127.1	131.1

Fig. 3. Energy diagram for the reaction between the methoxy and hydroxy species yielding formaldehyde and water. Initially the methoxy species is adsorbed on an fcc hollow site while the hydroxy species is adsorbed on a top site (dot-dashed line), an fcc site (solid line) and a long-hcp hollow site (dotted line). The formaldehyde and the water molecules in the final stage are in the gas phase.

However, the energy curve for reaction (6) is not shown in Fig. 3 because the steric effect for the co-adsorption of CH_3O and OH on the two neighbouring hollow sites (fcc and hcp) is very large. To avoid the large steric repulsion originating from the proximity of both radical oxygen atoms, the hydroxy radical moves to the contiguous fcc site. This was observed upon the geometry optimization of the co-adsorbed CH_3O and OH species. The methoxy species still adsorbed on the fcc hollow site.

The reaction barrier calculated for the reaction of the methoxy species with the hydroxy species adsorbed on the top site, shown in Fig. 1d, is 118.4 kJ mol^{-1}. This value is much lower than the most favourable decomposition route calculated for reaction on the clean copper surface. However, this reaction only occurs if the hydroxy radical is promoted previously from the fcc hollow to the

top site. As shown in Table 1, the adsorption energy difference between hydroxy adsorbed on the fcc site and on the top site is 61 kJ mol^{-1}, approximately. This means that the total energy required is 180 kJ mol^{-1}. This value is only 6 kJ mol^{-1} higher than the calculated energy barrier for the decomposition of the methoxy species with a methyl hydrogen approaching the long-hcp hollow site.

For the reaction scheme (7), where the co-adsorption of the hydroxy species on the long-hcp hollow site is modelled, the calculated reaction barrier is 162.3 kJ mol^{-1}. For the reaction scheme (8), with OH adsorbed on the fcc hollow site, the calculated reaction barrier is 165.4 kJ mol^{-1}. These two values are 8.5 and 11.6 kJ mol^{-1} lower than the reaction barrier for the most favourable CH_3O decomposition reaction on the clean copper surface. These differences appear to be too small

to justify the preference of the reaction schemes with co-adsorbed hydroxy with respect to the reaction without this radical.

The total energy of the co-adsorbed species adsorbed on hollow sites is more negative than the total energy of the products. The adsorption of H_2CO and H_2O is exothermic and its desorption requires energy. This is observed in experimental studies [4,6], where the desorption of H_2CO occurs only with increasing temperature.

From the geometrical parameters for the transition structures reported in Table 4, we see that the C—O axis tilting is much smaller than that in absence of the OH radical. This should be the main reason for the lower reaction barriers obtained when OH is present on the surface. In the presence of one surface defect such as a step, the reaction barrier for the C—H bond cleavage, in the absence of co-adsorbed OH, should become smaller than that obtained for a clean terrace. This is because when methoxy is adsorbed near a step the C—H cleavage is facilitated if the hydrogen atom is adsorbed on the upper terrace. The geometrical parameters of the transition structure for the situation where the hydroxy radical is located on the long-hcp hollow site show that the C—O

axis tilting is larger because of the larger distance between the two radicals. The internal parameters in the OCH_2—H species vary significantly from reaction scheme to reaction scheme except for the carbon to hydrogen distance. Atomic charges variations upon reaction are small except in the case of the hydrogen atom which suffers C—H bond scission. The distance of the methoxy hydrogen atom suffering cleavage to the hydroxy oxygen atom is close to 1.2 Å. The oxygen to surface distance is very large for the OH species adsorbed on the hollow sites. The calculated distances for this transition structure are much closer to the those for hydroxy adsorbed on the top site (1.96 Å, Table 1) than to those for adsorption on the fcc site (1.49 Å). This is a sign of oxygen to surface bond weakening since hollow sites have previously been found [25] to stabilize the water molecule formed in the reaction in a less efficient way than the top and bridge positions do.

4. Conclusions

The cluster model approach has been used to study the decomposition reaction of the methoxy

Table 4
Transition structures for the reaction of the methoxy species with co-adsorbed hydroxy radical on top, long-hcp and fcc sites (reactions (5), (7) and (8)) yielding gaseous formaldehyde and water

Adsorbed species	Parameter	Values for the following sites		
		OH_{top}	$OH_{long\text{-}hcp}$	OH_{fcc}
CH_3O	d (O—Surf.) (Å)	1.480	1.440	1.430
CH_3O	d (O—Cu) (Å)	2.086	2.060	2.052
CH_3O	d (C—O) (Å)	1.399	1.483	1.435
CH_3O	d (C—H) (Å)	1.104	1.102	1.104
CH_3O	d (C$\cdots$H) (Å)	1.427	1.318	1.380
CH_3O	tilt (C—O) (°)	18.6	36.6	19.8
CH_3O	ang (O—C—H) (°)	112.1	106.6	110.3
CH_3O	ang (O—C$\cdots$H) (°)	95.6	111.4	93.9
CH_3O	ang (H—C—O—H) (°)	125.2	114.0	121.4
OH	d (H$\cdots$O) (Å)	1.200	1.200	1.150
OH	d (O—Surf.) (Å)	2.017	1.815	1.915
OH	d (O—Cu) (Å)	2.017	2.240	2.298
OH	d (O—H) (Å)	0.967	0.967	0.967
OH	tilt (O—H) (°)	2.2	9.6	5.7
OH	ang (H$\cdots$O—H) (°)	108.6	117.4	108.9
OH	ang (H—O—ads. site) (°)	135.0	137.1	135.1

radical on a clean Cu(111) surface and on the same surface with co-adsorbed hydroxy species. The energy profiles for a series of well-defined reaction paths have been obtained using the DFT within the B3LYP hybrid method. The motivation of this work arises from the previous quantum chemical results obtained for the adsorption of the methoxy species on the clean copper surface [8,9,11,20]. These works suggested that the C—O axis tilting causes a large destabilization in the adsorption energy. This result may be used to interpret the experimental evidence that co-adsorbed oxygen increases formaldehyde production. However, this interpretation is in conflict with the majority of the experimental studies, which assume that the CH_3O decomposition occurs without reaction with any other species adsorbed on the metal surface. It is thought that only the OH bond scission in methanol is increased in the presence of co-adsorbed atomic oxygen.

In this work we have considered four different reaction schemes starting with the methoxy radical adsorbed on the fcc hollow site (the most favourable adsorption site). In all these reaction schemes, the final products were gas phase formaldehyde and adsorbed hydrogen. The main difference in these reactions concerns the surface site where the hydrogen atom is located and the extent of C—O axis tilting. The four different adsorption sites for the adsorbed hydrogen reaction product were the top, short-hcp, long-hcp and fcc positions. The results obtained suggest that the most favourable decomposition route is that in which the methyl group is tilted with one hydrogen atom approaching the hcp site that connects the fcc hollow site where the methoxy radical is adsorbed by one copper atom. For this situation, the calculated energy barrier is ~ 174 kJ mol^{-1}. The reaction of the methoxy and hydroxy radicals on the copper surface yielding gas phase formaldehyde and water has also been studied. In this case, a co-adsorbed hydroxy radical is also present on the surface in the four adsorption sites considered above. The preferred decomposition route is that in which the hydroxy radical adsorbed on the top site captures the hydrogen atom. The reaction barrier is ~ 118 kJ mol^{-1}. However, we should keep in mind that the hydroxy radical is preferen-

tially adsorbed on the fcc hollow site. The energetic difference between adsorption on both sites is ~ 61 kJ mol^{-1}. The total energy needed for the promotion of the hydroxy radical to the top site and for the subsequent decomposition reaction is ~ 180 kJ mol^{-1}. For the same reaction with the hydroxy radical adsorbed on the long-hcp and fcc sites, the energy barrier is 162 and 165 kJ mol^{-1}, respectively. From these results it is clear that the reaction is more favoured when OH is present on the surface. The energetic difference calculated for reaction with or without the adsorbed hydroxy is ~ 10 kJ mol^{-1}. Whiles this energy difference is significant it would not be sufficient to make the reaction scheme with co-adsorbed OH the one that is observed experimentally. In the view of present results it is very likely that both routes can coexist and that the presence of adsorbed oxygen-containing species serves to capture the H atoms produced in the reaction thus avoiding the recombination to methanol. The resulting OH radicals can indeed slightly favour the conversion to formaldehyde, generating water which is eliminated from upon heating the surface. The co-adsorbed OH species permits the C—H bond cleavage without the methoxy destabilization and the formation of two reaction products, H_2CO and H_2O, which are stable in the gas phase.

Acknowledgements

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