A density functional theory study of site-specific methyl reaction on MoO_3(010): The effects of methyl coverage

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We report density functional theory calculations, using pseudopotentials with a plane wave basis, of methyl adsorbed on the MoO_3(010) surface at 0.5 and 1.0 ML coverages. The MoO_3 surface is modeled by a one-layer slab. Methyl is adsorbed most strongly over the terminal oxygen, where methoxy is formed. Over the bridging oxygens, qualitatively different results are obtained depending on the coverage of methyl. At 0.5 ML, methoxy is formed over the bridging oxygens, with an associated relaxation of the surface caused by a repulsion between the methyl and the terminal oxygen. For the 1.0 ML coverage, methyl is not stable and decomposes. Over the asymmetric bridging oxygen, methyl reacts to form formaldehyde and hydroxyl, while over the symmetric bridging oxygen a formyl species and water are produced. The hydroxyl and water are formed via hydrogen transfer to a terminal oxygen. The bonding and reaction of methyl over the various oxygen species are analyzed and discussed using charge density difference plots as well as the crystal orbital overlap projection (COOP). For the 0.5 ML methyl coverage, this analysis shows that the tilting of the terminal oxygen bond weakens this bond slightly. For the 1.0 ML methyl coverage, the COOP plots indicate that the decomposition of methyl over the bridging oxygens is not as stable as methyl over the terminal oxygen because the presence of the carbon fragments affects the electronic structure, and causes a weakening of the Mo–terminal oxygen bond. These results are discussed in the context of partial oxidation reactions. © *2000 American Institute of Physics.* [S0021-9606(00)70521-6]

I. INTRODUCTION

One of the most important problems in heterogeneous catalysis is the partial oxidation of alkanes, especially methane. The catalytic partial oxidation of alkanes poses a particular challenge because they are very unreactive and do not readily form strong bonds to other species. As a result, high temperatures are generally required for C–H bond activation, the rate-limiting step in alkane reaction. Unfortunately, the high temperatures also favor nonselective secondary reactions, such as combustion. An effective catalyst must therefore balance the desire to achieve high conversion rates with the goal of high selectivity for partial oxidation.

In recent years, a commercial catalytic process for methane conversion to formaldehyde based on molybdenum trioxide has been patented.[1] As a result, there has been considerable interest in understanding what controls selectivity and activity in methane oxidation catalyzed by MoO_3-based materials.[2–7] Unfortunately, high selectivity for formaldehyde production is only achieved for low conversions. For example, formaldehyde is produced with 80%–90% selectivity at conversions of ~1% on SiO_2-supported MoO_3, but it drops below 40% for conversions on the order of 3%.[8]

Several studies of working catalysts have shown that the activity and selectivity for formaldehyde production is dependent on the oxidation states present on the surface,[5–7,9] the structure of the oxide material,[4–7,10–13] and the nature of the oxygen species present.[9] For example, higher selectivity for formaldehyde formation was reported on catalysts with a larger fraction of exposed MoO_3(010) planes, which contain Mo=O moieties.[12] However, due to the complex nature of the catalyst, it is not possible to determine how these factors affect the elementary steps in methane oxidation. The conversion and selectivity of the methane oxidation is dependent on both C–H bond breaking and C–O bond formation. Because the catalyst must play several roles, it is likely that the active sites for promoting specific steps are different.

While experimentally it is difficult to obtain detailed information about the electronic nature of each specific binding site, accurate density functional theory calculations allow a thorough and efficient examination of these issues. To date, there have been no *ab initio* calculations of methyl or methane on the MoO_3 surface. An earlier theoretical study of methane on the MoO_3 surface was performed by Mehandru *et al.*,[14] using small clusters to model the (100) and (010) surfaces with a variant of the semiempirical extended Hückel theory. These authors investigated the activity of surface O^- species on the activation of methane, and found that methyl was bound to unsaturated molybdenum atom sites as well as O^- atoms with approximately equivalent stability. Irigoyen *et al.*[15] used the same semiempirical theory to perform cal-

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culations of methane and its fragments on a cluster model of the $MoO_3(100)$ surface, and analyzed the resulting geometries and energetics. They found that the (100) face with exposed molybdenum atoms was more favorable towards methane dissociation, while the face with exposed oxygen atoms was unreactive towards methane. In the present study of the MoO_3 catalyst, we use one layer of the ideal $MoO_3(010)$ surface. Furthermore, in order to examine the oxidation process after the first C–H bond is broken in methane, we study the adsorption of methyl at two coverages over different sites on the $MoO_3(010)$ surface.

II. COMPUTATIONAL DETAILS

All calculations were performed using the commercially available version of CASTEP,[16] a density functional theory plane wave pseudopotential code. In these calculations, the local-density approximation is used for electron exchange and correlation. The local density approximation has been shown to produce bond lengths and vibrational frequencies in good agreement with experiment; generally, binding energies are too large, but qualitatively correct answers are obtained. The bare MoO_3 slab and the MoO_3+CH_3 systems were relaxed until the forces on all atoms were less than 0.05 eV/Å. The optimized norm-conserving pseudopotential for Mo including states up to $4d$ was generated with $r_{c,s}=r_{c,p}=r_{c,d}=1.7$ a.u. from a singly ionized reference configuration of $[\mathrm{Kr}]4s^2 4p^6 4d^5$ and is expressed in the fully separable Kleinman–Bylander form.[17] Optimization[18] was performed with $q_{c,s}=q_{c,d}=6.5\,\mathrm{Ry}^{1/2}$ and $q_{c,p}=7.5\,\mathrm{Ry}^{1/2}$ and 6, 4, and 4 Bessel functions for the *s*, *p*, and *d* orbitals, respectively. The soft oxygen pseudopotential was generated according to the scheme of Troullier and Martins[19] with core radii $r_{c,s}=1.3$ and $r_{c,p}=1.65$ a.u. An optimized norm-conserving pseudopotential was also used for C, with core radii $r_{c,s}=1.0$ and $r_{c,p}=r_{c,d}=1.4$ a.u., while a filtered Coulomb potential was used for hydrogen. As a test of these pseudopotentials, the equilibrium lattice parameters of the $\alpha-MoO_3$ bulk system was determined by finding the volume which minimizes the total energy while keeping the ratio of the lattice vectors fixed to the experimental value. The equilibrium volume was found to be 191.0 $Å^3$, slightly lower than the experimental value of 203.0 $Å^3$. We fix the lattice parameters at the experimental values for subsequent calculations of the MoO_3 surface. Relaxation of the ionic positions at both the experimental and relaxed lattice constants yields bond lengths in excellent agreement with experimental values.[20] The carbon pseudopotential was tested for both bulk diamond and an acetylene molecule, giving excellent agreement with experimental bond lengths, lattice parameters, and bulk moduli.

The model for the $\alpha-MoO_3$ surface consists of a single layer of the (010) face, repeated periodically in three dimensions with about 14 Å of vacuum between layers. Four special *k* points in the irreducible Brillouin zone were used with a 700 eV cutoff for the plane wave basis states. For the adsorption of methyl, two coverages are used: 0.5 and 1.0 ML. Because there are two inequivalent lattice constants in the plane of the surface, there are two choices for the 0.5 ML coverage, a 1×2 or a 2×1 unit cell. In each case, the unit cell was chosen so as to maximize the distance between the methyl fragments. For example, for methyl over the terminal oxygen and the symmetric bridging oxygen a 1×2 cell is used, while a 2×1 cell is employed for methyl over the asymmetric bridging oxygen. For the 1.0 ML coverage, one methyl is adsorbed per one surface unit cell.

Analysis of the calculations was performed using the crystal orbital overlap population (COOP).[21] The COOP is a projection of two individual atomic orbitals onto a crystal wave function, weighted by the overlap of the two atomic orbitals. The sign of the COOP is an indication of the bonding or antibonding contribution of the two orbitals to the crystal wave function, and the magnitude is indicative of the strength of the interaction. Thus, the COOP can be used as a specific indicator of the nature of covalent bonding in the system.

III. RESULTS

A. 0.5 ML coverage of methyl over $MoO_3(010)$

Adsorbed methyl is stable and forms methoxy (CH_3O) via bonding to each of the different types of oxygen. The most stable form of methoxy results from methyl binding to the terminal oxygen site, with the asymmetric bridging oxygen site very close in energy. Binding to the symmetric bridging oxygen is the least energetically favorable configuration. Over the terminal oxygen, methyl is adsorbed to the oxygen atom, forming an angle of 136° between the Mo, O, and C atoms, similar to hydrogen adsorbed over the terminal oxygen [Fig. 1(a)]. The Mo–terminal O bond length is lengthened from 1.67 to 1.86 Å, consistent with a change from a double to a single bond of the terminal oxygen. The carbon atom is bound to the oxygen atom with a bond length of 1.38 Å, while the hydrogens are bound to the carbon at a length of 1.10 Å. These lengths are very similar to bond lengths of methanol in the gas phase, which has a C–O bond length of 1.43 Å and a C–H bond length of 1.1 Å.

Methyl bound over the bridging oxygens also forms methoxy; however, the formation of methoxy is accompanied by a significant relaxation of the surface. There are two general features of the surface relaxation resulting from methyl adsorption over the bridging oxygens. First, there is repulsion between the methyl fragments and the terminal oxygens which causes a tilting of the terminal oxygens away from the methyl. Second, the bridging oxygens are pulled out of the surface as a result of adsorption to methyl. The extent of these relaxations is different for the symmetric and asymmetric sites.

Methyl adsorbed over the asymmetric bridging oxygen [Fig. 1(b)] has intermediate stability; it is 0.6 eV higher in energy than methyl over the terminal oxygen. The asymmetric bridging oxygen bound to the methyl is pulled out of the surface by 0.7 Å in the fully relaxed structure, and the short Mo–O bond is lengthened by 0.15 Å, while the long Mo–O bond increases from 2.33 to 2.68 Å. As for the symmetric bridging site, there are significant repulsions between the terminal oxygens and the methyl species. The terminal oxygen closest to the methyl fragment is tilted the most, at an angle of 22.5°. The more distant terminal oxygen is not substantially perturbed; the tilt angle is 5.1° when 0.5 ML of CH_3 is

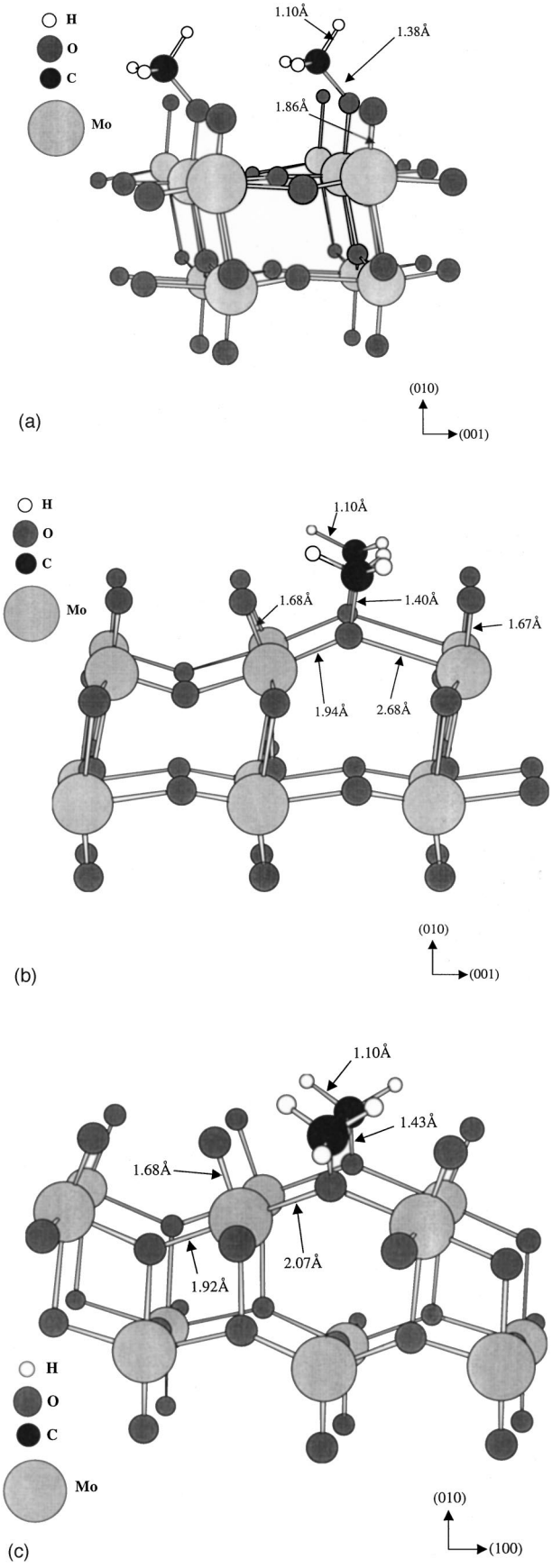

FIG. 1. Scale models of methoxy formed from CH_3 addition to oxygen. The total methyl coverage is 0.5 ML in all cases and a plane of symmetry in the (001) direction is enforced. (a) Methyl bound to terminal oxygen (Mo═O sites); (b) Methyl bound to asymmetric bridging oxygen; (c) Methyl bound to symmetric bridging oxygen.

TABLE I. Selected OPDOS for 0.5 ML coverage of methyl over MoO_3(010).

	OPDOS
C $2sp$–O $2p$	
Methyl over symmetric bridging O	0.29
Methyl over asymmetric bridging O	0.31
Methyl over terminal O	0.31
Mo $4d$–terminal O $2p$	
Methyl over terminal O	0.16
Methyl over symmetric bridging O	0.23
Methyl over asymmetric bridging O	0.23
Clean surface	0.28

bound to the asymmetric bridging oxygens, compared to a tilt of 4.9° for MoO_3 with no methyl adsorbed. The C–O bond length is 1.40 Å, with C–H bond lengths in methyl being 1.1 Å, similar to methyl over the terminal oxygen.

The degree of surface relaxation is greatest for methyl binding to the symmetric bridging oxygen [Fig. 1(c)]. Methyl adsorption on this site is 1.7 eV less stable than over the terminal oxygen site. The symmetric bridging oxygen is lifted out of the surface by 1.5 Å as a result of bonding to the methyl. Consequently, the long bond to the Mo atom beneath the symmetric bridging oxygen is increased from 2.33 Å in unperturbed MoO_3 to 3.80 Å in the relaxed structure after adsorption of 0.5 ML of methyl; the long Mo–O bond is effectively broken. In addition, the symmetric bridging oxygen O–Mo bond becomes asymmetric; one bond increases in length from 1.95 to 2.07 Å, while the other bond decreases to a bond length of 1.92 Å. The presence of the methyl also induces a tilting of the terminal oxygens towards the unoccupied symmetric bridging site, indicating a strong repulsion of the terminal oxygen from the methyl. In this case, the terminal oxygens are tilted by 19.7° from the surface normal, and the methyl is tilted by 39° in the (001) direction when it is bound to the symmetric bridging oxygen. The C–O bond length is 1.43 Å, 0.04 Å longer than for the terminal site, while the C–H bond lengths of methyl are 1.1 Å. The energy of the fully relaxed methoxy structure at the symmetric bridging sites is 1.7 eV higher than the most stable terminal sites.

In order to probe further the origin of the differences in the stability of methyl bound to the various oxygen sites at 0.5 ML coverage, the overlap population density of states (OPDOS) was calculated. The OPDOS is a summation of the COOP over all occupied states and yields a number which is a measure of the overall bonding or antibonding contributions of the two atomic orbitals.

The OPDOS and structural features indicate that the differences in binding energies are from steric repulsion and changes in Mo–O bonding. The OPDOS of the C–O bond is very similar for all three types of oxygen, indicating that each oxygen binds the methyl fragment almost equally (Table I). The closeness in the C–O bond lengths for CH_3 bound to all three oxygens supports this argument. Therefore, the difference in the overall binding energy must arise

from other factors. Steric repulsion between methyl bound to the bridging oxygens and the terminal oxygens is indicated by a tilt of the terminal oxygens away from the methyl group. The energetic cost of this steric repulsion must be 0.6 eV or less, which is the difference in binding energy between methyl over the terminal oxygen and methyl over the asymmetric bridging oxygen. Methyl over the symmetric bridging oxygen causes a substantial tilt in two terminal oxygens, which partially explains the significantly lower binding energy with respect to the other binding sites. The other factor leading to the small binding energy of methyl over the symmetric bridging oxygen is that the methyl pulls the symmetric bridging oxygen out of the surface by a large amount, effectively breaking one of the Mo–O bonds and thus lowering the binding energy. The strength of the bond which is broken can be roughly estimated in the following manner: the energetic cost to tilt a terminal oxygen is about 0.6 eV, based on the difference in the binding energy of methyl over the terminal oxygen and methyl over the asymmetric bridging oxygen. In the case of the symmetric bridging oxygen, two terminal oxygens are tilted, resulting in an approximate energy cost of 1.2 eV. Note that this is not quantitatively accurate, since the amount of tilt differs between the asymmetric bridging and the symmetric bridging sites. The remaining decrease in binding energy (~0.5 eV) is attributed to a combination of the loss of bonding between the symmetric bridging oxygen and the Mo atom beneath and the longer C–O bond length compared with methoxy bound to other oxygen sites.

The tilting of the terminal oxygen has some effect on its bonding to the Mo atom. The OPDOS of the Mo *d*–terminal O *p* interaction shows that the bonding is decreased slightly (Table I), and the COOP plots indicate that the tilting of the terminal oxygen lowers an antibonding state below the Fermi level (Fig. 2). A comparison of the COOP plots between the tilted terminal oxygen species for methyl over the bridging oxygens and that of the clean surface shows the close similarity in the bonding states between all three systems. However, in the tilted terminal oxygen species there is an occupied Mo–O antibonding state just below the Fermi level that is not present on the clean surface. It is the occupation of this state which slightly reduces the bonding strength between the Mo and the terminal oxygen in the tilted case. The bonding of this tilted species is intermediate between that of the Mo–terminal oxygen double bond for the clean surface and the Mo–O single bond for methyl bound to the terminal site. The Mo–O bond COOP for the latter case (Fig. 2) also has an antibonding state immediately below the Fermi level, while the interaction between the oxygen $2p$ and Mo $3d$ states is less due to poorer overlap caused by the increased bond length.

B. 1.0 ML coverage of methyl over MoO_3(010)

Increasing the methyl coverage to 1 ML results in qualitative changes in the binding over the bridging oxygens. Specifically, methyl over the bridging sites decomposes via loss of hydrogen. Methyl bound to the terminal oxygen remains intact and is still the lowest energy site (Table II).

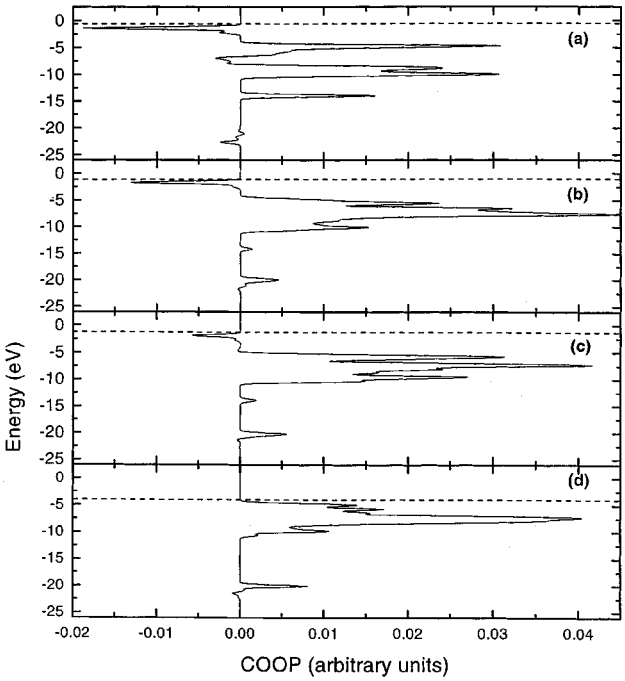

FIG. 2. COOP plots of the Mo $4d$–terminal O $2p$ interaction for methyl adsorbed over the bridging oxygen sites (0.5 ML coverage). For comparison, the COOP plot for the clean surface is also shown. Methyl bound to terminal oxygen; (b) Methyl bound to symmetric bridging oxygen; (c) Methyl bound to asymmetric bridging oxygen; (d) Clean surface.

The structure of methoxy formed from methyl (1.0 ML) bonding to the terminal oxygen is nearly the same as for a methyl coverage of 0.5 ML (Fig. 3). The Mo–terminal oxygen bond again increases in length from 1.67 to 1.88 Å, as the double bond to the Mo is reduced to a single bond. There is minimal relaxation of the lattice due to CH_3 adsorption. The only difference is a decrease in the bond length between the Mo atom to which methoxy is bound and the underlying symmetric bridging oxygen, from 2.3 to 2.1 Å [Fig. 3(a)].

A COOP analysis of the Mo–terminal O bond [Fig. 4(c)] indicates that the main bonding is still through the Mo $4d$–O $2p$ interaction, but the magnitude of the bonding is decreased by half compared with clean MoO_3, consistent with a reduction of bond order from 2 to 1. The OPDOS of the Mo–terminal oxygen bond is 0.16, identical to the value of the OPDOS in the 0.5 ML case. This number is indicative of a Mo–O single bond, as can be seen by comparison of the OPDOS for the Mo═O bond in clean MoO_3, 0.28. The methoxy is tilted by 38° with respect to the surface normal, similar to that of hydrogen adsorbed over the terminal oxygen site. The amount of tilting for the 1 ML case is identical

TABLE II. Relative stabilities of CH_3 over MoO_3(010). Note: Energies are relative to the most stable system, methyl over the terminal oxygen.

Binding site	Energy (eV)	
	0.5 ML	1.0 ML
Symmetric bridging O	1.7	3.3
Asymmetric bridging O	0.6	2.2
Terminal O	0.0	0.0

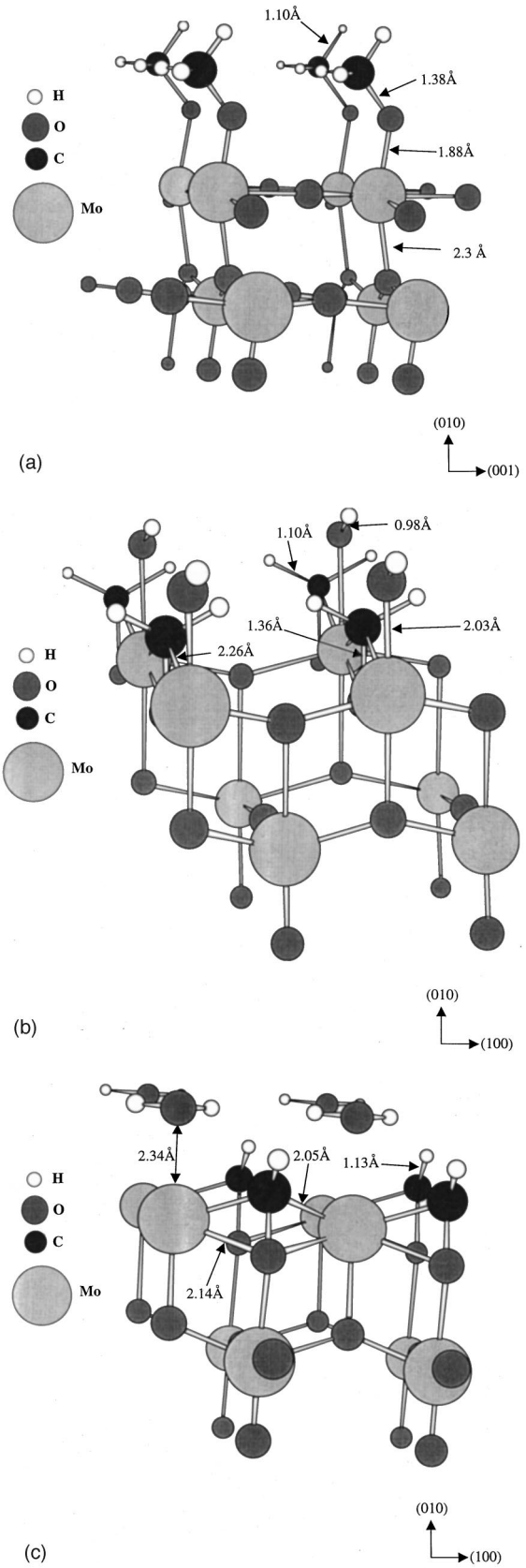

FIG. 3. Scale models of the products resulting from methyl adsorption to oxygen. For relaxation, a plane of symmetry in the (001) direction is enforced. The total methyl coverage is 1.0 ML in all cases and a plane of symmetry in the (001) direction is enforced. (a) Methyl bound to terminal oxygen; (b) Formaldehyde and hydroxyl formed from methyl binding to asymmetric bridging oxygen; (c) Formyl and water formed from methyl binding to symmetric bridging oxygen.

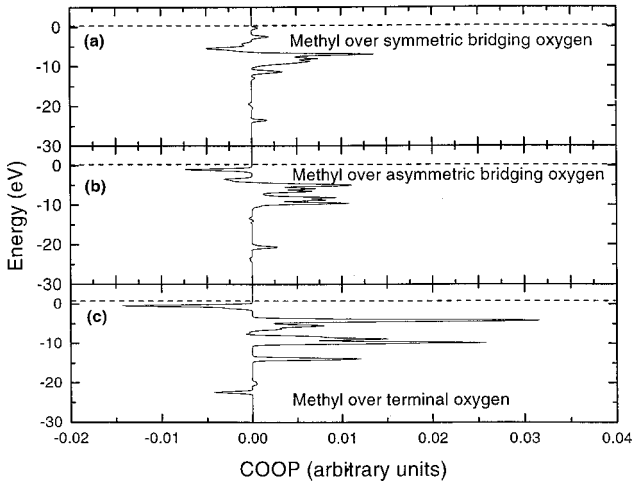

FIG. 4. COOP plots of the Mo $4d$–terminal O $2p$ interaction for the three different methyl adsorption sites (1.0 ML coverage). Methyl binding to symmetric bridging oxygen (water formed over terminal oxygen); (b) Methyl binding to asymmetric bridging oxygen (OH formed over terminal oxygen); (c) Methyl binding to terminal oxygen (methoxy formed over terminal oxygen).

to that in the 0.5 ML coverage. The C–O and C–H bond lengths are 1.38 and 1.10 Å, respectively, compared to 1.42 and 1.10 Å for gas-phase methanol. The bonding between the oxygen and the carbon atom is consistent with what one would expect, with a carbon sp^3 hybrid orbital bonding with a hybridized oxygen $2p$ orbital.

The asymmetric bridging oxygen site represents an intermediate case between the terminal and the symmetric bridging oxygen sites. One hydrogen is transferred from methyl to a terminal oxygen site, leaving formaldehyde above the asymmetric bridging oxygen when 1.0 ML of CH_3 approaches the asymmetric bridging oxygen [Fig. 3(b)]. Interestingly, the hydroxyl over the terminal site is different from hydroxyl formed from hydrogen atom adsorption[22] in that the Mo–terminal O bond length is unusually long, about 2.03 Å, in contrast to hydrogen adsorption at the Mo═O site on clean MoO_3, in which case the same bond length is 1.8 Å long. The asymmetric bridging oxygen also becomes more symmetric, with bond lengths of 1.95 and 2.17 Å, compared to 1.79 and 2.33 Å for clean MoO_3. The adsorbed formaldehyde has a C–O bond length of 1.36 Å and C–H bond lengths of 1.10 Å; these values are slightly higher than the analogous gas-phase values for formaldehyde, 1.23 Å for the C–O bond, and 1.06 Å for the C–H bonds. The lengthened C–O bond in adsorbed formaldehyde is due to the presence of the metal atom, which is also involved in bonding to the carbon.

As in the 0.5 ML case, the symmetric bridging oxygen is the least energetically favorable site. In contrast to the 0.5 ML case, methyl decomposes to HCO and water [Fig. 3(c)]. Water forms via hydrogen transfer to the terminal oxygen, it is not bound strongly to the Mo given that the distance above the surface is 2.34 Å. This indicates that water is eliminated from the surface, which relieves steric repulsion between the hydrocarbon moiety and the terminal oxygens. The carbon is actually bound closer to the Mo atoms than the symmetrically bridging oxygens, at distances of 2.05 vs 2.14 Å, re-

TABLE III. OPDOS of Mo–C and Mo–O bonding for 1.0 ML coverage of methyl over MoO_3(010).

	OPDOS
Mo $4d$–terminal O $2p$	
Methyl over terminal O	0.16
Methyl over asymmetric O	0.05
Methyl over symmetric O	0.04
Methyl over asymmetric bridging O	
Mo $4d$–asymmetric bridging O $2p$	0.07
Mo $4d$–C $2p$	0.10
Mo $4d$–C $2s$	0.10
Methyl over symmetric bridging O	
Mo $4d$–symmetric bridging O $2p$	0.05
Mo $4d$–C $2p$	0.09
Mo $4d$–C $2s$	0.06

spectively, indicating competition for Mo electron density. The OPDOS of the Mo–C and Mo–O interactions (Table III) shows that the covalent bonding between the Mo and the C atom is due to Mo $4d$ and C $2s,p$ orbitals, and is greater than that between the Mo and the symmetric bridging oxygen. There is also little covalent bonding between the Mo atom and the terminal oxygen, due to the poor overlap of orbitals caused by the large Mo–terminal O distance.

The OPDOS (Table III) indicates a weakened covalent bond between the asymmetric bridging oxygen and the Mo atom, and significant covalent bonding between the C atom and the Mo atom. They also indicate that there is less covalent bonding between the Mo and the terminal oxygen, as a result of the longer Mo–terminal oxygen bond [Fig. 4(b), Table I]. Furthermore, the bonding between the asymmetric bridging oxygen and the Mo is predominately through the Mo $4d$ and O $2p$ orbitals, in contrast to the Mo–asymmetric bridging oxygen bonding in clean MoO_3, which takes place through the Mo $5p$ and O $2p$ orbitals. The OPDOS also shows that there is in fact more bonding between the Mo and C atoms than between the Mo and asymmetric bridging O atoms (Table III); the orbitals involved are the Mo d and the C sp^2.

No local minimum for 1 ML of intact methyl over the asymmetric bridging site was found. In one attempt, the surface was held rigid while the methyl, initially placed 2 Å above the asymmetric bridging oxygen site, was allowed to move; in this case, the methyl still decomposed into OH and formaldehyde. In another, the methyl was fixed while the surface was allowed to relax. For this calculation, there was also no convergence to a local minimum. It is possible that the decomposition of methyl over the bridging sites of MoO_3 at 1.0 ML coverage proceeds without a barrier as long as CH_3 is sufficiently close to the oxygen; however, there is probably a barrier to adsorption when the methyl is further away, due to steric repulsion from the terminal oxygens.

IV. DISCUSSION

This study demonstrates that the coverage of an adsorbate has a significant effect on the qualitative result of the calculations. Steric interactions are the dominant factor in determining the favorability of bonding at both coverages examined in the present study; however, the way that the steric interactions are relieved is different depending on the coverage. The fact that the most favorable binding site for methyl at both coverages is the same, the terminal site, confirms this hypothesis. This is the position that minimizes steric interactions; methyl bound at the bridging oxygens at both coverages encounters repulsion with the neighboring terminal oxygen. Choosing a 1 ML coverage of CH_3 on MoO_3(010) imposes a high symmetry on the problem. The terminal oxygens are fixed in place because of methyl species on both sides, and no tilting is allowed when CH_3 is brought near the bridging oxygens. The steric strain is reduced in this case by hydrogen transfer from the methyl to the terminal oxygen, allowing Mo–C bonding to occur. On the other hand, at a 0.5 ML coverage, the terminal oxygen has freedom to move, and tilts away from the methyl in order to relieve the steric repulsion. Furthermore, a 1 ML coverage of methyl on MoO_3(010) is probably not a realistic coverage, because steric repulsion would lead to a high barrier to the formation of this structure.

Nevertheless, the calculation of the 1 ML methyl overlayer yields some interesting information. For methyl adsorbed over the symmetric bridging oxygen at 1 ML coverage, two hydrogens are transferred to the terminal oxygen to form water which is not bound to the surface. This demonstrates that while hydrogen is most favorably bound to the terminal oxygen, as shown by previous calculations,[22] water can be formed and removed from the surface. Therefore, the addition of hydrogen to the terminal oxygen is not a kinetic ''dead end;'' the Mo–terminal oxygen bond can be reduced by the elimination of water. The elimination of water also leaves behind a possible active site for reaction, an exposed Mo atom. Alternatively, the terminal oxygen site can be regenerated by mobile oxygen atoms at higher temperatures. Thus, the catalyst can be regenerated after reaction with incoming hydrocarbons. This terminal oxygen vacancy could be important for methyl addition to the bridging oxygens, because removal of one of the terminal oxygens would relieve the steric repulsion caused by the presence of the methyl. Calculations investigating the addition of methyl to this vacancy site are currently underway.

Our results have some implications for the activation of methane over MoO_3 catalysts. First, the binding site on the surface of MoO_3 is strongly dependent on the local environment, specifically on the steric interactions with terminal oxygens. This means that for the fully or nearly stoichiometric oxide surface, binding to the terminal oxygen is probably preferred. Second, the abstraction of hydrogen by the terminal oxygen could occur at areas of locally high methyl coverages. It is only when the terminal oxygen is constrained that hydrogen abstraction becomes a possibility.

Comparisons with the semiempirical studies by Mehandru *et al.* and Irigoyen *et al.* cannot be made in this case. Although both previous studies examine methyl on the MoO_3 surface, different binding sites were not tested; rather, adsorption over the terminal oxygen site was assumed. Furthermore, because the semiempirical calculations use cluster models of the MoO_3 surface, the effects of coverage are not

accessible. Both of these calculations compare the bonding of methyl to both terminal oxygen and exposed Mo atoms. On the (010) surface of MoO_3, there are no exposed Mo atoms, and therefore we do not consider this possibility. Calculations of methyl addition to a terminal oxygen vacancy site that are currently in progress will address this issue.

It is also important to note that the results found from the geometry optimization yield the lowest energy structure, but not necessarily the kinetically accessible intermediates. Indeed, it is likely that kinetic factors will play an important role in the selectivity for addition of methyl to a specific type of oxygen. Further work including dynamical simulations is needed in order to determine the kinetic effects involved in the partial oxidation process as well as to probe the role of the terminal oxygen vacancy in the binding of methyl.

V. CONCLUSIONS

Our calculations show that the most stable product for methyl adsorbed over MoO_3(010) is methoxy over the terminal oxygen site at both 0.5 and 1.0 ML coverages. At the lower coverage of 0.5 ML, methoxy is also formed over the bridging oxygens; this formation is accompanied by a tilting of the terminal oxygen away from the methoxy species as well as an upward movement of the bridging oxygen out of the surface. The lower binding energy for methyl over the bridging oxygens at the 0.5 ML coverage is partially due to the repulsion between the methyl and the terminal oxygen. Interestingly, methyl over the bridging oxygen sites at the higher 1.0 ML coverage forms the partial oxidation products of formaldehyde and formyl over the asymmetric bridging and symmetric bridging oxygens, respectively, via transfer of hydrogen from methyl by the terminal oxygen. The reason for the energetic instability of the 1.0 ML methyl+bridging oxygen systems relative to 1.0 ML methyl+terminal oxygen system is due to bond weakening of the Mo–terminal oxygen bond caused by the presence of the CH_x fragments, as shown by the COOP analysis. Dynamical simulations are necessary to determine which pathways are kinetically accessible.

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