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A Water-Promoted Mechanism of Alcohol Oxidation on a Au(111) Surface: Understanding the Catalytic Behavior of Bulk Gold

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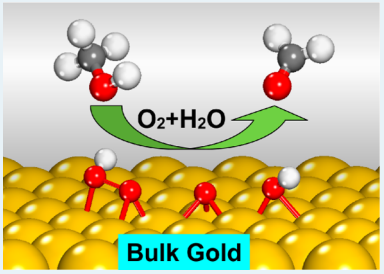
Supporting Information

ABSTRACT: To understand the catalytic mechanism of alcohol oxidation with molecular oxygen on bulk metallic gold catalysts, we have systematically studied the oxidative dehydrogenation of methanol on Au(111) using density functional theory. It is found that molecular oxygen can be activated via a hydroperoxyl (OOH) intermediate produced by abstracting a hydrogen atom from co-adsorbed methanol or water. Interestingly, extra water molecules significantly promote the hydrogen-transfer reactions between $CH_3OH\cdots O_2$ and $H_2O\cdots O_2$ co-adsorbates, lowering the activation barrier of OOH formation from ~0.90 to ~0.45 eV. The formed OOH intermediate either directly reacts with methanol to produce formaldehyde or dissociates into adsorbed atomic oxygen and hydroxyl. Further calculations demonstrate that the oxidative dehydrogenation of methanol by OOH, atomic oxygen, and hydroxyl is extremely facile with low barriers between 0.06 and 0.30 eV. These results provide an explanation for the activation mechanism of molecular oxygen on bulk gold and reveal a possible pathway for alcohol oxidation with dioxygen.



KEYWORDS: *methanol oxidation, bulk gold, O_2 activation, hydroperoxyl, water, density functional theory*

1. INTRODUCTION

The selective oxidation of alcohols to aldehydes is one of the most fundamental transformations in both laboratory and industrial chemistry.[1,2] Aldehydes are valuable both as important intermediates for organic synthesis and as high-value components for fine chemicals.[1] Currently, many stoichiometric oxygen-containing oxidants such as permanganate and chromate are commonly used to accomplish this transformation. However, such processes bear severe limitations of high cost and the production of a large amount of nondesired byproducts.[3−5] To address the environmental and atom-efficient concerns, significant efforts have been made to design highly efficient heterogeneous catalysts for aerobic oxidations using either molecular oxygen or air as an oxidant that is readily available and generating water as the only byproduct.

Recently, the selective oxidation of alcohols on gold has attracted extensive attention because its selectivity is higher than those of other metal catalysts.[6−13] While gold nanocrystals in an aqueous medium, especially under alkaline conditions, are found to be highly effective for the oxidation of alcohols in the presence of O_2, the dominant products are the corresponding monoacids instead of aldehydes.[10,11,14−17] Under mild solvent-free conditions, supported gold catalysts also exhibit extraordinary activity and selectivity in the oxidation of alcohols to aldehydes or ketones with O_2,[18−21] which arouses considerable interest because of environmental benefits and convenient recycling of the catalysts. Despite the importance of these experimental findings, little is known on an atomic level about the selective oxidation of alcohols by molecular O_2. A particularly controversial issue is the manner in which O_2 is activated on gold.

While gold is the noblest metal, <5 nm nanosized gold particles or subnano clusters show exceptional catalytic properties for the CO oxidation reaction.[22,23] However, gold does not seem to be very size-sensitive in the selective oxidation of alcohols in the gas or liquid phase.[18,21,24,25] For example, in the selective oxidation of glycerol and propane-1,2-diol, gold particles with a broad size distribution (5−50 and 25 nm on average) present excellent activity and selectivity to yield the corresponding aldehydes.[21] Of particular importance is the discovery by Angelici and co-workers that bulk gold powders (~50000 nm in size) or large-sized gold particles (>50 nm) also show considerable activity in the oxidative dehydrogenation of alcohols and amines.[26,27] These unexpected experimental findings demonstrate that large-sized or even bulk gold catalysts are able to catalyze some specific reactions.[22,28,29]

To understand the catalytic behavior of bulk gold, Mullins and co-workers conducted a series of experimental investigations of a single-crystal Au(111) surface,[30−32] indicating that a bulk gold surface precovered with atomic oxygen is highly reactive and selective for the partial oxidation of alcohols to aldehydes or ketones. The high activity of atomic oxygen-

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precovered Au(111) was also established for the oxidative self-coupling of methanol to form esters by Friend et al.[33,34] While these studies provide insights into the catalytic ability of bulk gold, the model catalysts they used all involve atomic oxygen-precovered Au(111), which requires a continuous supply of an oxygen-containing resource. Some of the key issues in alcohol oxidation on bulk gold include activation of molecular oxygen to provide active oxidative species and the dehydrogenation mechanism of alcohols on clean Au(111) under solvent-free conditions.

In addition, as a common ingredient in the gas feed, water (e.g., moisture) is known to play a significant role in a variety of O_2-involved reactions, including CO oxidation,[35−39] propene epoxidation,[40−42] and alcohol oxidation.[43] Water is thought to assist in O_2 adsorption and activation, thus accelerating the reactions.[43−47] Shang and co-workers systematically investigated the effects of water along with the O_2 activation mechanism using density functional theory (DFT) calculations and found that the presence of water can double the O_2 adsorption energy to ∼0.4 eV at commonly available edge sites of nanoparticles.[17] In the practical system for alcohol oxidation, the existence of water vapor and water as a reaction product are nearly never avoidable, and its potential effects need to be thoroughly investigated. Besides the known role of water, one might wonder if it has some other functions in the catalytic process.

To address these issues, we performed DFT studies to elucidate the mechanism of alcohol oxidation using molecular O_2, the catalytic behavior of bulk gold, and the effect of water in alcohol oxidation reactions. The selective oxidation of methanol to formaldehyde on Au(111) is used as a model reaction. Our investigations reveal that molecular O_2 can be activated on Au(111) via a critical OOH intermediate produced by the transfer of hydrogen from methanol or H_2O. Water is found to facilitate OOH formation via constructing a hydrogen bonding chain. The formed *OOH species as well as its decomposed fragments (O* and *OH) are the key active species in allowing the oxidative dehydrogenation of methanol, where the asterisk represents the adsorbed state.

2. COMPUTATIONAL DETAILS

All the DFT calculations were performed by using DMol^3 code[48,49] as implemented in the Material Studio package. The generalized gradient approximation (GGA) with the PBE functional[50] and double-numerical quality basis set with polarization functions (DNP) were used for all the atoms. The core electrons of metal atoms were treated using effective core potentials (ECP) developed by Berger et al.,[51] in which the mass−velocity and Darwin relativistic corrections were included. A thermal smearing of 0.002 hartree and a real-space cutoff of 4.5 Å were adopted.

A Au(111) surface was modeled by a periodic four-layer slab repeated in a 3 × 3 surface unit cell with a vacuum region of 15 Å between clean slabs. A 3 × 3 × 1 k point sampling was applied in our calculations. To examine the accuracy of 3 × 3 × 1 k points, a much denser k point sampling, 7 × 7 × 1, was used to calculate the adsorption energies of considered species and yielded results similar to those calculated by 3 × 3 × 1 k points (Table S1 of the Supporting Information), indicating a 3 × 3 × 1 k point sampling is accurate enough for this system. The adsorbate(s) together with the two "top" layers of metal atoms was allowed to relax during geometry optimizations. The convergences of energy, gradient, and maximal displacement were set as 10^{-5} hartree, 2×10^{-3} hartree/Å, and 5×10^{-3} Å, respectively. The adsorption energy E_{ad} or desorption energy ($E_{des} = -E_{ad}$) of an adsorbate was calculated as $E_{ad} = E_{ads/sub} - (E_{ads} + E_{sub})$, where $E_{ads/sub}$ is the total energy of the slab covered with the adsorbate in the optimized geometry, E_{ads} is the total energy of the adsorbate in the gas phase, and E_{sub} is the total energy of the clean substrate. With these definitions, a negative value of E_{ad} implies a release of energy or a stable adsorption on the surface.

All the transition states of the reactions were determined using a complete LST/QST (linear synchronous transit and quadratic synchronous transit) approach[52] and mode eigenvector following method.[53] All the optimized transition states were confirmed to possess only a single imaginary frequency, and the corresponding vibration mode was verified to connect the reactant and product.

3. RESULTS AND DISCUSSION

3.1. Direct Dehydrogenation of Methanol to Formaldehyde. Before we address the oxidative dehydrogenation (ODH) reactions, we first investigate the direct dehydrogenation of methanol (CH_3OH) to formaldehyde (CH_2O) in the absence of O_2 on a Au(111) surface as a reference. For the sake of convenience, we refer to the hydrogen bound to oxygen as α-H and to the hydrogen bound to carbon as β-H. From previous studies,[54,55] dehydrogenation of methanol proceeds in two elementary steps ($CH_3OH \rightarrow CH_3O + H$ and $CH_3O \rightarrow CH_2O + H$), as depicted in Figure 1.

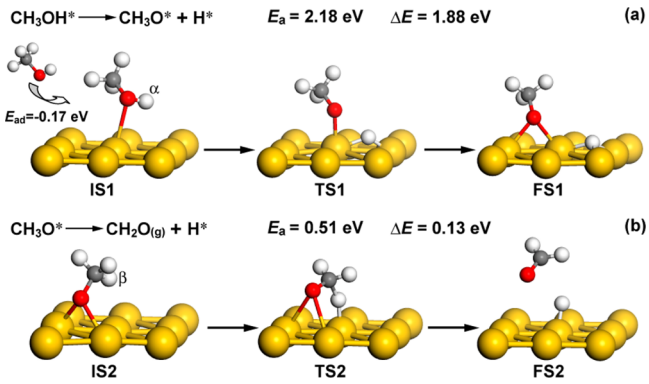

Figure 1. Direct dehydrogenation of methanol to formaldehyde on a Au(111) surface. (a) Transfer of α-H to form an adsorbed methoxy and a hydrogen atom. (b) Transfer of β-H to form gas-phase formaldehyde and an adsorbed hydrogen atom. E_{ad} is the adsorption energy, E_a the activation barrier ($E_{TS} - E_{IS}$), and ΔE the reaction energy ($E_{FS} - E_{IS}$). An asterisk denotes the adsorbed state.

Our calculations show that methanol preferably adsorbs on the top site of a Au atom on Au(111) via an oxygen atom. Both the adsorption energy (−0.17 eV) and the Au−O bond length (2.82 Å) imply a relatively weak interaction between methanol and the Au(111) surface. In the first dehydrogenation step (Figure 1a), with the cleavage of the O−H bond, the resulting methoxy species and a hydrogen atom bind to a bridge and a hollow site, respectively. The activation barrier is calculated to be as high as 2.18 eV, and the reaction is drastically endothermic, with a calculated reaction energy of 1.88 eV. These unfavorable thermodynamic and kinetic energetics are primarily due to the weak bonding of hydrogen atom with a gold surface.[56,57] Because the methoxy radical is electronically

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unsaturated, the subsequent dehydrogenation of β-H becomes more favorable with a substantially lower activation barrier of 0.51 eV and a reaction energy of 0.13 eV (Figure 1b). As long as formaldehyde is formed on Au(111), it desorbs into the gas phase immediately.[58] Our results reveal that direct dehydrogenation of methanol on a clean Au(111) surface is prohibitively difficult under ambient conditions, consistent with previous theoretical studies[10,34] and experimental observations.[30]

3.2. Adsorption and Activation of O_2 on a Au(111) Surface. *3.2.1. Mystery of O_2 Activation.* Experimental studies show that the reaction rate for methanol dehydrogenation is much higher in the presence of O_2 than that of direct dehydrogenation.[59] Utilization of O_2 or air as the oxidant is the final goal for environmentally benign oxidation reactions. However, how O_2 is activated on gold remains under debate. Except for the dissociation of O_2 on small-sized gold clusters,[60] several other pathways have also been proposed, including the activation of O_2 by formation of superoxo (O_2^-) or even peroxo (O_2^{2-}) complexes,[59,61−65] direct O_2 dissociation promoted by pre-adsorbed oxygen atoms, water, or reactants,[66−69] and activation via an intermediate hydroperoxyl (OOH) species.[20,70,71] The activation of molecular O_2 on inert Au(111) seems to be particularly enigmatic because it neither adsorbs nor dissociates on bulk gold.[60] Our calculated activation barrier for gas-phase O_2 dissociation on Au(111) is 2.44 eV, indicating that it is highly unlikely that O_2 is activated by direct cleavage of the O−O bond under ambient conditions (Figure S1 of the Supporting Information). Therefore, unraveling how O_2 is activated on a Au(111) surface is the key point in understanding the oxidative mechanism of O_2 in the methanol dehydrogenation reaction as well as the catalytic activity of bulk gold.

3.2.2. Formation of OOH. Previous study has demonstrated that an O_2 molecule can be activated by forming an OO−L (L = Xe^+, etc.) complex with the π^* orbitals of O_2 partially occupied via (p−π^*)σ bonding.[72] Our recent study has shown that O_2 can be readily activated on a gold cluster and nanoparticle by the formation of hydroperoxyl via the H-transfer reaction (O_2* + H_2O* → OOH* + OH*).[70] Zope et al. also found that in an alkaline aqueous solution O_2 is activated through the catalytic decomposition of a peroxide intermediate.[10] A similar channel for O_2 activation is conceivable in the presence of alcohol because the α-H of alcohol is quite analogous to the hydrogen atom in H_2O despite the different acidity. Indeed, our calculations show that the existence of methanol makes the adsorption of O_2 on a clean Au(111) surface feasible, as displayed in Figure 2 (black). Methanol first spontaneously adsorbs on a Au(111) surface with a slight release of energy (−0.17 eV). The pre-adsorbed methanol acts as an abstractor for O_2 to form the co-adsorbed complex ($CH_3OH\cdots O_2$)* by means of hydrogen bonding interaction. The distance between α-H and O_2 (1.84 Å) is in the range of a typical hydrogen bond,[73] and the Au−O bond distances between Au and O_2 are 2.50, 2.64, and 2.84 Å, implying an effective bonding interaction. In contrast, upon removal of methanol from the co-adsorbed complex, O_2 will promptly desorb into the gas phase, indicating the hydrogen bonding interaction with methanol is critical for attracting O_2 to a Au(111) surface.

From the calculated energy profile (Figure 2, black), the adsorption of O_2 is an endothermic process by 0.61 eV. As Behler et al.[74] explained, O_2 probably converts from its triplet ground state to an excited singlet state when approaching the metal surface. In IS3, the O−O bond length increases from 1.21 Å in the free O_2 molecule to 1.30 Å, which is close to the distance in superoxide O_2^- species (1.25−1.30 Å) but much shorter than that in peroxide O_2^{2-} species (1.30−1.55 Å).[75] Mulliken charge population shows that the adsorbed O_2 carries negative charges (Figure S2 of the Supporting Information), consistent with O_2 being transferred to a superoxo-like species on the surface.[59,61−65] Although the dissociation of O_2 under this state has been notably enhanced by the neighboring adsorbed methanol compared with pure O_2 dissociation (Figures S1 and S3 of the Supporting Information), the reaction remains difficult because of the quite high barrier of 1.49 eV.

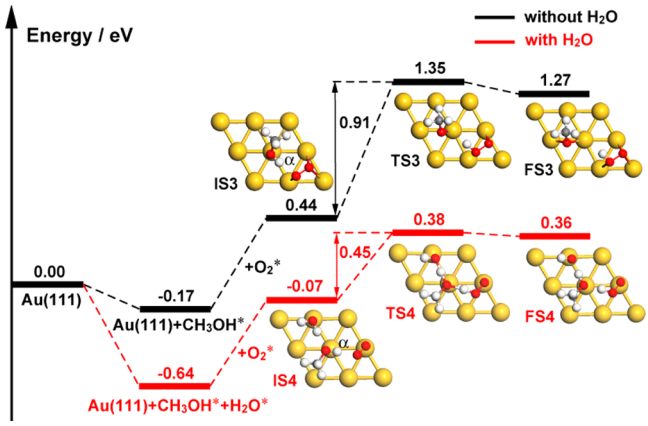

Figure 2. Optimized structures and energy profile for the formation of OOH via the transfer of α-H in methanol to adsorbed O_2 without (black) and with (red) the involvement of H_2O on a Au(111) surface.

With the co-adsorbed $CH_3OH\cdots O_2$ complex as a starting point, O_2 can abstract the hydrogen atom of the OH group in methanol to yield OOH* species [($CH_3OH\cdots O_2$)* → CH_3O* + OOH*], with a barrier of 0.91 eV (TS3 in Figure 2), much lower than that of direct O−O bond dissociation. In FS3, because of the (s−π^*)σ bonding between H and O_2, the O−O bond is further elongated to 1.45 Å. The O−O bond is now some 20% longer than that in free O_2, indicating molecular O_2 has already been substantially activated on a bulk Au(111) surface. As reported in the literature, formation of OOH is also a critical elementary step in the direct synthesis of hydrogen peroxide.[76−78]

3.2.3. Promotional Effect of Water in OOH Formation. In the aerobic oxidation of benzyl alcohol to benzaldehyde, the presence of water was reported to improve the conversion of benzyl alcohol by 7-fold.[43] Herein, we examined the effect of H_2O in the initial O_2 activation step, i.e., ($CH_3OH\cdots O_2$)* → CH_3O* + OOH*. Results of calculations (Figure 2, red) show that the co-adsorption energy of a CH_3OH and a H_2O is −0.64 eV, much higher (in absolute value) than the sum of the individual adsorption energies (−0.32 eV) because of the hydrogen bonding interaction. The subsequent adsorption of O_2 is also thermodynamically unfavorable by 0.57 eV. Surprisingly, the barrier to the formation of OOH in the presence of H_2O was notably reduced to 0.45 eV in contrast with a value of 0.91 eV without H_2O. According to the structure of TS4 (Figure 2), the three-molecule reaction follows an SN_2-like mechanism: while the α-H of methanol transfers to O_2, a hydrogen atom of H_2O transfers to methanol simultaneously, resulting in the final species OOH, CH_3OH, and OH. The overall reaction can be expressed as

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$(H_2O\cdots CH_3OH\cdots O_2)^* \rightarrow OH^* + CH_3OH^* + OOH^*$, where methanol is not consumed in the whole reaction but just acts as a mediator for hydrogen transfer. The ultimate result of this reaction is that a hydrogen atom of H_2O is shifted to O_2 via methanol. Another possibility is H_2O being located in the middle of O_2 and methanol (Figure S4 of the Supporting Information), yielding OOH, H_2O, and CH_3O species, which can be expressed as $(CH_3OH\cdots H_2O\cdots O_2)^* \rightarrow CH_3O^* + H_2O^* + OOH^*$. The co-adsorption energy of $(CH_3OH\cdots H_2O\cdots O_2)$ is −0.08 eV, comparable with the co-adsorption energy (−0.07 eV) of $(H_2O\cdots CH_3OH\cdots O_2)$ in Figure 2. In this reaction, H_2O serves as the mediator for hydrogen transfer, and the corresponding barrier (0.56 eV) and reaction energy (0.45 eV) are comparable with those for methanol located between O_2 and H_2O. From the catalytic point of view, the mediator (CH_3OH or H_2O) in the middle position serves as a catalyst promoter that effectively lowers the activation barrier without being consumed.

We also examine the activation of molecular O_2 by pure H_2O. One or two H_2O molecules per unit cell were considered (Figure 3). With one H_2O (Figure 3, black), the barrier for O_2

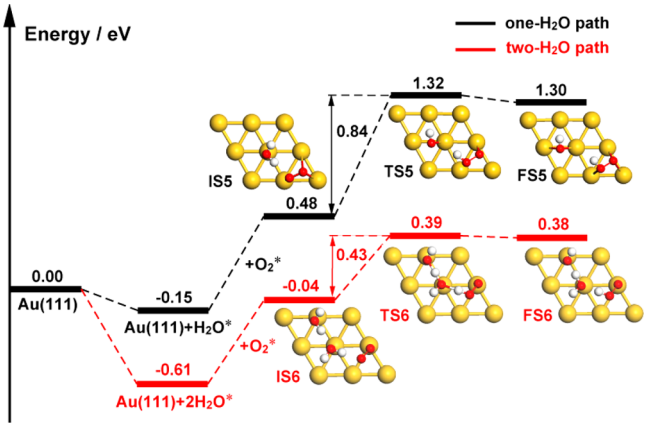

Figure 3. Optimized structures and energy profile for the formation of OOH via transfer of a hydrogen atom in H_2O to adsorbed O_2 with the involvement of one (black) or two (red) H_2O molecules on a Au(111) surface.

abstracting one hydrogen atom from H_2O (0.84 eV) is slightly lower than that for abstracting one hydrogen atom from methanol (0.91 eV) but is much higher than the corresponding barrier (0.26 eV) on a Au_{38} nanoparticle.[70] Via introduction of a second H_2O into this reaction (Figure 3, red), the activation barrier is dramatically reduced to 0.43 eV, analogous to that of the aforementioned $H_2O\cdots CH_3OH\cdots O_2$ case, where the middle H_2O molecule bridges a channel for the hydrogen transfer from the end-on H_2O to O_2. The energy profile in Figure 3 bears the same trend as in Figure 2, verifying the similarity of methanol and H_2O in activating O_2. In both cases, the extra H_2O reduces the apparent activation barrier to <0.40 eV, implying that in principle the formation of OOH can be achieved under less severe conditions. It is worth noting that although the neighboring water molecule can promote the dissociation of O_2 by reducing the activation barrier from 2.44 to 1.51 eV (Figure S3 of the Supporting Information), the barrier is still much higher than that of OOH formation (0.84 eV).

From the discussion above, both methanol and H_2O are able to stabilize molecular O_2 on a Au(111) surface and further activate it by forming the OOH species. Our findings of the involvement of a second H_2O remarkably favoring the hydrogen-transfer reaction by constructing a hydrogen bonding chain might provide a reasonable explanation for the enhanced role of H_2O in many heterogeneous catalytic reactions. In particular, one can expect that water may follow the same mechanism in other H-transfer reactions. A similar promoting role of water has also been reported in the CO_2 hydrogenation reaction on Cu(111)[79] and some gas-phase reactions.[80,81]

3.2.4. Dissociation of OOH. A Fourier transform infrared spectroscopic study[43] demonstrates the adsorbed OOH species is a precursor for the formation of atomically adsorbed oxygen and hydroxyl on Au/TiO_2, providing strong evidence of the dissociation of OOH on gold. In the initial configurations, OOH freely walks from the top site of the Au atom to the bridge site with little diffusion barrier (Figure S5 of the Supporting Information). The dissociation of OOH* to O* and OH* has an activation barrier of 0.79 eV and a reaction energy of −0.18 eV. The optimized geometric structures are displayed in Figure 4. In TS7, the O−O bond length is

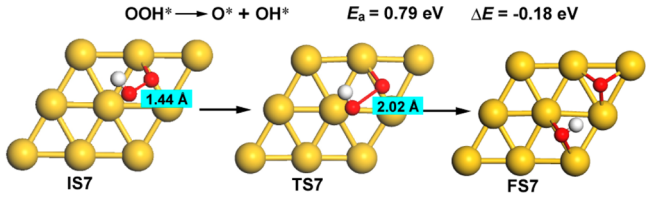

Figure 4. Dissociation of OOH* to O* and OH* on a Au(111) surface.

extended to 2.02 Å from an initial length of 1.44 Å. In the final geometry (FS7), the dissociated fragments, O* and OH*, are anchored at the hollow site and bridge site, respectively.

Furthermore, we have also examined the effect of water on the dissociation of OOH. In the presence of a neighboring water molecule, the activation barrier of OOH dissociation is increased by 0.01 eV (Figure S6 of the Supporting Information), indicating water has little effect on this process. Inasmuch as atomic oxygen and hydroxyl have been identified as the active species for alcohol oxidation on Au(111),[10,11,17,30−34] the easy formation of the OOH intermediate clearly paves the way for an effective activation of molecular O_2 on a bulk gold surface.

3.3. Dehydrogenation of Methanol to Formaldehyde by OOH*, O*, and OH*. As an alternative to the dissociation of OOH* species to form O* and OH*, the OOH* species itself can abstract a hydrogen atom from methanol to form H_2O_2 and formaldehyde. Similarly, the dissociated atomic O* and OH* can also react with methanol to produce formaldehyde. According to our calculations (Figures S5 and S7 of the Supporting Information) and those of Xu et al.,[34] the surface species (CH_3OH, CH_3O, OOH, O, and OH) can diffuse very easily, facilitating facile reactions between each other.

3.3.1. Dehydrogenation of Methanol by OOH.* As stated above, the dehydrogenation of methanol by OOH* is predicted to be a likely step. Figure 5a depicts the transfer of α-H of methanol to OOH* to form adsorbed methoxy and H_2O_2 with an endothermic energy of 0.27 eV, which is followed by β-H elimination (Figure 5b) to yield formaldehyde and another molecule of H_2O_2 with a huge energy release of −2.00 eV. The low calculated barriers, 0.30 and 0.06 eV, for the two aforementioned steps demonstrate that the direct hydro-

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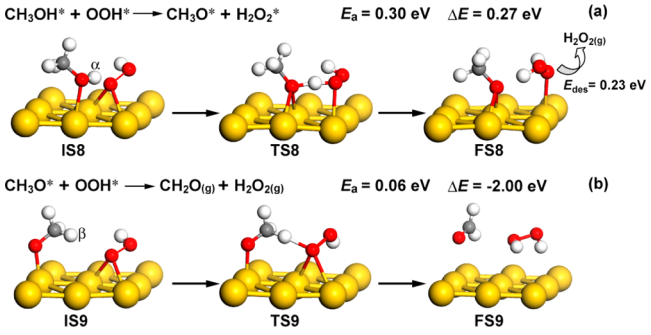

Figure 5. Dehydrogenation of methanol to formaldehyde via OOH*. (a) Transfer of α-H to OOH* to form methoxy and hydrogen peroxide. (b) Transfer of β-H to OOH* to form formaldehyde and hydrogen peroxide.

genation of OOH* is more favorable than its dissociation pathway. In other words, in the aerobic oxidation of alcohols, formation of a moderate oxidant H_2O_2 is more favorable than that of the strong oxidant O* and OH* species.

In addition, the H_2O_2 molecule formed in the first step is weakly adsorbed on the surface with an adsorption energy of −0.23 eV, whereas H_2O_2 formed in the second step cannot be adsorbed, because of the hydrogen bonding interaction between H_2O_2 and methoxy instead of formaldehyde. The low barrier for the formation of H_2O_2 as well as its facile desorption might explain why Ketchie et al. experimentally observed an appreciable concentration of H_2O_2 in the product mixture of alcohol oxidation.[25]

*3.3.2. Dehydrogenation of Methanol by O**. Despite a clean Au(111) surface being unfavorable for the adsorption or activation of molecular O_2, it does easily chemisorb oxygen in its atomic form.[82] Experimental[30−33] and theoretical[34] studies have shown that atomic oxygen-covered gold surfaces are highly active for alcohol oxidation reactions. Kandoi et al. revealed atomic oxygen can be facilely hydrogenated to OH and H_2O on a Au(111) surface.[83] According to our results (Figure 6), the dehydrogenation of methanol by atomic oxygen is extremely easy. Transfer of α-H to the neighboring oxygen adatom can be readily achieved by overcoming a low barrier of 0.13 eV. The successive β-H elimination step is almost a barrierless downhill process (E_a = 0.07 eV; ΔE = −2.06 eV), generating formaldehyde in the gas phase. For this reaction to

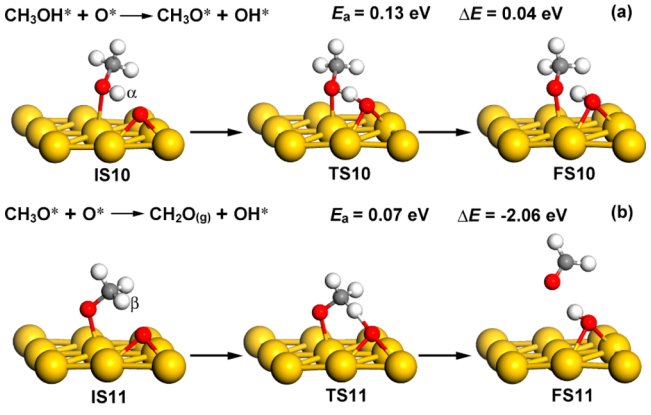

Figure 6. Dehydrogenation of methanol to formaldehyde via O*. (a) Transfer of α-H to O* to form methoxy and hydroxyl. (b) Transfer of β-H to O* to form formaldehyde and hydroxyl.

occur, the oxygen adatoms need to move from a 3-fold hollow site to a 2-fold bridge site. In the transition-state structures, hydrogen is shared by the donor (methanol or methoxy) and its acceptor (atomic oxygen).

*3.3.3. Dehydrogenation of Methanol by OH**. Similar to OOH* and O*, OH* is also a reactive species for the oxidation of alcohols. The corresponding barriers and reaction energies are listed in Figure 7. The water molecule generated in this

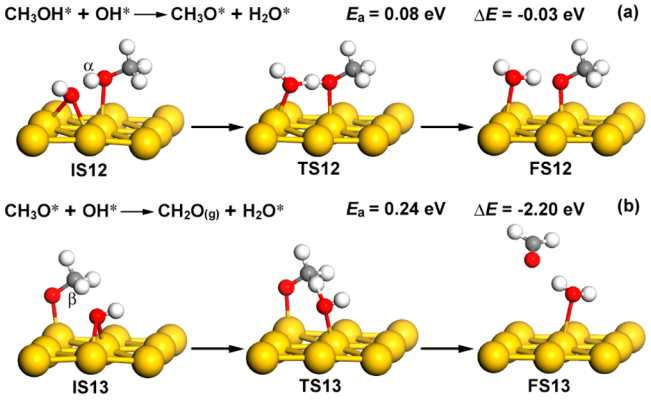

Figure 7. Dehydrogenation of methanol to formaldehyde via OH*. (a) Transfer of α-H to OH* to form methoxy and H_2O. (b) Transfer of β-H to O* to form formaldehyde and H_2O.

process as a byproduct can be re-used to promote the formation of the OOH* intermediate as described in a previous section. In fact, the dehydrogenation of methanol by adsorbed OH in the gas−solid phase is entirely similar to the alcohol oxidation catalyzed by OH^- anion under aqueous alkaline conditions.[10,11,17,84,85] However, the absence of solvents and alkaline bases in the gas−solid system is more ideal for a benign effect on the environment and green chemistry.[19]

3.4. Complete Reaction Network. On the basis of our computational results, the selective oxidation of methanol to formaldehyde follows either a direct pathway or an indirect pathway assisted by molecular O_2 and its derived species. The key elementary steps are listed sequentially below in eqs 1−14.

Direct pathway:

$$CH_3OH^* \rightarrow CH_3O^* + H^* \quad (1)$$

$$CH_3O^* \rightarrow CH_2O_{(g)} + H^* \quad (2)$$

OOH-mediated pathway:

$$\begin{cases} (CH_3OH\cdots O_2)^* \rightarrow CH_3O^* + OOH^* & (3) \\ (H_2O\cdots O_2)^* \rightarrow OH^* + OOH^* & (4) \end{cases}$$

$$\begin{cases} (CH_3OH\cdots H_2O\cdots O_2)^* \\ \quad \rightarrow CH_3O^* + H_2O^* + OOH^* & (5) \\ (H_2O\cdots CH_3OH\cdots O_2)^* \\ \quad \rightarrow OH^* + CH_3OH^* + OOH^* & (6) \\ (H_2O\cdots H_2O\cdots O_2)^* \\ \quad \rightarrow OH^* + H_2O^* + OOH^* & (7) \end{cases}$$

$$OOH^* \rightarrow O^* + OH^* \quad (8)$$

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$$\begin{cases} CH_3OH^* + OOH^* \\ \quad \rightarrow CH_3O^* + H_2O_2\,^* \end{cases} \quad (9)$$

$$\begin{cases} CH_3O^* + OOH^* \\ \quad \rightarrow CH_2O_{(g)} + H_2O_{2(g)} \end{cases} \quad (10)$$

$$\begin{cases} CH_3OH^* + O^* \rightarrow CH_3O^* + OH^* & (11) \\ CH_3O^* + O^* \rightarrow CH_2O_{(g)} + OH^* & (12) \end{cases}$$

$$\begin{cases} CH_3OH^* + OH^* \rightarrow CH_3O^* + H_2O^* & (13) \\ CH_3O^* + OH^* \rightarrow CH_2O_{(g)} + H_2O^* & (14) \end{cases}$$

The direct pathway without O_2 can hardly occur under ambient conditions because of very high barriers and a large endothermicity. In the OOH-mediated pathway, O_2 is activated by the formation of an important intermediate hydroperoxyl (OOH), as shown in eqs 3 and 4, which is the rate-determining step with the highest barrier (~0.90 eV). The involvement of one more H_2O (eqs 5−7) notably lowers the barrier of OOH* formation to ~0.45 eV and thus changes the rate-determining step to the dissociation of OOH* (eq 8). The subsequent dehydrogenation of methanol can be readily achieved by OOH*, O*, and OH* (eqs 9−14). Although the initial formation of OOH is thermodynamically unfavorable, the heat released from the following steps makes the whole catalytic cycle exothermic.

4. CONCLUSIONS

A systematical study of the selective oxidation of methanol to formaldehyde on Au(111) has been performed by DFT calculations. We have proposed a possible pathway for oxidative dehydrogenation of methanol with molecular O_2 on a bulk Au(111) surface. The main conclusions drawn from our calculations are as follows. (1) The pre-adsorbed reactant, such as methanol or H_2O, is able to make the adsorption of O_2 on a Au(111) surface feasible via hydrogen bonding interaction. Furthermore, O_2 can abstract a hydrogen atom from the reactant (CH_3OH or H_2O) to form a hydroperoxyl species (OOH), which is identified as a vital intermediate for subsequent oxidations. (2) By constructing a hydrogen bonding chain with H-containing reactants, water is found to notably facilitate hydrogen-transfer reactions, which lowers the formation barrier of OOH species from ~0.90 eV (without water) to ~0.45 eV (with water). This novel mechanism might lead to a new understanding of the significant role of H_2O in related hydrogen-transfer reactions. (3) OOH species and the further dissociated atomic oxygen and hydroxyl are highly reactive for the dehydrogenation of methanol. The calculated barriers fall between 0.06 and 0.30 eV.

Our results provide mechanistic insight into the aerobic oxidation of alcohols and an understanding of the catalytic behavior of a large-sized or bulk gold surface via formation of hydroperoxyl radical. Of particular importance is the finding that water or methanol can significantly promote the H-transfer reactions by a synergetic hydrogen bonding chain. Such a pathway for O_2 activation via α-H transfer can also be extended to other alcohols and hydrogen-containing reactants such as amine, acid, thiol, etc. Further investigations of the role of hydroperoxyl radical in other catalytic organic reactions will be interesting.

■ ASSOCIATED CONTENT

Supporting Information

Supplementary data as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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