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The adsorption of methyl on Rh_{10} clusters: selective C–H bond weakening

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Abstract

The adsorption of methyl on an Rh_{10} cluster was studied by ab initio density functional calculations as a model for the Rh(1/1/1) surface. The surface was modeled by a three-layer, 10 atom Rh cluster. The most stable binding site was found to be the threefold site, and the most stable geometry was a methyl species tilted 20° from the surface normal towards the onefold site of the Rh. Crystal orbital overlap populations were calculated and showed that the tilted methyl was energetically preferred because of a bonding interaction between the *d* states of the Rh and one of the C–H antibonding orbitals in the methyl. Electron donation from the *d* states to this C–H orbital causes a selective weakening of the bond, possibly explaining experimental vibrational data in which a softened C–H stretch mode is observed. A discussion of the advantages and the limitations of the cluster approximation is also presented.

Keywords: Wavefunction; Orbitals; COOP

1. Introduction

The partial oxidation of methane is currently a very active area of research, as it would be commercially lucrative to directly convert methane into simple organic compounds such as methanol or formaldehyde. Methane, however, is a very stable molecule, and the energy needed to break the first C–H bond is quite large. Moreover, after the first C–H bond is broken, the most energetically favorable products are the complete oxidation products of CO_2 and H_2O. Therefore, it is difficult to stop the oxidation in order to extract the desired partial oxygenates. An important part of these combustion processes is the activation of C–H bonds in surface-bound hydrocarbons. Rhodium in particular is known to effectively activate C–H bonds of adsorbed hydrocarbons, including methyl. In this work, the adsorption of methyl is studied on Rh in order to understand the electronic factors that lead to C–H bond activation.

Experimental studies of methyl on clean Rh(1/1/1) reveal the presence of a softened C–H stretching mode around 2600 cm^{-1}, in addition to other C–H modes in the expected 2900–3000 cm^{-1} region [1]. The presence of a softened C–H mode has also been observed with cyclohexane and methyl on Mo(1/1/0) [2,3], and for CH_3 on a wide variety of transition metal surfaces [4–6]. The mode softening could be due to electron donation from the metal into a C–H antibonding

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orbital, or donation from a C–H bonding orbital to the metal. For cyclohexane on Mo(1/1/0), donation from the metal to a C–H antibonding orbital was indicated, based on experimental studies of coadsorbed electronegative species [2]. However, studies on other metal surfaces have maintained that donation from the C–H bonding orbital to the metal *d* band leads to the low-frequency mode, indicating that different metals behave differently [7].

Accordingly, we undertook electronic structure calculations of methyl on Rh in order to determine the geometry of methyl on the surface as well as the mechanism for mode softening. Our results indicate that the most stable configuration of CH_3 on the Rh_{10} cluster is tilted and in the threefold site. In contrast, Yang and Whitten [8] performed a cluster study of methyl on Ni(1/1/1) with configuration interaction calculations and found that although the mode softening occurred for a tilted methyl species, it was energetically less favorable than the upright species. A semi-empirical calculation of methyl on Rh(1/1/1) using clusters determined that the most stable binding site was the onefold site [9]. We discuss these differences as well as the possible effect of cluster size on CH_3 bonding to Rh.

2. Calculation details

All calculations were performed with the Amsterdam Density Functional program [10–12]. The local spin density approximation was used [13], along with the gradient corrected functionals of Perdew and Wang [14]. A 10 atom cluster was used to model the (1/1/1) face of Rh. This three-layer cluster was designed as a balance between an accurate representation of the surface and computation time. Its high symmetry ensures that computational demands will not be excessive. Furthermore, the presence of three layers in the cluster also reduces the amount of distortion in the cluster when relaxing ionic positions to their ground state. This cluster was used in a previous work involving oxygen adsorption, and has been shown to yield qualitatively correct results with regards to experimental bond lengths and binding energies [15].

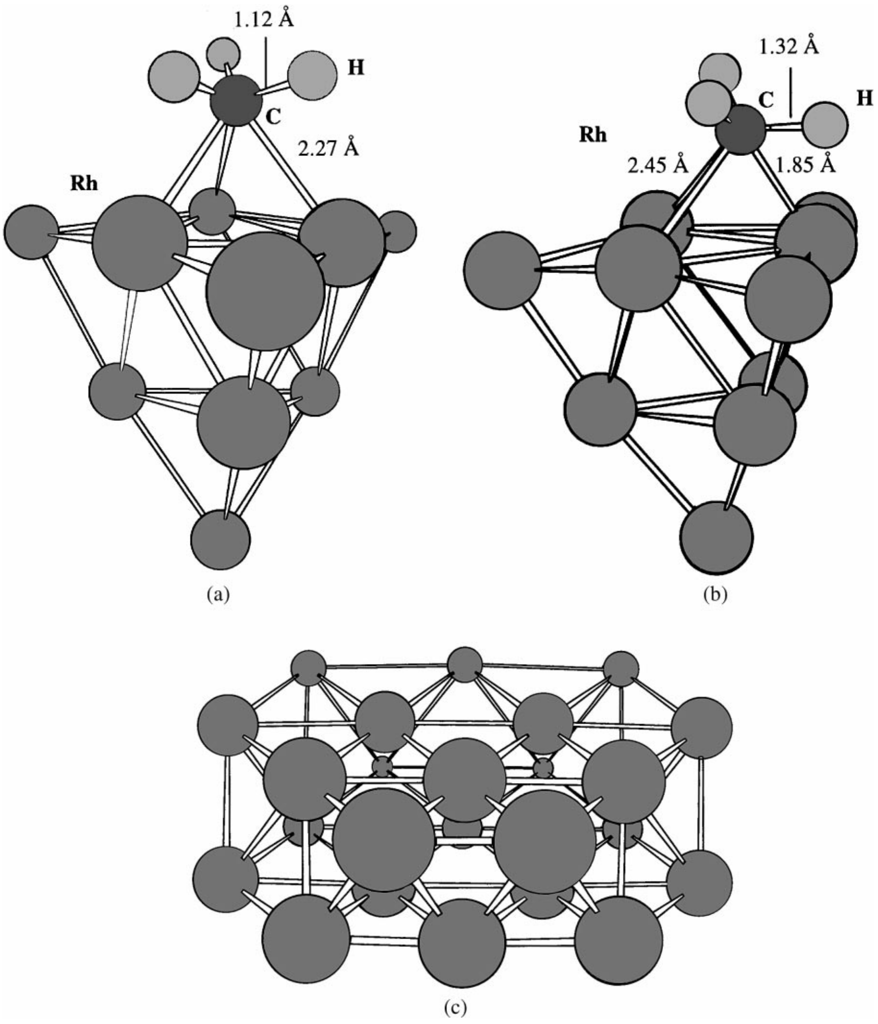
The basis sets in the calculations consisted of Slater-type orbitals with polarization functions. The Rh atoms were described by a double zeta basis with core electrons frozen up to the 4*p* level. The carbon and hydrogen atoms were described by a triple-zeta basis, with two polarization functions added. It was previously shown that the basis set had very little effect on this same cluster in the determination of bond lengths and binding energies [15]. For all calculations, except as noted, the ionic positions were relaxed until the energy converged to within 0.001 hartree and the gradients on the atoms were below 0.005 a.u./Å. Furthermore, each system was relaxed to its electronic ground state.

Orbital analysis was performed using in-house software that provided the crystal orbital overlap population (COOP) [16]. The COOP, originally developed by Hoffman [17], is a measure of the bonding or antibonding character of the interaction between two orbitals:

$$\mathrm{COOP}(\epsilon) = \sum_n \langle \varphi_i | \psi_n \rangle \langle \varphi_j | \psi_n \rangle S_{ij} \delta(\epsilon - \epsilon_n),$$

where φ refers to the fragment orbitals, ψ to the molecular wavefunction, and S_{ij} to the overlap between the two fragment orbitals. In our presentation of the COOP curves we have broadened the discrete levels of the cluster by 0.5 eV in order to simulate the infinite surface. This assumes that bonding is primarily local in nature, which is intrinsic to the cluster approximation of a surface. In this case there is a smooth transition between the discrete eigenvalue spectrum of a cluster to the density of states of an extended surface. In addition, a slight smoothing of the states also leaves a more general picture of the bonding, making it easier to observe overall trends in bonding.

For the methyl+Rh system we are interested not in the COOP between individual atomic orbitals, but in the COOP between the Rh *d* orbitals and the molecular orbitals of the methyl. Therefore, the fragment orbitals referred to above in the definition of the COOP are the molecular orbitals of methyl. These orbitals are calculated by taking the methyl coordinates of the relaxed methyl+Rh system and doing a calculation of the molecular orbitals for isolated methyl. It is these wavefunctions that are projected onto the molecular wavefunctions of the complete system when obtaining the COOP values for the CH_3 bound to Rh_{10}.



(a) (b)

(c)

Fig. 1. (a) Ten atom Rh cluster with upright methyl; (b) 10 atom Rh cluster with tilted methyl adsorbed; (c) 24 atom cluster (C_{3V} symmetry) used for binding site studies of methyl on Rh.

The most favorable binding site for the methyl was determined by placing it into the different sites of a two-layer 24 atom cluster (Fig. 1(c)). The 10 atom cluster was not used for this purpose because the cluster was too small. For example, to test the onefold site would have required placing it on an atom with different coordination than those involved in the threefold site. Therefore, the binding sites were tested on the larger cluster; however, the computational requirements for the larger cluster dictated that the remaining calculations be performed on the 10 atom cluster. Initial ionic relaxation of the methyl was performed by placing the methyl upright in the threefold site, to preserve the C_{3V} symmetry of the system. Afterwards, the methyl was manually bent 10° at a time to determine the optimum tilt angle, keeping all atoms in the methyl rigid except for the M–C–H bond angle.

3. Results

Tests of the binding site on the larger 24 atom cluster revealed that the most stable position for methyl was the threefold site, with a binding energy of −24 kcal/mol on the 10 atom cluster. The ground state electronic configuration was a doublet state, which was determined by testing different spin states to find the lowest energy configuration. Binding energies were calculated relative to the energies of the bare cluster and the gas-phase methyl. The gas-phase methyl ground state geometry was a planar state. The adsorbed methyl had its hydrogens pointing towards the atop site of the Rh atoms. With the hydrogens pointing towards the twofold site, the binding energy was reduced to −17 kcal/mol, implying a rotational barrier of at least 7 kcal/mol. The methyl itself is slightly flatter than the normal tetrahedral geometry, with a H–C–H bond angle of 107.3°. The C–H bond length is 1.1 Å, which is slightly longer than that of gas-phase methyl; however, this is not surprising because of the different hybridization of the two species. As is usual for an adsorbate on a cluster, the methyl induces a slight upward movement of the central three Rh atoms by 0.2 Å. This effect has also been observed with oxygen adsorbed on this same cluster.

The effect of bending the methyl cluster off vertical was also investigated. When the methyl was tilted towards the Rh atom, the binding energy reached a maximum at a 20° tilt from normal, to −33 kcal/mol. There was also energy lowering when the methyl was tilted towards the twofold position. The energy was lowered by 7 kcal/mol for a tilt angle of 10°. This was still 2 kcal/mol higher in energy than for the minimum energy configuration tilted toward the atop site (Figs. 2 and 3).

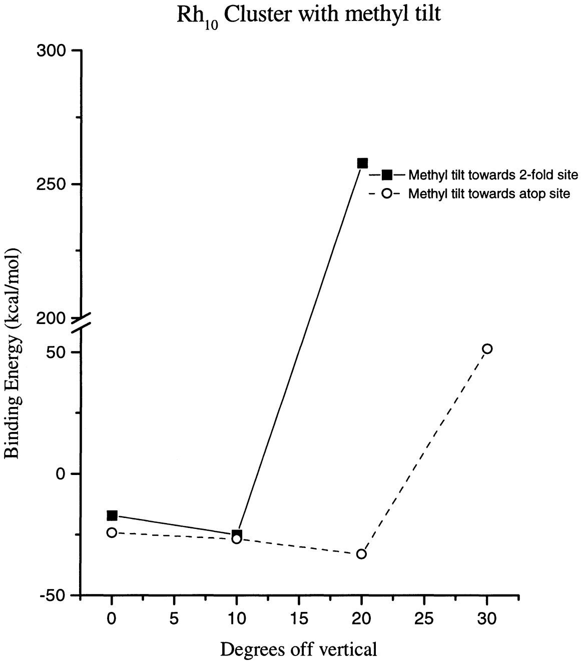
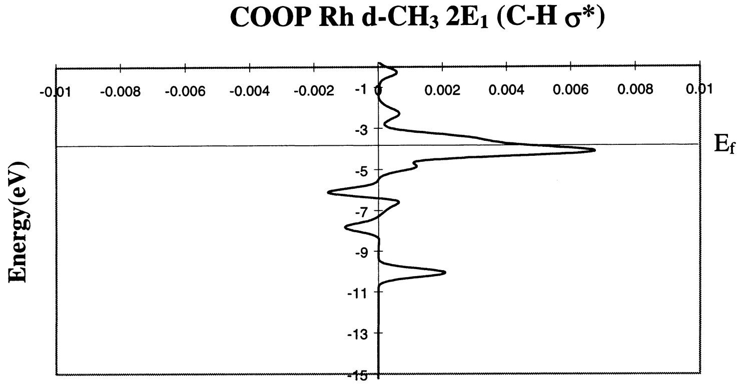


Fig. 2. Plot of tilting angle vs. binding energy for methyl adsorbed on the Rh_{10} cluster. Data for bending towards the twofold site and the atop site are shown.

4. Discussion

The calculated geometries agree in some respects with several calculations of methyl on Ni(1/1/1). Yang and Whitten [8] find that the threefold site is most favorable, with the methyl hydrogens pointing towards the metal atoms. However, the tilting of the methyl on Ni(1/1/1) destabilizes the system by 4 kcal/mol. This may be due to electronic differences between Ni and Rh. The threefold site is preferred from the calculations of Kratzer et al. [18] on Ni(1/1/1), and they also observe a flattening of the methyl pyramid, although their H–C–H bond angle is 100°, compared to 107.5° in our case. This is in contrast to calculations by Burghgraef et al. [19], also on Ni, where the onefold site was preferred. A comparison between the semi-empirical study of de Koster and van Santen [9] of methyl on Rh(1/1/1) and this study shows some disparity. For example, they find that the onefold site is the most stable. However, this may be due to the fact that atomic positions are not relaxed, and the methyl was kept at the perfect tetrahedral angle of 109°. In fact, the COOP analyses demonstrate that the threefold site should be the most favorable for the upright geometry, because this site allows maximum overlap between the methyl antibonding and the Rh *d* orbitals.

It is interesting to analyze the differences in bonding between the two types of methyl considered here: the upright and the tilted. By examining the detailed electronic structure of both species, one can deduce the reason for the greater stability of the tilted species. Orbital analysis of the upright methyl bonded to the Rh cluster indicates that bonding occurs primarily through a covalent interaction between the *sp* hybrid


COOP Rh d-CH_3 $2E_1$ (C-H σ*)

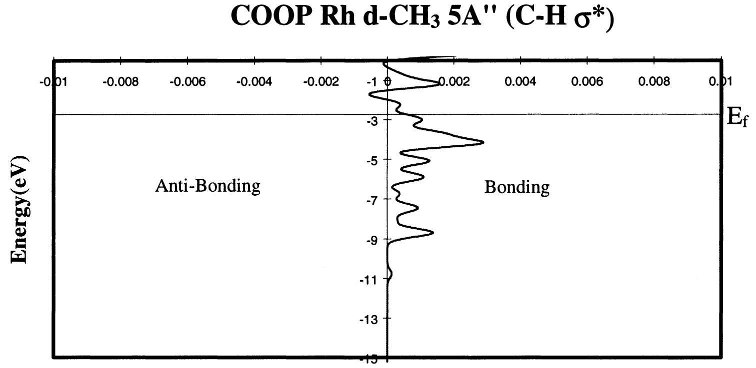

COOP Rh d-CH_3 5A" (C-H σ*)

Fig. 3. (a) COOP plot of the Rh *d* orbitals with the $2E_1$ orbital of upright methyl. Note that the relative intensites given above refer to three equivalent C–H bonds; (b) COOP plot of the Rh *d* orbitals with the 5A$''$ orbital of tilted methyl.

orbital on the carbon and the empty *p* band of the Rh. There is also a bonding contribution between the carbon *sp* orbital and a linear combination of the Rh d_{xz} and d_{yz} orbitals. While this interaction is the main bonding interaction, there is also a minor interaction between the Rh *d* band and the $2E_1$ orbital of the upright methyl. The $2E_1$ orbital is a CH_3 σ^* orbital, and there is a small (0.06 e^-/C–H bond) donation into this orbital. This interaction is slightly bonding, and explains why the geometry of the upright methyl is distorted from the ideal tetrahedral positions, with the C–H bonds bent slightly towards the surface.

The tilted methyl is similar to the upright species in that the main bonding is between the Rh *p* band and the *sp* orbital of the carbon. On the other hand, the tilt of the methyl now allows greater electron donation from the metal into the C–H antibonding orbital. The COOP curves demonstrate that the interaction between the Rh orbitals and the 5A$''$(C–H σ^*) orbital is completely bonding below the Fermi level. The amount of donation into this one orbital is now 0.15 e^-, 2.5 times the amount of donation into the C–H bond of the upright species. This accounts for the increase in binding energy for the tilted methyl, also resulting in a selective weakening of the C–H bond closest to the surface. This result is in qualitative agreement with experiments that show C–H bond softening has been observed experimentally for methyl on the Rh(1/1/1) surface, indicated by a low-frequency C–H stretching mode.

An attempt to calculate the vibrational frequencies of the C–H stretches in the tilted methyl species was unsuccessful. The methyl positions were relaxed, keeping the Rh atoms fixed. With the convergence for the gradients set at 0.005 a.u./Å, the hydrogen atom closest to the surface detached itself from the methyl and was bound to the Rh atom. We tentatively ascribe this to an edge effect; since the edge Rh atom has a lower coordination than in the bulk, it could be more likely to bind H. The ionic positions were successfully relaxed when a less stringent convergence limit of 0.01 a.u./Å was used. The full force constant matrix for the C–H stretches was then calculated. The diagonal elements were found by displacing a small amount (0.05 Å) of each atom separately along the bond axis on either sides of the equilibrium position. The total energy of the perturbed system was calculated, and the resulting force constant was found from fitting the energies to a parabola. The off-diagonal elements were obtained by displacing two atoms at a time, calculating the total energy, and then finding the resulting force constant by solving the total energy equation. The vibrational frequencies and normal modes can then be obtained by diagonalizing the force constant matrix multiplied by appropriate mass factors.

The vibrational frequencies found from this method were substantially different than those measured experimentally. There are two possible sources of error in the method described above. First, since we diagonalized a subspace of the force constant matrix, the basis functions (C–H stretches) used in the construction of the partial matrix may not be valid. However, it is known experimentally that the stretches lie significantly higher in energy than any other methyl modes; therefore, we do not expect coupling between the stretches and other vibrational modes, and the stretches are a good basis for the partial force constant matrix. The second source of error is the size of the cluster. Vibrational frequencies depend sensitively on the shape of the potential energy surface. Any cluster calculation that aims to calculate accurate vibrational frequencies for a surface must then reproduce quantitatively the shape of the potential energy function for that surface. In this case, the tilted methyl has a hydrogen close to an edge Rh atom which has lower coordination than an Rh atom on a surface. Hence, this could create an error associated with the fact that the edge Rh atom binds hydrogen more strongly than it would on a surface and could change the calculated shape of the potential energy surface. Our results suggest that finite-size effects become important for even small polyatomic adsorbates and suggest that a full two-dimensional slab calculation is necessary to model such hydrocarbon–surface interactions.

5. Conclusions

The binding of methyl to a 10 atom Rh cluster designed to mimic the (1/1/1) surface was calculated using density functional theory. The most stable binding site was the threefold site, with the relaxed geometry being a tilted methyl species. The tilted methyl species had electron donation from the metal to the C–H antibonding orbital, which strengthened the bonding of the methyl to the surface, but selectively weakened the tilted C–H bond, perhaps explaining experimental results which observe a softened C–H mode with vibrational spectroscopy. This calculation also illustrates the shortcomings of cluster calculations. Good clusters can predict bond lengths, binding energies, and electronic structure; however, a finite cluster size could have effects on the shape of the potential energy surface which make it difficult to accurately calculate vibrational frequencies. Therefore, it is necessary to use caution when selecting a cluster to model a surface. Comparisons with experimental data are crucial in order to ensure that a given cluster can qualitatively model an extended surface.

Acknowledgements

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