

Cluster model study of methoxy radical adsorption on the Cu (111) surface

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Abstract

Results of quantum density functional theory calculations on the adsorption of the methoxy radical on the Cu (111) metallic surface are reported. The metal surface is modeled by clusters of up to 7 atoms and the cluster size effect is discussed. It is found that the hollow site on the surface is the preferred site for adsorption and the C–O bond is quasi perpendicular to the surface. The methyl group has a small barrier (5.5 kJ mol^{-1}) for rotation around the C–O bond. The calculated vibrational frequencies of the adsorbed species are in good agreement with the experimental data available. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many commercially important products can be prepared with high efficiency depending upon the use of transition metal surfaces as catalysts [1]. The synthesis of methanol over Cu/ZnO catalysts [2] is one of those reactions. Another reaction that involves both methanol and transition metal surfaces as a catalyst is the oxidation to formaldehyde. So, the interaction of methanol with this type of catalysts has been widely investigated [3–6].

In the course of these reactions, the methoxy fragment ($\text{CH}_3\text{O}\cdot$) appears as a stable species and it seems to be a key intermediate. The methoxy radical is easily formed on most of these metal surfaces via O–H bond cleavage in methanol.

It was found experimentally [7, 8] that methoxy binds to the Cu(111) metal surface with its C–O axis perpendicular to the surface, on a hollow site,

with its oxygen atom pointing towards the surface. Hofmann et al [8] have found a Cu–O bond distance of 1.32 Å.

In this paper, the adsorption of $\text{CH}_3\text{O}\cdot$ on the Cu (111) surface is described using a density functional theory (DFT) approach. The goal is to evaluate the energetics of the $\text{CH}_3\text{O}\cdot$ adsorption and to compare the chemisorptive properties of the radical as a function of surface site and cluster size. Vibrational frequencies are also calculated and compared with available experimental data in order to test the validity of the approximations used.

2. Method

For the present study, Cu_nOCH_3 , $n = 1-7$, clusters are considered to model the Cu (111) surface– CH_3O chemisorption interaction. The metal clusters Cu_n , $n = 1-7$, are selected as portions of the ideal Cu (111) surface where the bulk value for Cu–Cu nearest neighbor distance 2.551 Å is used. Furthermore, the

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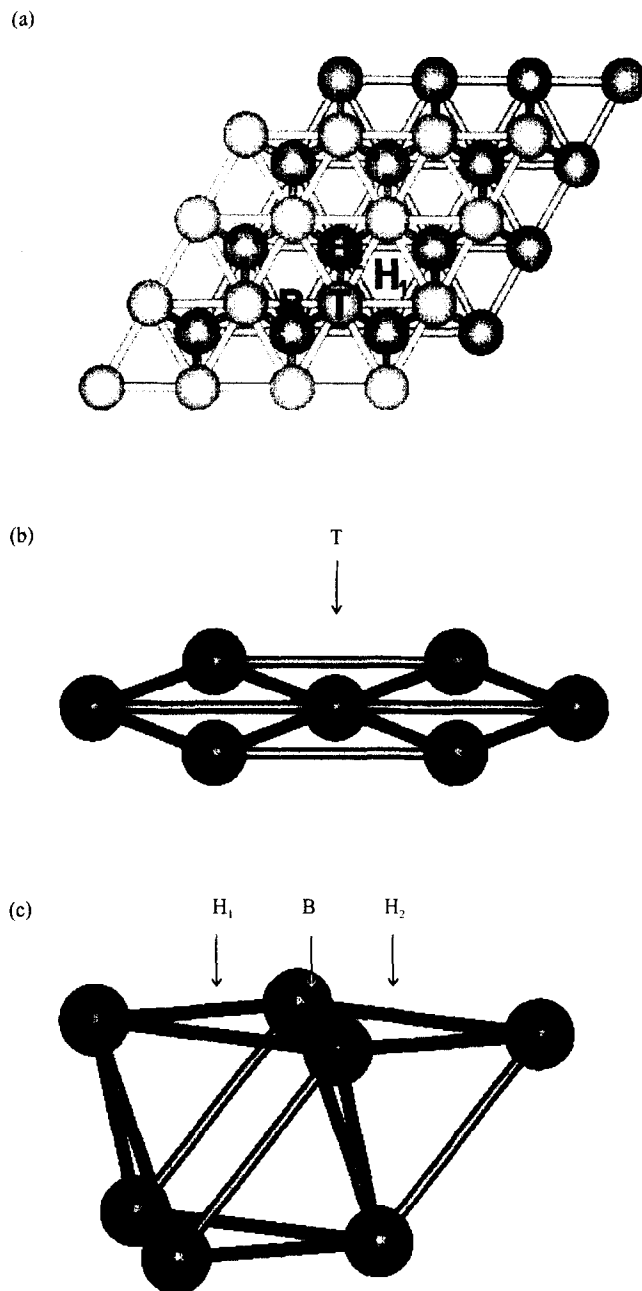


Fig. 1. Representation of adsorption sites on copper. The arrows represent the oxygen atom of methoxy radical. (a) Top view of a Cu (111) surface. T and B indicate the top and bridge and H₁ and H₂ are the two different hollow sites on the metallic surface. (b) Cu₇ cluster used for CH₃O· adsorption study on a top site. (c) Cu₇ cluster used for CH₃O· adsorption study on a bridge site and on hollow sites. As the adsorption on the hollow site H₁ is slightly preferred, all calculations reported here refer to this and not to the H₂ site.

Table 1

Adsorption energies and optimal distances for methoxy radical on a Cu (111) surface. The first column shows the size, the type of site, for each cluster and, in parenthesis, the number of metal atoms on each layer.

n	E_a (CH ₃ O on Cu _{n}) (kJ mol ⁻¹)	d (O–Cu _{n}) (Å)
1 top (1,0)	- 118.7	1.882
2 bridge (2,0)	- 141.5	1.558
3 hollow (3,0)	- 310.4	1.506
4 hollow (3,1)	- 392.0	1.461
5 hollow (3,2)	- 275.2	1.449
6 hollow (6,0)	- 109.2	1.524
7 top (7,0)	- 155.5	1.937
7 bridge (4,3)	- 192.1	1.569
7 hollow (4,3)	- 231.1	1.462

clusters used to model the top, bridge and hollow sites are shown in Fig. 1.

The geometry of the methoxy radical is kept fixed throughout the calculations and taken from the total optimization of the radical with an overall C_{3v} symmetry. C–O and C–H bond distances of 1.3684 and 1.1046 Å, respectively, were used and the O–C–H angle was fixed at 113.6°.

The calculations of the methoxy–Cu _{n} system were performed in two steps. First, the methoxy in a C_{3v} conformation was placed over and perpendicular to the metal cluster and the distance between the

oxygen atom and the first copper layer was optimized. This step was repeated for all Cu _{n} clusters with $n = 1–7$. Secondly, for the largest ($n = 7$) cluster, the methoxy radical was then allowed to bend and rotate, the COCu angle and the HCOCu dihedral angle being optimized. The vibrational frequencies of the methoxy radical were calculated for this optimal conformation.

These calculations were done with the three parameter hybrid method proposed by Becke [9] which includes a mixture of Hartree–Fock (HF) and density functional theory (DFT) exchange terms, associated with the gradient corrected correlation functional of Lee, Young and Parr [10]. The DFT method was used in order to reduce the computational effort and include some correlation effect.

The 3d¹⁰ 4s¹ Cu valence shell was described by a minimal basis set. The effects of the inner shell electrons were included in the effective core potential by Hay and Wadt [11]. To describe the oxygen, carbon and hydrogen atoms in the methoxy radical, the 6-31G** basis set (double zeta plus p polarization functions in hydrogen atoms and d functions in oxygen and carbon atoms) was used.

Calculations were performed on IBM Risc 6000 and DIGITAL Alpha workstations using the GAUSSIAN 94 [12] package.

Table 2

Methoxy adsorption properties on the different Cu₇ clusters representing on-top, bridge and hollow sites. d (O–Cu) is the perpendicular distance of oxygen atom to the copper surface, E_a is the methoxy adsorption energy and $q(X)$ is the atomic charge, in a.u., on oxygen and on the nearest to oxygen Cu atom(s). All frequencies are in cm⁻¹ and are scaled by a factor of 0.9614 [13].

	Top normal	Top tilted	Bridge normal	Bridge tilted	Hollow normal	Experimental
d (O–Cu) (Å)	1.94	1.98	1.57	1.60	1.46	1.32 ^a
E_a ^b (kJ mol ⁻¹)	156	177	192	200	231	
q (O)	- 0.70	- 0.67	- 0.74	- 0.72	- 0.77	
q (Cu)	0.60	0.56	0.28	0.27	0.29	
ν_{as} (CH ₃)	2823	2841	2868	2867	2847	2888 ^c
ν_s (CH ₃)	2799	2750	2828	2828	2830	2808 ^c
δ_{as} (CH ₃)	1432	1441	1459	1459	1471	1464 ^c
δ_s (CH ₃)	1428	1420	1471	1450	1424	1435 ^c
ν (CO)	1173	1126	1200	1200	1215	1039 ^c
ρ (CH ₃)	1130	1104	1155	1154	1133	1150 ^c
ν (CuO)	360	409	364	364	350	328 ^c

^a Backscattering photoelectron diffraction experiments, see Ref. [8].

^b Positive values are exothermic.

^c EELS value, see Ref. [14].

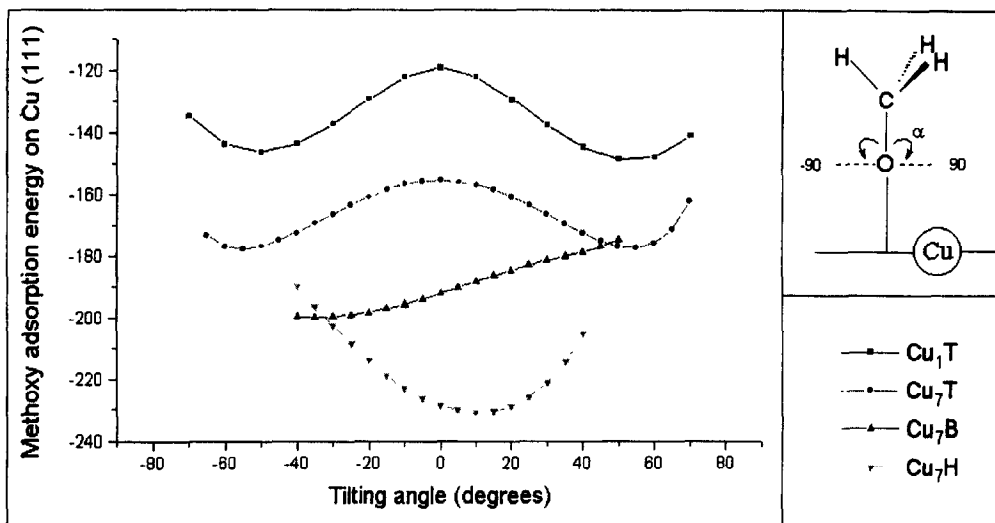


Fig. 2. Comparison of C–O axis tilting effect of methoxy radical adsorbed on top (Cu_1T and Cu_7T), bridge (Cu_7B) and hollow (Cu_7H) sites of the Cu (111) surface for Cu_n ($n = 1$ and 7) clusters.

3. Results

Table 1 lists the computed adsorption energy of methoxy radical on different Cu_n clusters modeling the Cu (111) surface, at the hollow, bridge and top sites (see Fig. 1). These results were obtained for $\text{CH}_3\text{O}\cdot$ adsorption with the C–O axis of methoxy radical at a C_{3v} conformation and with its symmetry axis perpendicular to the surface. As the properties of the hollow sites H_1 and H_2 are similar, only the results for the preferred site H_1 are reported throughout this paper.

The adsorption energy E_a presented in Table 1 is defined as

$$E_a(d) = -[E_{\text{tot},d}(\text{Cu}_n\text{OCH}_3) - E_{\text{tot}}(\text{Cu}_n) - E_{\text{tot}}(\text{CH}_3\text{O}\cdot)]$$

where $E_{\text{tot},d}(\text{Cu}_n\text{OCH}_3)$ is the total energy of the Cu_nOCH_3 cluster with d equal to the optimized distance of the oxygen atom from the plane of the surface metal atoms, $E_{\text{tot}}(\text{Cu}_n)$ is the total energy for the surface cluster and $E_{\text{tot}}(\text{CH}_3\text{O}\cdot)$ is the total energy of the methoxy radical.

From the results in Table 1 it is predicted that the methoxy radical adsorbs on all the clusters considered. The higher values of E_a are obtained for

methoxy adsorption on hollow sites. The top site is the one that stabilizes $\text{CH}_3\text{O}\cdot$ more poorly.

Several calculated properties of methoxy adsorbed on Cu_7 clusters are reported on Table 2. The calculated adsorption energies, oxygen to surface equilibrium distances, charges and vibrational frequencies are reported for methoxy adsorbed at three sites of the copper cluster and compared with the experimental data for adsorption on the copper (111) surface.

The calculated Cu–O distances are 1.98, 1.60 and 1.46 Å for top, bridge and hollow positions. The value obtained for methoxy radical adsorption on a Cu(111) surface hole is in good agreement with the photoelectron diffraction value [8] of 1.32 Å.

The variation of methoxy adsorption energy on a $\text{Cu}_7(111)$ cluster with the tilting angle, α , of the C–O axis away from the surface normal is shown in Fig. 2. On hollow sites, the methoxy radical prefers a quasi perpendicular orientation to the surface. In fact, a very small tilt is observed due to the repulsion between the hydrogen atoms and the metal surface. For top and the bridge sites, the C–O axis of $\text{CH}_3\text{O}\cdot$ is found to be tilted from the surface normal by 53° and 40° . The tilting effect above the Cu(111) surface is higher for adsorption on a top site and it is well demonstrated by the increase in the adsorption energy of 21 kJ mol^{-1} for $\alpha = 53^\circ$. For bridge sites the increase is only of 8 kJ mol^{-1} for $\alpha = 40^\circ$. This is probably due to the

Table 3

Comparison of the vibrational frequencies calculated imposing a C–O distance of 1.368 Å (the optimal bond length of CH₃O· in a vacuum) and 1.42 Å (the experimental bond length) with the ones obtained for the optimized C–O distance of 1.396 Å. The distance of the oxygen atom to the surface is not much changed by this full optimization, staying at ca 1.46 Å.

	Calculated			Experimental
	1.368	1.396	1.42	
$d(\text{C-O})$ (Å)	1.368	1.396	1.42	1.42
$\nu_{\text{as}}(\text{CH}_3)$	2847	2895	2891	2888
$\nu_{\text{s}}(\text{CH}_3)$	2830	2835	2831	2808
$\delta_{\text{as}}(\text{CH}_3)$	1471	1490	1480	1464
$\delta_{\text{s}}(\text{CH}_3)$	1424	1458	1436	1435
$\rho(\text{CH}_3)$	1133	1146	1125	1150
$\nu(\text{CO})$	1215	1124	1021	1039
$\nu(\text{CuO})$	350	351	321	328

higher value of the distance between the oxygen atom and the metal surface in this case and the consequent free motion of the methyl groups.

The comparison of the adsorption energy variation with the tilting angle α for top adsorption on Cu₁ and on Cu₇ clusters is also reported in Fig. 2. The tilting effect is similar but on the bigger cluster the gain on adsorption energy is smaller than on Cu₁. This is probably due to the fact that despite the O–copper surface long distance, for α near 50° the hydrogen atoms of CH₃O· are not far from the metallic surface which will hinder the tilt.

The calculated vibrational frequencies presented in Table 2 are in good agreement with experimental work [3, 14]. The stretching Cu–O vibrational frequencies lie on the range 350–364 cm⁻¹ for CH₃O· adsorbed on all sites considered except for the tilted methoxy adsorbed on a top site where a stretching Cu–O frequency of 409 cm⁻¹ is found. These values are close to the experimental $\nu(\text{Cu-O})$ value of 328 cm⁻¹. The C–O stretching frequencies obtained for methoxy adsorbed at different sites are higher than those obtained experimentally. This is likely to be due to the use of a value of 1.368 Å for the C–O distance instead of the experimental value of 1.42 Å. The vibrational frequencies calculated for the C–O bond length of 1.368 Å estimated by the quantum calculations of methoxy in a vacuum are compared in Table 3 with those obtained for an optimized adsorbed conformation ($d_{\text{C-O}} = 1.396$ Å) and for the experimental bond length of 1.42 Å. It can be

seen that the C–O stretching frequency is improved with the full optimization of the adsorbed species but a better agreement with experiment is found when the experimental bond length is used in the calculations. For the Cu–O stretch, a similarly good agreement with experiment is obtained when $d_{\text{C-O}} = 1.42$ Å is used.

Charges on the oxygen atom of the methoxy radical are close to -0.7 a.u. and are compensated by positive charges on the metal atoms near the adsorption site. This means that the O–Cu bond has a partial ionic character.

Understandably the variation of methoxy radical rotation energy for the different adsorption sites is minimal. The highest value is obtained for hollow sites (~ 5.5 kJ mol⁻¹) and this is due to the higher proximity of the hydrogen atoms of the methyl group to the surface. It can be seen that the normal methoxy radical can freely rotate above the Cu (111) metallic surface.

4. Conclusions

The density functional theory results reported above show that a seven atom copper cluster gives a reasonable description of the surface allowing a good prediction of structural and energetic features of the adsorbate. Methoxy is found to adsorb in any of the positions tested, on top of a metal atom, on the bridge between two atoms or on the hollow formed by three neighboring atoms. The hollow site is the preferred one with the methoxy C–O bond quasi perpendicular to the surface and the methyl group rotating almost freely. When adsorbed at the top or at the bridge sites, the C–O bond tilts away from the perpendicular to the surface with an important energy gain. This energy gain is especially large for the top position and is due to the interplay between the usual bonding preferences of the oxygen atom and the interaction of methyl with other surface copper atoms when it tilts. In fact, this energy gain is about 50% larger when a single metal atom is used to represent the surface. Curiously, the preferred angle is almost unchanged at ca 50°. The estimates of the vibrational frequencies agree with experimental data. It was found that the agreement of the C–O and the O–Cu stretching frequencies could be much improved if the

experimental C–O bond length is used in the calculation instead of those obtained in calculations of isolated $\text{CH}_3\text{O}\cdot$ or for $\text{CH}_3\text{O}\cdot$ adsorbed on the copper surface.

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