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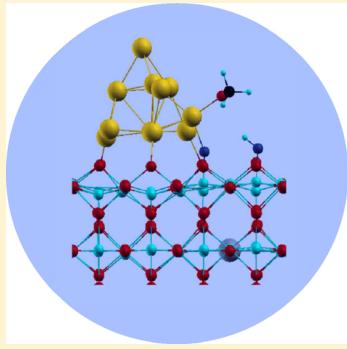
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Nature and Role of Activated Molecular Oxygen Species at the Gold/Titania Interface in the Selective Oxidation of Alcohols

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ABSTRACT: The heterogeneously catalyzed selective oxidation of alcohols has been studied by using methanol on gold nanoparticles supported on reduced titania surfaces. Our density functional theory based simulations shed light on the atomistic details of the mechanism responsible for the CH_3OH oxidation toward formaldehyde, CH_2O , at these complex Au/TiO_2 interfaces. The selectivity and high catalytic activity of the Au/TiO_2 nanocatalyst in the oxidation of methanol is traced back to the presence of active sites right at the interface between the Au nanoparticle and the TiO_2 support where preadsorbed molecular oxygen is activated as a result of significant metal–support interactions. The activation of O_2 at such dual perimeter sites occurs via charge transfer from Au/TiO_2 leading to the formation of peroxide species, $\text{O}_2^{\delta-}$. These activated $\text{O}_2^{\delta-}$ species open up an efficient low-temperature reaction channel for the oxidation of methanol to yield formaldehyde and water.



I. INTRODUCTION

Gold nanoclusters prepared in different ways and supported on reducible metal oxides such as titania, TiO_2 ,^{1–8} are able to catalyze many important chemical reactions such as partial oxidation of hydrocarbons, hydrogenation of unsaturated hydrocarbons, water gas shift, and CO oxidation.^{9–13} In particular, it became clear long ago that the size of the gold particles substantially affects the catalytic activity.¹⁴ The gold clusters should be smaller than about 3 nm in diameter for high catalytic activity to occur, suggesting the key importance of interfacial metal–support interactions on the nanometer to atomic scale.¹⁴ In fact, oxide-supported metal nanoparticles display “Metal–Support Interaction” (MSI) effects, which give rise to structural and electronic properties unique to the combined system and not present in the separate materials.

Multiple mechanisms have been proposed to explain the high catalytic activity of oxide-supported Au for CO oxidation,^{15–17} which serves as both a model and reference reaction. The origin of the high catalytic activity of Au/oxide catalysts, however, has not been fully clarified at the atomistic level. In particular, controversies still exist on the nature of the active sites, on the interactions between supports and gold particles, and on the chemical nature of the activated molecular oxygen species.

Recently, theory as well as experiment have shown that active interfacial sites for nanometer Au/ TiO_2 catalysts, located at the interface between the Au nanoclusters and the TiO_2 support, catalyze reactions such as CO oxidation,^{18–24} H₂ oxidation,²⁵ acetic acid oxidation,²⁶ oxidative dehydrogenation of carboxylic acids,²⁷ and methanol oxidation.^{28,29} In the case of CO oxidation, CO molecules are delivered to the active sites at the interface between Au nanoparticles and TiO_2 supports via diffusion, where they assist O–O bond dissociation and react with oxygen at these interfacial sites. In particular, infrared-kinetic measurements indicate that the O–O bond scission is activated by the formation of a CO– O_2 complex at dual Ti–Au

sites at the Au/TiO_2 interface²² for the simple case of CO oxidation. Moreover, it has been shown that TiO_2 -supported Au^{3+} ions can catalyze CO oxidation at very low temperature.²⁴ These results²⁴ demonstrate that sites consisting of or including Au^{3+} provide CO oxidation rates well comparable with those obtained with Au^0 clusters, but at very low apparent activation energies. Concerning H₂ oxidation at the Au/TiO_2 interface it has been shown²⁵ that active sites for the $\text{H}_2 + \text{O}_2$ reaction over the Au/TiO_2 nanocatalyst are located at dual perimeter sites at the interface between Au and TiO_2 , where O_2 is activated. Similar results have been found in the case of the partial oxidation of acetic acid and the oxidative dehydrogenation of carboxylic acids.^{26,27} The high reactivity of interfacial sites of gold/titania nanocatalysts toward methanol decomposition has also been suggested.^{28,29}

Motivated by these findings we present here a detailed mechanistic study of the selective oxidation of a polyatomic molecule, methanol, toward formaldehyde, using a quite realistic Au/TiO_2 nanocatalyst model. The quest for efficient catalysts in the partial oxidation of alcohols for the production of fine and specialty chemicals has indeed attracted great interest in the past years.³⁰ Thus, providing an atomistic understanding of alcohol oxidation by using activated O_2 at gold/titania catalysts appears timely.

Anticipating our key results, we find that the high catalytic activity and selectivity of the Au/TiO_2 catalyst originate from the presence of active sites at the interface between the Au nanoparticle and the reduced TiO_2 surface. In particular, the activation of molecular O_2 is shown to occur via charge transfer from the interfacial Au/TiO_2 system, thus forming highly reactive $\text{O}_2^{\delta-}$ species at dual perimeter sites.

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II. COMPUTATIONAL DETAILS

The density functional theory (DFT) calculations have been performed with use of the Car–Parrinello Molecular Dynamics CPMD³¹ and Quantum Espresso³² codes. All calculations have been performed by using spin-polarized GGA+U based on the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.³³ The spin-polarized Kohn–Sham equations were solved in the plane-wave and pseudopotential framework by using Vanderbilt's ultrasoft pseudopotentials³⁴ with a cutoff of 25 Ry, using the Γ -point. In line with our previous work^{17,35} we made use of the linear response LDA+U approach of de Gironcoli and Cococcioni with a fixed value of $U = 4.2$ eV that has been determined by using the self-consistent approach.^{36,37} The occupations of the d-orbitals are calculated by using atomic-like wave function projectors.

The $\text{TiO}_2(110)$ surfaces have been modeled by four O– Ti_2O_2 –O trilayer (4×2) supercell slabs separated by more than 10 Å of vacuum; we refer to ref 38 for the definition of the model and the trilayers. The bottom of the slab was passivated with pseudohydrogen atoms of nuclear charge +4/3 and +2/3 to achieve well converged results, which is our benchmarked “standard setup”.³⁸ The two lowest trilayer atoms were constrained to their equilibrium positions, while all the other atoms were free to move until the maximum force was less than 0.02 eV/Å.

The reaction mechanism for methanol oxidation has been studied by means of the climbing image nudged elastic band (CI-NEB)^{39,40} method that was used to identify the minimum energy paths on the potential energy surface (PES). These calculations have been performed in the supercells described above including up to 20 replica images.

Adsorption energies have been calculated as usual

$$E_{\text{ads}} = E_{\text{tot}} - [E_{\text{sub}} + E_X]$$

where E_{tot} is the total energy of the combined system (namely the adsorbate X bound to the substrate), E_{sub} is the energy of the substrate alone, and E_X is the total energy of the adsorbate in the gas phase. Accordingly, the difference charge density has been evaluated by using the usual expression

$$\Delta\rho(\vec{r}) = \rho_{\text{tot}}(\vec{r}) - [\rho_{\text{sub}}(\vec{r}) + \rho_X(\vec{r})]$$

where ρ_{tot} , ρ_{sub} , and ρ_X represent the charge density of the whole system, the isolated substrate, and the adsorbate, respectively.

Additional calculations have been performed by using plain PBE to compare the PBE+U results with the ones obtained by removing the Hubbard U correction. In particular, we have selected important reaction pathways to be discussed later in the paper for which we have recomputed the activation energies after switching off the Hubbard correction, see Table 1; note

Table 1. Comparison between Activation Energies of Selected Reaction Pathways (denoted by the respective figure label) Obtained by Using PBE+U and Plain PBE Functionals

energy barrier	PBE+U	PBE
Figure 4	0.05 eV	0.03 eV
Figure 5	0.49 eV	0.82 eV
Figure 6	0.69 eV	0.58 eV
Figure 8	0.33 eV	0.47 eV
Figure 10	2.65 eV	2.73 eV

that the full pathways have been reoptimized by using plain PBE. It is clear from Table 1 that the energy barriers computed by using PBE+U and plain PBE are in qualitative agreement for reasons that have been explained earlier.³⁸ Thus, the Hubbard correction is only required to localize the excess charges of reduced titania surfaces at specific Ti sites.^{17,35}

III. RESULTS AND DISCUSSION

A. Nanocatalyst Model Systems with Preadsorbed Molecular O₂. The study of the CH_3OH oxidation reaction over an Au/TiO₂ catalyst requires a realistic model of an Au_n cluster supported on a TiO₂ metal oxide surface. Oxygen vacancies, being always present on the rutile surface thus generating F-centers and excess electrons, result in stable anchoring sites for Au adatoms.³ It is noted in passing that the vivid correlated dynamics of such excess electrons close to oxygen vacancies on TiO₂(110), predicted by us several years ago,³⁵ has been confirmed recently by sophisticated STM experiments.⁴¹

As we will see later, the high selectivity and reactivity of Au/TiO₂ nanocatalysts originate from the presence of active sites at the interface where O₂ molecules become activated. It is therefore important to provide evidence that such O₂–Au/TiO₂ systems with Au clusters of different size and shape display qualitatively similar electronic properties, which result into O₂ activation irrespective of the atomistic details of the particular cluster model.

To this end, we have performed a set of static calculations where Au_n clusters of different size and morphology, using $n = 11–16$, were grown on TiO₂(110) surfaces where a surface oxygen vacancy (O_v) acts as an anchoring site for initial Au nucleation. We note in passing that this O vacancy, marked as a pink sphere in Figure 2a, is always present on the TiO₂ surface even if not highlighted in all figures of the paper. Cluster growth was done by cycles of adding more and more Au atoms and relaxing the obtained clusters, taking the lowest energy structure as the starting point for the next such cycle. These usual structural relaxations were followed by short room temperature Car–Parrinello ab initio molecular dynamics (AIMD) simulations⁴² to check the stability of the optimized Au_n/TiO₂ structures. Next, a O₂ molecule was adsorbed at the interface between the supported metal clusters and the TiO₂(110) surface, which is where the active sites reside (vide infra). The most stable structures found by using that procedure are the ones depicted in Figure 1, which might be global or local minima. Based on these structures, we have performed Löwdin charge analyses of the Au_n/TiO₂(110) systems depicted in Figure 1 in the presence of the activated O₂ molecule at the interface as shown, but also in its absence as a reference.

The average Löwdin charge values, $\overline{\text{Au}}$, of the Au_n clusters depicted in Figure 1 without and with activated O₂ molecule at the Au/TiO₂ interface are reported in Table 2. It is clear from Table 2 that $\overline{\text{Au}}$ is almost the same not only for metal clusters of different size and shape, but also in the presence or absence of the activated O₂ molecule at the Au_n/TiO₂ interface. In addition, the charge of O₂ preadsorbed at the metal/oxide interface is almost constant regardless of the shape and size of the neighboring Au_n cluster, suggesting that the O₂ molecule is activated in the same way by all model systems such as those depicted in Figure 1. As will be analyzed in the next section, the O₂ species is activated via charge transfer from the substrate to

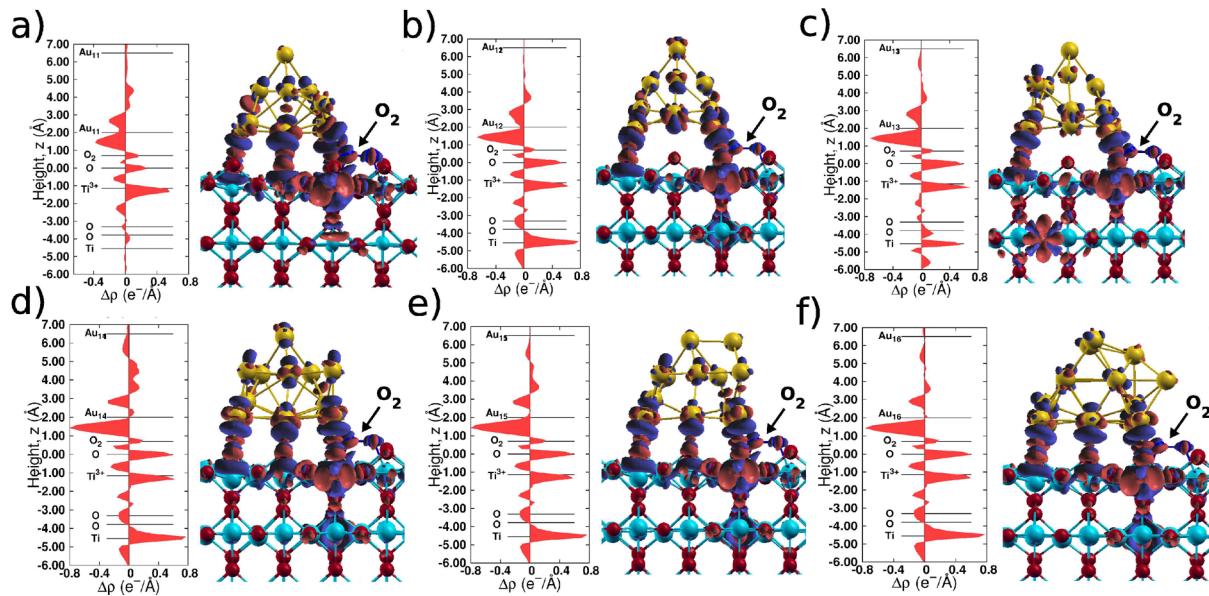


Figure 1. Bonding charge $\Delta\rho$ for selected Au_n ($n = 11, \dots, 16$) clusters supported by the reduced $\text{TiO}_2(110)$ surface in the presence of a preadsorbed O_2 molecule as indicated. The left subpanels represent the bonding charges integrated in planes perpendicular to the surface and are plotted as a function of the height from the surface. The right subpanels depict the corresponding bonding charge isosurfaces in real space plotted at $0.06 \text{ lel}/\text{\AA}^3$; electron accumulation and depletion are represented by red and blue isosurfaces, respectively.

Table 2. Löwdin Charges Analyses of the Six $\text{Au}_n/\text{TiO}_2(110)$ Nanocatalyst Models Depicted in Figure 1, with and without Preadsorbed O_2 at the Gold/Titania Interface^a

	Au_{11}	Au_{12}	Au_{13}	Au_{14}	Au_{15}	Au_{16}
$\overline{\text{Au}}(/ \text{TiO}_2)$	11.04 lel	11.03 lel	11.04 lel	11.01 lel	11.03 lel	11.00 lel
$\overline{\text{Au}}(/ \text{TiO}_2/\text{O}_2)$	11.03 lel	11.00 lel	11.00 lel	11.01 lel	11.00 lel	11.00 lel
O_2	12.57 lel	12.58 lel	12.58 lel	12.57 lel	12.57 lel	12.57 lel
$\text{Au} \rightarrow \text{O}_2-\text{TiO}_2$ charge transfer	0.468 lel	0.512 lel	0.571 lel	0.476 lel	0.562 lel	0.550 lel
Δq	0.05	0.06	0.09	0.06	0.10	0.02

^aFirst row: Average Löwdin charge value ($\overline{\text{Au}}$) of the Au_n clusters in the absence of the preadsorbed O_2 molecule at the Au/TiO_2 interface. Second row: Average Löwdin charge value ($\overline{\text{Au}}$) of the Au_n clusters in the presence of the activated O_2 molecule. Third row: Löwdin charges of the O_2 molecule when adsorbed at the interface (the corresponding Löwdin charge of an isolated O_2 molecule, 11.89 lel, serves as reference). Fourth row: Amount of charge transferred from the Au_n nanoclusters to the O_2-TiO_2 substrate (obtained by integrating the bonding charge on planes parallel to the surface from the middle of the vacuum region to the middle of the $\text{Au}-\text{O}$ bond lengths at the interface between the Au_n clusters and the $\text{TiO}_2(110)$ substrate). Fifth row: Löwdin charge difference Δq between the particular Au atom of the gold nanocluster that is closest to O_2 before and after the adsorption of the O_2 molecule at the interface.

molecular oxygen. In the absence of the preadsorbed O_2 molecule three Ti^{3+} sites are present in the substrate. Upon O_2 adsorption at the Au_n/TiO_2 interface two of these three electrons are transferred to the O_2 molecule that becomes activated by turning formally into a peroxide species, O_2^{2-} , to be discussed in detail in the next section. Interestingly enough, upon O_2 adsorption the Au atom of the gold nanocluster closest to the O_2 molecule becomes slightly positively charged as revealed by the Δq values compiled in Table 2. In addition to computing Löwdin charges, we have performed a bonding charge analysis of the various $\text{O}_2-\text{Au}_n/\text{TiO}_2$ nanostructures, $\Delta\rho$, which are shown in Figure 1 for Au_n clusters supported by the defective $\text{TiO}(110)$ surface in the presence of the activated O_2 species. Here, $\Delta\rho$ has been computed as a difference between the charge density of the whole $\text{O}_2-\text{Au}_n/\text{TiO}_n$ system and the sum of the charge densities of the separated Au_n nanoclusters and the remaining defective TiO_2 support together with the preadsorbed O_2 molecule, i.e. O_2-TiO_n , without relaxing any of these separated structures. This analysis reveals that charge is transferred from the metal cluster to the substrate with preadsorbed O_2 once the Au_n nanoclusters are

adsorbed on the surface; the amount of charge transferred is reported in the fourth row of Table 2. It is clear from these data that, in all the nanocatalysts considered, a similar amount of charge is transferred from the Au_n nanocluster to the support with preadsorbed O_2 , thus resulting in slightly positively charged $\text{Au}_n^{\delta+}$ clusters. This is consistent with the enhanced reactivity of positively charged Au sites for oxidation that has been observed in recent experiments.^{24,29}

Overall these results suggest that, at the interface where the oxidation of methanol takes place, the behavior of Au_n nanoclusters of different shape and morphology is qualitatively the same. In what follows we have thus selected the smallest nanocatalyst, i.e. $\text{Au}_{11}/\text{TiO}_2(110)$ as depicted in Figure 1a, to investigate the reactivity and selectivity for CH_3OH oxidation at the gold/titania interface in terms of an atomistically detailed reaction mechanism.

B. Activation and Diffusion of Molecular O_2 on Reduced Au/TiO_2 Surfaces. Our proposed catalytic cycle for CH_3OH oxidation starts with the adsorption of a O_2 molecule at the interface between the gold cluster, here Au_{11} , that is pinned by an F-center on the $\text{TiO}_2(110)$ surface.

Let us first discuss this nanocatalyst model in the absence of preadsorbed molecular oxygen.⁴³ The removal of an O atom from the ideal $\text{TiO}_2(110)$ surface gives rise to two excess electrons that localize on two Ti atoms occupying specific Ti-3 d orbitals, thus formally creating two Ti^{3+} sites.^{17,35} Next, the binding of the Au_{11} cluster on such a reduced $\text{TiO}_2(110)$ support entails a strong charge rearrangement at the metal/oxide contact, the adsorption energy being -2.19 eV. Such adsorption of a gold cluster on the reduced oxide support without preadsorbed O_2 induces a strong charge rearrangement at the metal/oxide contact through the MSI effect. Inspection of spin density and bonding charge reveal that roughly 0.4 lel are transferred from the metal cluster to the defective $\text{TiO}_2(110)$ surface.⁴³ This charge transfer from Au_{11} to the defective support reduces the substrate even more, thus formally turning one more Ti^{4+} ion into a Ti^{3+} site. Therefore, the Au_{11} cluster, once adsorbed, leaves a strongly reduced substrate with all together (formally) three Ti^{3+} ions⁴³ in the absence of O_2 , which results in a slightly positively charged $\text{Au}_{11}^{\delta+}$ cluster.

As a second step, preadsorption of molecular oxygen is carried out to analyze in depth the activation of the O_2 species at the gold/titania interface. Figure 2 depicts the $\text{Au}_{11}/\text{TiO}_2(110)$ nanocatalyst before (in panel a) and after O_2 adsorption at the interface in three different configurations b, c, and d. In the lowest-energy preadsorbed configuration depicted in panel b of Figure 2, the O_2 molecule is strongly bound at the gold/titania interface, its adsorption energy being

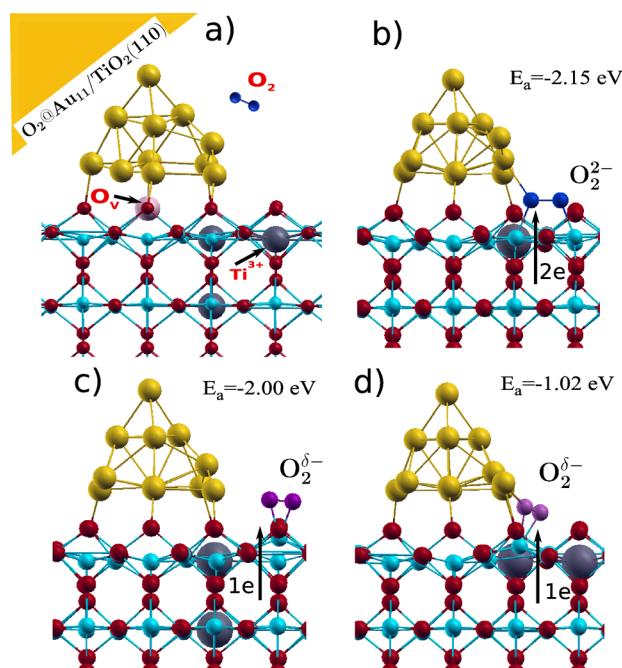


Figure 2. Panel a shows a ball and stick model of the $\text{Au}_{11}/\text{TiO}_2(110)$ catalyst model with the Au_{11} cluster sitting on a surface O vacancy. Panels b–d show three low-energy configurations with O_2 adsorbed at the interface between the Au_{11} cluster and the $\text{TiO}_2(110)$ surface; the corresponding binding energies for O_2 adsorption on $\text{Au}_{11}/\text{TiO}_2(110)$ are reported in the panels. The Au, Ti, and O atoms are depicted in yellow, light blue, and red, respectively, whereas the O_2 molecule is shown in dark blue. The big dark blue spheres represent the reduced Ti^{3+} sites, while the O vacancy, denoted by O_v , is depicted as a pink sphere in panel a. Although the O vacancy is shown for illustration only in panel a, it is present in all the figures presented in the paper.

-2.15 eV. In this structure, each O site of the O_2 molecule binds to one 5-fold-coordinated Ti site, Ti_{5c} , the two O– Ti_{5c} bond lengths being 1.93 and 1.98 Å. Note that the longer bond is the one that involves the O site that is closer to the Au_{11} gold cluster. The computed O–O bond length is found to be 1.44 Å, see Table 3, which is very much extended compared to a

Table 3. Löwdin Charges and Bond Lengths of an Isolated Oxygen Molecule $\tilde{\text{O}}_2$ in the Triplet State, an Isolated $\tilde{\text{O}}_2^-$ Superoxide, and an Isolated $\tilde{\text{O}}_2^{2-}$ Peroxide Species Compared to the Corresponding Values of the Activated O_2^- Superoxide and O_2^{2-} Peroxide Species Adsorbed at the Interface between the Au_{11} Cluster and the TiO_2 Interface^a

species	charge	bond length
$\tilde{\text{O}}_2$	11.89 lel	1.23 Å
$\tilde{\text{O}}_2^-$	12.40 lel	1.30 Å
$\tilde{\text{O}}_2^{2-}$	12.60 lel	1.38 Å
O_2^-	12.47 lel	1.44 Å
O_2^{2-}	12.57 lel	1.44 Å

^aOn the basis of Löwdin charge and spin density analyses two different O_2 species adsorbed at the interfacial region were identified. The O_2^- species corresponds to the structures depicted in Figure 2, panels c and d. Here, the O_2 molecule is sitting on top of a single 5-fold coordinated surface Ti site, therefore the two O atoms of the O_2 molecule are bound to the same Ti atom. The O_2^{2-} species corresponds to the structure depicted in Figure 2b and has been classified as a peroxide. In this case, each atom of the O_2 molecule binds to a different 5-fold coordinated surface Ti site. See text for remarks on the underlying electronic structure method.

noninteracting neutral O_2 molecule, 1.23 Å, and comes close to the reference value computed for a peroxide species, O_2^{2-} , which is roughly 1.38 Å.

The computed Löwdin charge of this activated O_2 species is 12.57 lel, which is in accord with that computed for the free peroxide, 12.60 lel, see Table 3. Note that for an isolated O_2 molecule in the triplet state, the same computational method yields an O–O bond length of only 1.23 Å and a Löwdin charge of 11.89 lel, see Table 3. The charge of the preadsorbed O_2 species which sits on top of a single 5-fold coordinated surface Ti site, corresponding to the structures depicted in Figure 2c,d, which are less stable than that in panel b, amounts to 12.47 lel and is thus close to that of a free superoxide, 12.40 lel, see Table 3. In the context of such comparisons, it must be kept in mind that any partial charge analysis, such as that of Löwdin, can offer only qualitative insights into charge transfer processes rather than providing absolute numbers. Furthermore, we stress that simple GGA density functionals, such as PBE, are not expected to provide highly accurate numbers for dioxygen species as a function of their charge state, in particular for the dianionic case. Keeping this in mind, the data reported in Table 3 can merely provide a consistent set of noninteracting O_2 reference species in different charge states which have been obtained by using the same computational approach as that used to investigate the catalytic cycle on the nanocatalyst slab model.

Thus, an O_2 molecule once preadsorbed at the perimeter of the gold/titania nanocatalyst is found to be strongly negatively charged and is characterized by a significantly elongated O–O bond length.

In addition, the adsorption of the O_2 molecule induces a further change in the degree of reduction of the supporting substrate. The calculations predict that two of the three

electrons originally occupying Ti 3d orbitals are transferred from the TiO_2 substrate to the adsorbed O_2 molecule, which “formally” turns into a peroxide species, O_2^- . This charge flow, driven by a subtle interplay between the TiO_2 surface and co/adsorbates, leads to a $\text{O}_2\text{-Au}/\text{TiO}_2/\text{O}_2$ interface where a single Ti^{3+} ion remains present within the TiO_2 substrate as marked by the big blue sphere in Figure 2b, whereas three such sites are observed in panel a in the absence of preadsorbed O_2 .

Besides this most stable peroxide state of Figure 2b, the calculations allowed us to identify higher-energy configurations for O_2 adsorption on the $\text{Au}_{11}/\text{TiO}_2(110)$ catalyst. These optimized structures are depicted in Figure 2c,d, where the O_2 molecule is sitting on top of a single Ti_{5c} surface site either far away or next to the supported Au_{11} gold cluster, respectively, the corresponding binding energies being -2.00 and -1.02 eV. The O_2 molecule has an O–O bond length of 1.45 Å, while the O– Ti_{5c} bond lengths are ~ 1.9 Å in both cases. Our calculations show that when the O_2 molecule is adsorbed on top of the same surface Ti_{5c} atom, the resulting charge rearrangement differs significantly from that obtained from the lowest energy adsorption site of Figure 2b, where the two O atoms of dioxygen are bound to different surface Ti sites. It is clear from Figure 2c,d that in these cases formally only one of the three excess electrons populating Ti 3d orbitals of the substrate is transferred to the O_2 adsorbate (see the remaining two big blue spheres in these panels). The computed Löwdin charge of this species is 12.47 lel in both configurations, see Table 3, i.e. such preadsorbed O_2 species are less negatively charged compared to the energetically preferred one from panel b in Figure 2. Inspection of the spin density reveals that this “excess charge” is now shared between the adsorbed O_2 molecule and the Au_{11} gold cluster. Thus, the resulting simplified picture is that one unpaired electron is transferred in such configurations from the substrate to the adsorbate and subsequently shared between the O_2 molecule and the gold cluster. This suggests that the formation of a superoxide species O_2^- is discouraged in such energetically higher-lying configurations.

As anticipated, the most stable structure, namely the one with lowest energy depicted in Figure 2b, has been employed as the starting structure for investigating the selective oxidation process of methanol involving the activated $\text{O}_2\text{-Au}_{11}/\text{TiO}_2(110)$ nanocatalyst system.

Before doing so, however, let us first consider the diffusion process of the O_2 molecule on the reduced $\text{Au}_{11}/\text{TiO}_2(110)$ surface. Figure 3 shows a computed migration pathway that leads to an interchange of preadsorption sites for O_2 in terms of the stationary points, where all energy differences are referred to the initial state (IS). In the IS the O_2 molecule is sitting on top of a surface Ti_{5c} atom, which is the configuration shown in Figure 2c, whereas the final state (FS) is the O_2 molecule coadsorbed at the interface between the supported Au_{11} gold cluster and the $\text{TiO}_2(110)$ surface, thus reaching the lowest energy configuration that is depicted in Figure 2b. The IS and FS are separated by an intermediate state (IS1) and thus two transition states, TS1 and TS2, with activation energies of 0.47 and 0.45 eV, respectively. It is noted in passing that in the IS and TS1 two Ti^{3+} ions are present in the substrate, whereas the remaining part of not only the migration pathway, but also the entire catalytic cycle to be discussed later is characterized by the presence of a single Ti^{3+} ion in the substrate. Thus, along the migration path leading from IS to FS an electron populating the substrate in IS is transferred to the O_2 molecule leading to the formation of a peroxide species in the FS. The FS configuration

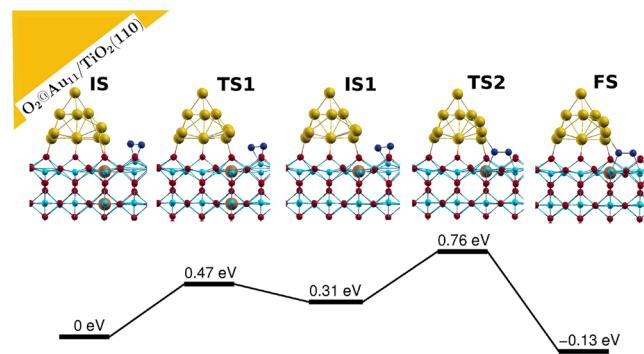


Figure 3. Reaction path and corresponding energies for the O_2 migration and activation processes on the $\text{Au}_{11}/\text{TiO}_2(110)$ catalyst. The energy differences of the intermediate state (IS1), the final state (FS), and the transition states (TS1, TS2) are referred to the initial state (IS).

has a total energy that is 0.13 eV lower with respect to the IS, but despite such small energy difference the two structures differ considerably. The more stable FS configuration is the one employed to study the selective CH_3OH oxidation on the $\text{Au}_{11}/\text{TiO}_2(110)$ surface. We anticipate that the adsorption of O_2 directly at the metal/oxide interface plays a prominent role in the proposed catalytic process. The strong interface activity of molecular O_2 can be traced back to the aforementioned charge transfer from $\text{Au}_{11}/\text{TiO}_2(110)$ leading to the formation of activated $\text{O}_2^\delta-$ species, the charge state of which depends on the particular adsorption site as discussed.

C. Methanol Coadsorption on the Activated Catalyst.

The activation of molecular O_2 at the $\text{Au}_{11}/\text{TiO}_2(110)$ interface analyzed up to this point is followed by the coadsorption of a CH_3OH molecule close to the activated O_2 species. Figure 2 shows the computed reaction path for methanol coadsorption at the metal/oxide catalyst interface. The coadsorption of CH_3OH proceeds with a negligible activation energy barrier of ~ 0.05 eV as given by the transition state. In the final state, the H atom of CH_3OH points toward the activated O_2 molecule, while its O atom is pointing in the direction of the neighboring Au atoms of the supported Au_{11} cluster. The corresponding Au–O and H–O distances are 2.51 and 1.77 Å, respectively, and the coadsorption energy is -0.58 eV. In addition, electronic structure analyses along the coadsorption process show that one reduced Ti^{3+} site is preserved in the oxide support, cf. the single big blue sphere in each of the subpanels of Figure 4a.

We should mention in passing that different starting configurations for methanol coadsorption at the $\text{O}_2\text{-Au}_{11}/\text{TiO}_2(110)$ interface have been considered. Our calculations predict values for coadsorption energies on the order of only -0.3 eV when the CH_3OH molecule is placed on top of the supported Au_{11} cluster, whereas values on the order of -0.6 eV are obtained when the molecule occupies sites at the $\text{Au}_{11}/\text{TiO}_2(110)$ interface close to activated O_2 species. Thus, the catalytically favorable sites seem to be preferred over others.

In summary, these computations support the idea that the presence of preadsorbed and thus activated O_2 molecules stabilizes the interaction between CH_3OH and the $\text{Au}_{11}/\text{TiO}_2(110)$ catalyst. In particular, the activated O_2 species is seen to attract the acidic H atom of the methanol OH group, leading to a starting configuration that facilitates the CH_3OH oxidation process.

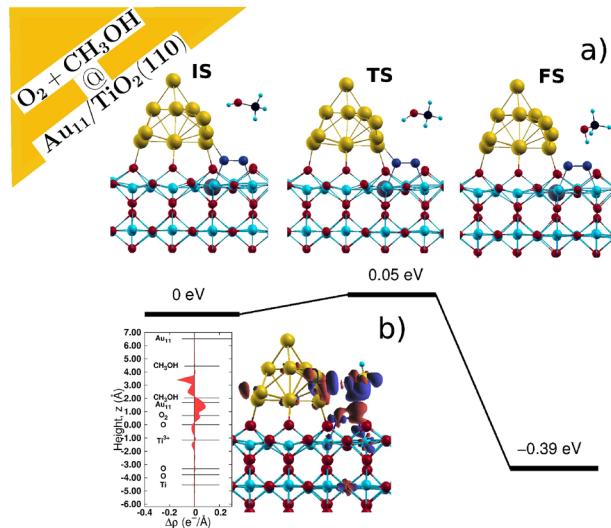


Figure 4. Reaction path and corresponding energies for CH₃OH coadsorption (panel a). Panel b shows methanol-induced charge flow in the final state (FS). Blue and red isosurfaces indicate depletion and accumulation of charge, respectively. The C and H atoms of the CH₃OH molecule are shown as black and small light blue spheres, respectively.

To further characterize the nature of the interaction between CH₃OH and the activated O₂ molecule in the FS of Figure 2a, we have computed the difference $\Delta\rho(\vec{r})$ between the charge

densities of the combined system and the separated components, namely CH₃OH and the substrate, while freezing all atomic positions. The methanol-induced charge flow is depicted in Figure 4b, where blue and red isosurfaces indicate depletion and accumulation of charge, respectively. Analyzing the chemical bonding qualitatively in three dimensions, we observe that electron charge accumulates between the first layer Au atoms and the substrate. A more quantitative analysis, where only the charge redistribution perpendicular to the support is considered (see the left panel of Figure 4b), reveals that upon adsorption of the Au₁₁ cluster on the surface with preadsorbed O₂, charge is transferred from the metal to the surface, part of which is transferred to the adsorbed O₂ species. The charge flow induced upon CH₃OH coadsorption suggests that additional charge is transferred from the methanol molecule to the preadsorbed O₂ molecule. We conclude that the activated O₂ species at the interface between the Au₁₁ nanocluster and the TiO₂ surface can efficiently bind a methanol molecule right at the active site, which is the starting point of the catalytic cycle.

D. Methanol Oxidation at the Interface. The coadsorption of CH₃OH at the active site of the O₂–Au₁₁/TiO₂(110) interface is followed by the first oxidation step, which yields a methoxy species, CH₃O, attached to the gold nanoparticle. The corresponding computed reaction path is shown in Figure 5. The CH₃OH molecule adsorbed at the O₂–Au₁₁/TiO₂ interface (see IS of Figure 5a) reacts directly with the activated O₂ species leading to a transition state via

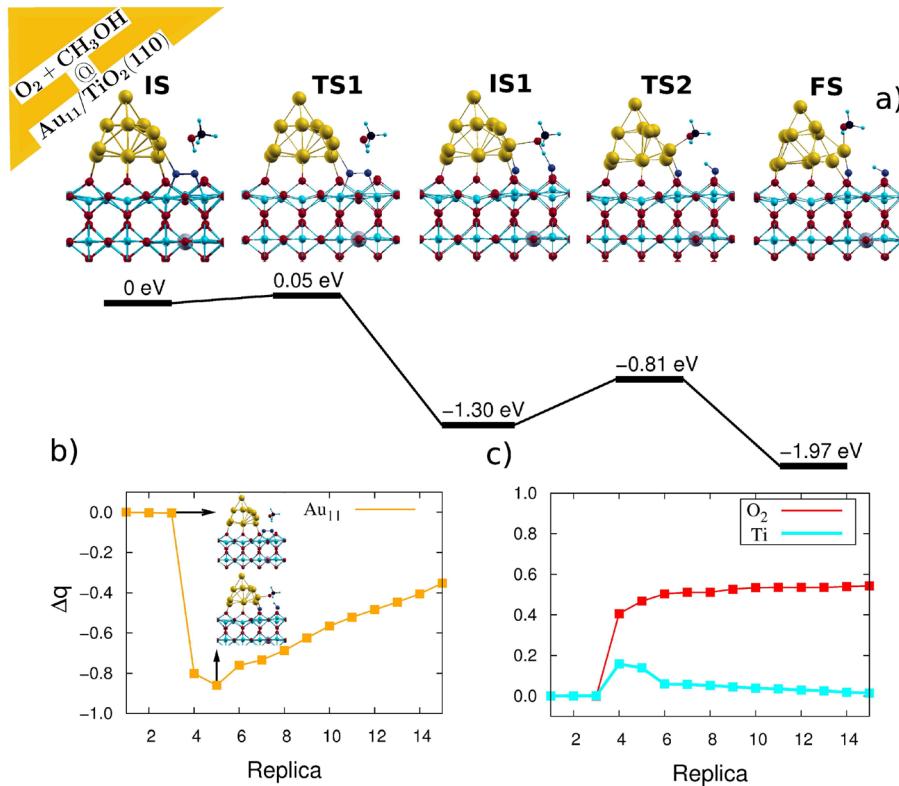


Figure 5. Reaction path and corresponding energies for CH₃OH oxidation are given in panel a. Panels b and c show the difference in the Löwdin charges, Δq , between the initial configuration (IS) and the following nudged elastic band (CI–NEB) replica images that characterize the optimized pathway to the FS configuration as schematically depicted in panel a. Panel b depicts Δq of the entire Au₁₁ cluster, whereas panel c shows Δq obtained from the sum of the charges of the two adsorbed O sites as well as that obtained from summing the contributions of the two Ti_{Sc} sites to which these O atoms are bonded. Note that the abrupt changes from replica 3 to 4 and 5 correspond to the transformation of TS1 to IS1 and thus to the breaking of the O–O bond as indicated by the configuration insets in panel b.

interaction with the neighboring Au site right at the interface (see TS1 of Figure 5a). The very interaction with CH_3OH weakens the O–O bond of the preadsorbed O_2 species, which easily dissociates to the intermediate state IS1 of Figure 5. The computed activation energy is found to be only ~ 0.05 eV, whereas the intermediate is seen to be significantly stabilized by about -1.30 eV with respect to the initial state. In the IS1 structure, the distance between the two O atoms of the dissociated O_2 molecule is 2.82 Å, whereas the Au–O and H–O distances involving the CH_3OH molecule shorten to 2.29 and 1.37 Å, respectively. The O atom at the interface approaches the Au_{11} nanocluster, its distance with the closest neighboring Au atom being 2.16 Å.

This first step is followed by the actual CH_3OH oxidation via the transfer of the H atom of the methanol OH group to the O atom of the dissociated O_2 farthest away from the Au_{11} cluster. At the same time the thus formed CH_3O species binds to the neighboring Au atom (see TS2 of Figure 5a). The activation energy of this concerted rearrangement is 0.49 eV. In this TS2 configuration, the O–H and Au– CH_3O bond lengths are 0.98 and 2.00 Å, respectively, whereas the distance between the O atom at the interface and the Au atom of the Au_{11} cluster remains at a value of 2.16 Å.

This newly formed O–Au– CH_3O complex rearranges and reaches the configuration depicted in the final state of Figure 5a, where the methoxy species tilts such that the O–Au– CH_3O complex forms a quasi-linear molecular structure. In this final configuration the Au–O and CH_3O –Au bond lengths are 2.02 and 2.06 Å, respectively. The bond length of the surface OH group formed after the H release from the CH_3OH molecules is 0.99 Å. This process is accompanied by another sizable energy decrease, the energy difference between the IS and the FS being -1.97 eV.

The change in the electronic structure of the $\text{O}_2/\text{Au}_{11}/\text{TiO}_2$ nanocatalyst along the computed reaction pathway has been studied in detail to understand why the preadsorbed and activated O_2 species easily dissociate. We have computed the difference in the Löwdin charges, Δq , between the initial configuration IS and the following replica images that characterize the computed reaction pathway which links the IS to the FS (see Figure 5b,c). Panel b shows the evolution of Δq of the Au_{11} nanocluster, whereas panel c shows Δq of the entire O_2 molecule together with the Δq parameter obtained by adding the contributions of the two surface Ti_{5c} sites to which the O atoms of the activated O_2 molecule are bound as a function of the replica images that have been obtained upon the CI–NEB optimizations. The third and fifth replica images of Figure 5b,c represent the TS1 and the IS1 configurations, respectively. Thus, the dissociation of the activated O_2 molecule via interaction with CH_3OH takes place between the third and fourth NEB replicas of the reaction pathway. It is clear from Figure 5 that this dissociation is induced by a charge transfer out of the Au_{11} cluster to the substrate and the O–O atoms, giving further evidence of the key role played by MSI effects at the Au/TiO_2 interface. Interestingly, no further reduction of the substrate and thus generation of more than one Ti^{3+} site in the support is observed.

E. Methoxy Oxidation at the Gold Nanoparticle. The following step in the proposed reaction mechanism implies finally the formation of formaldehyde, CH_2O . The computed reaction path is depicted in Figure 6, where the energy differences are, as usual, referred to the initial state. The oxidation of CH_3O takes place through the transfer of an H

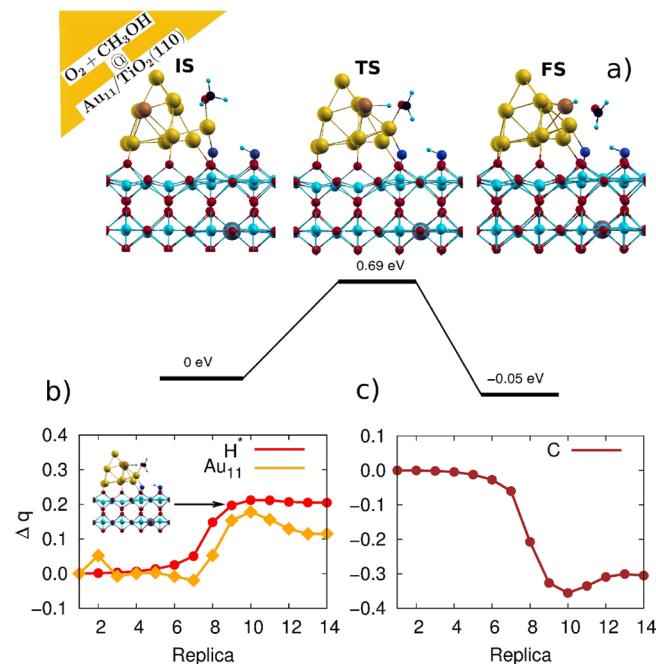


Figure 6. Reaction path and corresponding energies for CH_3O oxidation (panel a); the Au atom taking part in this reaction step by moving in the direction of the H atom transferred to it in the FS thus yielding CH_2O is depicted in orange. Panels b and c show the difference in the Löwdin charges, Δq , between the initial configuration (IS) and the following CI–NEB replica images that characterize the computed pathway to FS via TS. Panel b depicts Δq of the Au_{11} cluster together with the H atom, denoted as H^* , transferred from the CH_3O molecule to the metal adatom, whereas panel c shows Δq of the C atom of the CH_3 group.

species to a metal site of the Au_{11} cluster to which it adsorbs right upon formation. The CH_3O to CH_2O oxidation occurs in the following way: an Au atom of the supported metal cluster moves toward the quasi-linear O–Au– CH_3O complex that transfers an H atom of CH_3O to this Au site thus leading to the formation of CH_2O . The activation energy of this process is found to be 0.69 eV. In the transition state the Au– CH_2O distance elongates to 2.25 Å, whereas the Au–H bond amounts to 1.71 Å. In the final state, the distances between the formed CH_2O molecule and the Au_{11} cluster and the Au–H bond length are 2.4 and 1.6 Å, respectively. Thus, the Au_{11} supported on the TiO_2 surface behaves as a “storage device” accepting H atoms from the attached CH_3O species.

The changes in the electronic structure in terms of charge transfer are analyzed in the lower panels of Figure 6 which depict Löwdin charge changes Δq of selected atoms of the adsorbate/catalyst system. The left panel shows the evolution of Δq of the Au_{11} nanocluster as well as that of the H species transferred from CH_3O to the metal cluster, whereas the right panel depicts Δq of the C atom of the CH_3O molecule as a function of the CI–NEB replica images. As demonstrated by this analysis, the H species transfer from the methoxy group to the gold nanocluster is accompanied by a charge transfer away from the C atom of the newly formed CH_2O molecule to the Au_{11} cluster and to the H species transferred to the gold cluster. It is noted that close inspection suggests that no specific Au atom of the metal cluster dominates the change in the charge along the pathway, the additional charge being distributed among all metal atoms. Once the H species is transferred to the

metal cluster its charge transmutes from 0.8 to 1.0 lel, which formally corresponds to a neutral H atom.

F. Formaldehyde Desorption and Water Formation.

Let us now discuss the last part of our proposed catalytic cycle, which involves the desorption of CH₂O and the formation of water. The newly formed CH₂O molecule can easily desorb, the desorption energy being 0.29 eV. After that, the H atom adsorbed on the Au₁₁ cluster can migrate on the nanoparticle until it reaches the activated O atom that is located at the Au₁₁/TiO₂ interface where it becomes an OH group corresponding to hydroxyl formation on titania. The computed migration barrier amounts to approximately 1.5 eV, see Figure 7. This

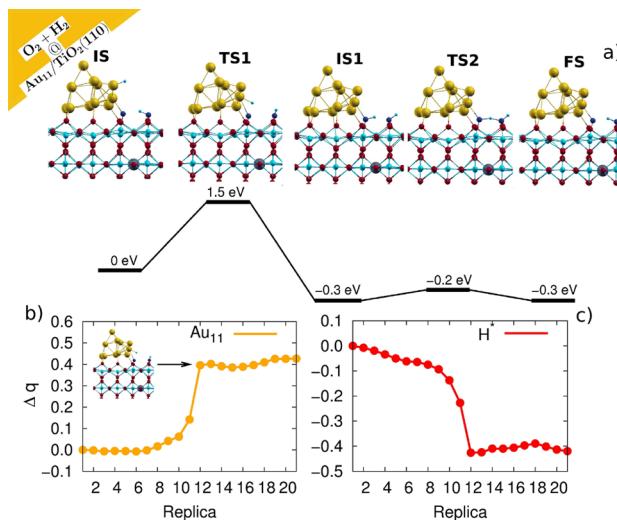


Figure 7. Reaction path and corresponding energies for H migration from the metal cluster to the activated O atom at the interface and water formation at the interface (panel a). Panels b and c show the difference in the Löwdin charges, Δq , between the starting configuration (IS) and the following CI-NEB replica images that characterize the computed pathway to FS via TS depicted in panel a. Panel b depicts Δq of the Au₁₁ cluster, whereas panel c shows Δq of the H species, denoted as H*, as it migrates to the gold/titania interface and finally to the available hydroxyl group thus forming an H₂O molecule.

seems pretty high, but it has been widely recognized that quantum effects on nuclear motion certainly play an important role in H diffusion on metal surfaces such as Cu(001), Pt(111), and Au(111).^{45–48} In particular, such quantum effects have been shown not only to significantly lower H diffusion barriers, but also to induce more efficient migration pathways even at unexpectedly high temperatures. Any quantitative investigation of such quantum effects on gold nanoclusters, however, would be a separate topic on its own right. Inspection of the projected density of states reveals that, along the path, the charge state of the migrating H species changes from close to 1.0 initially to about 0.5 lel, therefore transmuting from an H atom in the IS to a proton in the intermediate state IS1. This is clear from the lower panel of Figure 7 where the evolution of Δq of the Au₁₁ nanocluster (left panel) as well as of the H species (right panel) migrating on the metal particle is shown as a function of the NEB replica number. Clearly, during the migration process charge is transferred from the H species to the Au₁₁ nanocluster.

The proposed reaction mechanism ends with the transfer of the H species from the OH group formed by migration of the

H atom on the Au₁₁ cluster to the nearby OH group that has been formed earlier as a result of the first CH₃OH oxidation step. We have computed an activation energy of only 0.10 eV for this process. As depicted in the upper panel of Figure 7, a H₂O molecule is formed in the final configuration, FS, which is about -0.3 eV lower in energy relative to the initial state where the H species was bound to gold. This water molecule can desorb with a desorption energy of 0.90 eV, thus closing the cycle and leaving behind an activated O atom species at the interface, ready to oxidize another methanol molecule.

G. Methanol Oxidation at the Interface without Activated O₂ Species.

Let us finally investigate the oxidation of CH₃OH at the Au₁₁/TiO₂(110) interface in the absence of preadsorbed O₂ to work out its pivotal role in this heterogeneously catalyzed chemical reaction. We note in advance that also in this case the catalytic cycle does not modify the degree of reduction of the oxide support. In the absence of activated O₂, however, three Ti³⁺ ions instead of one, i.e. two from the F-center and one from the nanoparticle, are present in the titania support from the initial to the final state along the oxidation pathway that we are going to describe in what follows.

As depicted in Figure 8, for the Au₁₁/TiO₂(110) interface without activated O₂, the most stable initial configuration (IS)

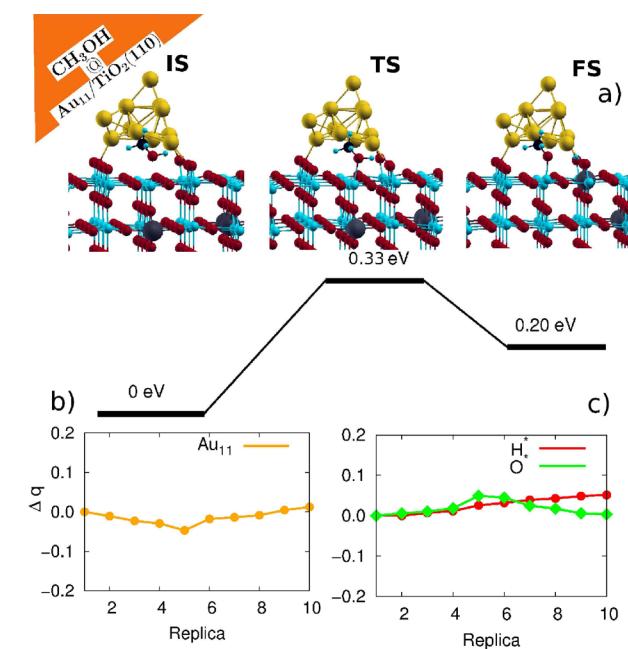


Figure 8. Reaction path and corresponding energies for CH₃OH oxidation in the absence of preadsorbed O₂ (panel a), to be compared to the mechanism obtained in the presence of activated O₂ as depicted in Figure 5. Panels b and c show the difference in the Löwdin charges, Δq , between the starting configuration (IS) and the following CI-NEB replica images that characterize the computed pathway to FS via TS depicted in panel a. Panel b depicts Δq of the Au₁₁ cluster, whereas panel c shows Δq of the O atom and H atom, denoted as H* of the OH group of the CH₃OH molecule, the H* being the one transferred from the CH₃OH molecule to a neighbor bridging O atom.

is the one where the CH₃OH molecule is adsorbed at a surface Ti_{sc} site, the binding energy being -1.13 eV. The distance between the O atom of the methanol molecule and the specific Ti_{sc} atom is 2.22 Å. Additional calculations show that similar values for the binding energy are obtained if methanol is

adsorbed on different Ti_{5c} surface sites at the interface between the Au cluster and the TiO_2 support. This suggests that no particular Ti_{5c} site close to the metal particle is preferred for methanol adsorption. Additional calculations showed that on the stoichiometric $\text{TiO}_2(110)$ surface and in the absence of gold the most stable configuration for methanol adsorption is again on Ti_{5c} surface sites. In the optimized structure the distance between the O atom and the Ti_{5c} is 2.21 Å and the methanol hydrogen (belonging to the OH group) is pointing to a nearby bridging oxygen site. The adsorption energy of the molecule at this site, however, is -0.86 eV in agreement with earlier data,⁴⁹ so that it can be concluded that methanol should preferentially adsorb at Ti_{5c} sites close to the supported gold cluster.

Figure 8 shows the computed reaction path for the first oxidation step of CH_3OH at the $\text{Au}_{11}/\text{TiO}_2(110)$ interface in the absence of O_2 to be compared to the one in Figure 5 when preadsorbed O_2 is present. The adsorbed CH_3OH molecule (see IS of Figure 8) transfers the H species (see below for analysis of its charge state) of its OH group to a bridging O atom (FS) in the neighboring oxygen row on $\text{TiO}_2(110)$. The IS and FS configurations are separated by a single TS with an activation energy of 0.33 eV. More importantly, the FS is found to be 0.20 eV higher in energy with respect to the IS indicating that on the $\text{Au}_{11}/\text{TiO}_2(110)$ interface in the absence of O_2 the CH_3OH molecule prefers the nondissociated state even at perimeter sites of the adsorbed gold nanoparticle.

This is in stark contrast to the CH_3OH oxidation mechanism at the $\text{O}_2-\text{Au}_{11}/\text{TiO}_2(110)$ interface where an O_2 molecule is activated by charge transfer and becomes catalytically active. As depicted in Figure 5 for the O-rich $\text{Au}_{11}/\text{TiO}_2(110)$ interface, the FS turns out to be much more stable with respect to the IS, actually being nearly 2 eV lower in energy after this first oxidation step to the methoxy species that is bound to the gold nanoparticle in the FS.

The lower panel of Figure 8 shows the evolution of Δq of the Au_{11} nanocluster and of the H and O species belonging to the OH group of the CH_3OH molecule a function of the replica images of the computed reaction path depicted in the upper panel. It is clear that no significant charge transfer is observed along the first oxidation step, in particular when directly contrasted to the distinct behavior unveiled by the respective analysis in Figure 5. The charge of the Au_{11} nanocluster as well as the site charges of the OH group involved in the oxidation of methanol are almost constant along the entire path, thus suggesting that the metal cluster does not take part in the reaction. Along the reaction path the H species transferred from the OH group of the CH_3OH molecule to a neighboring O bridging atom of the surface has constant charge close to about 0.5 lel. This is consistent with a protonic state both in the OH group of adsorbed methanol and after being transformed into a hydroxyl group on titania, thus leaving behind a methoxy species.

We have then explored possible routes for the interaction between methoxy, CH_3O , if formed as a result of CH_3OH dissociation on the $\text{Au}_{11}/\text{TiO}_2(110)$ interface in the absence of O_2 , and the supported gold nanoparticle. Interestingly, our calculations suggest that CH_3O does not interact with the neighboring $\widetilde{\text{Au}}$ site right at the interface, depicted as an orange sphere in Figure 9a in the presence of preadsorbed O_2 (which is the FS configuration of Figure 5). Once the CH_3O molecule is placed in proximity of this neighboring site, $\widetilde{\text{Au}}$, as in panel a

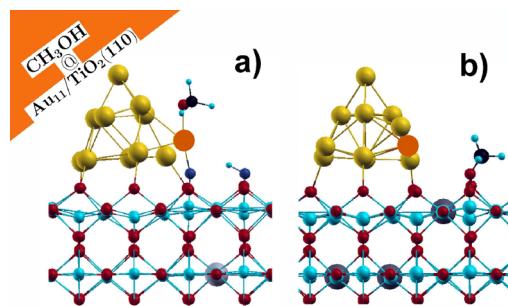


Figure 9. Structures of CH_3O adsorbed on the reduced TiO_2 surface where the activated O_2 species is present in panel a but absent in panel b. The Au atom depicted as an orange sphere is denoted by $\widetilde{\text{Au}}$ in the text.

but in the absence of O_2 , the molecule approaches the $\text{TiO}_2(110)$ surface by detaching from the supported gold cluster upon structural relaxation. This process leads to the very same configuration as the previously found FS configuration as depicted in Figure 8. We thus conclude from these calculations that the gold nanoparticle is essentially not involved in these processes, in contrast to its significant involvement when preadsorbed O_2 is present at the perimeter.

To gain deeper insight into why in the absence of O_2 at the $\text{Au}_{11}/\text{TiO}_2(110)$ interface the $\widetilde{\text{Au}}$ site prevents the formation of the $\text{CH}_3\text{O}-\text{Au}$ complex, which represents a key step in the CH_3OH oxidation on the O-rich $\text{Au}_{11}/\text{TiO}_2(110)$ surface, we have examined the difference in the electronic structures obtained for the configurations depicted in Figure 9, panels b and a, respectively. Close inspection of the computed Löwdin charges revealed that when O_2 is present at the interface, the O_2 molecule is activated by charge transfer from the Au/TiO_2 substrate, *vide supra*, and the particular Au atom bonded to the O_2 molecule results in a slightly positive charge, $\text{Au}^{\delta+}$. On the other hand, in the absence of the O_2 molecule, the very same Au site turns out to be negatively charged, $\text{Au}^{\delta-}$. The difference in the Löwdin charges between the negatively and positively charged gold atom is as large as about $\Delta q \approx 0.4$ lel.

We firmly conclude from these reference calculations that the high catalytic activity and selectivity of the $\text{Au}_{11}/\text{TiO}_2(110)$ nanocatalyst with preadsorbed O_2 originates from the presence of active interfacial sites, where the activation of O_2 occurs through charge transfer from $\text{Au}_{11}/\text{TiO}_2(110)$ forming highly active $\text{O}_2^{\delta-}-\text{Au}^{\delta+}$ complex species.

Finally, we address the question if the methoxy species, once formed in the absence of O_2 , could migrate to a more favorable position on the gold cluster that allows for further oxidation. Figure 10 shows the computed path for migration of the CH_3O species away from the gold/titania interface until it reaches a Au site on top of the gold particle that allows for the formation of a bound $\text{CH}_3\text{O}-\text{Au}$ species. The computed path starts with the methoxy species, which is attached on a surface Ti_{5c} site right at the $\text{Au}_{11}/\text{TiO}_2(110)$ interface but not bound to any gold atom, see the IS configuration of Figure 10 being identical to the FS of Figure 8. The CH_3O molecule indeed detaches from the surface and migrates on the metal cluster until it forms a stable complex with two top Au atoms; the activation energy of this process is 2.65 eV. In the FS, the distances between the two specific Au sites of the Au_{11} cluster and the O atom of the CH_3O molecule are 2.17 and 2.22 Å. However, as depicted in the lower panel of Figure 10, again no significant change is observed on the Δq of the Au_{11} cluster, in stark contrast to the

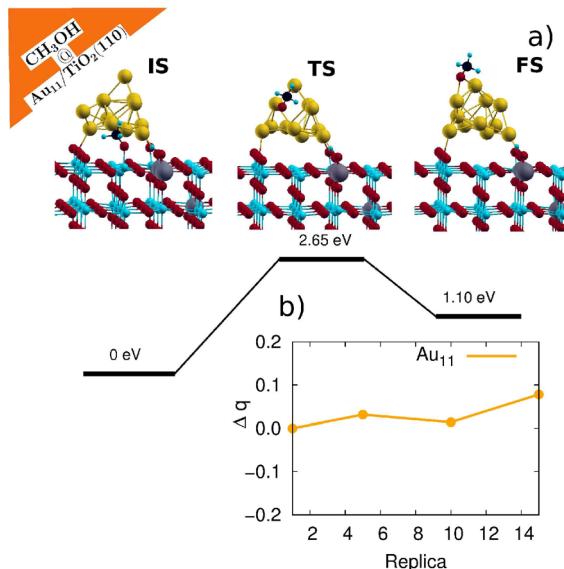


Figure 10. Migration path and corresponding energies for CH_3O on $\text{Au}_{11}/\text{TiO}_2(110)$ in the absence of preadsorbed O_2 are given in panel a. Panel b shows the difference in the Löwdin charges, Δq , between the starting configuration (IS) and the following CI-NEB replica images of the Au_{11} nanocluster that characterize the computed pathway to FS via TS depicted in panel a.

case in which activated O_2 is present at the interface. In view of the huge activation energy of this process in conjunction with a much higher energy of the on-top state versus the on-surface state of methoxy, it does not make sense to proceed with the next step of the catalytic cycle, namely the CH_3O oxidation to yield formaldehyde.

We summarize that, according to these calculations, a gold nanocluster supported on titania is not a good catalyst for partial oxidation of methanol to formaldehyde in the absence of preadsorbed dioxygen at the metal/oxide interface, which gets activated to a peroxidic form. This conclusion based on mechanistic analyses based on electronic structure is in full agreement with experimental data where the effect of O_2 preadsorption and methanol coadsorption has been explicitly probed.²⁹

IV. CONCLUSIONS AND OUTLOOK

In summary, we have shown that the selectivity and high catalytic activity of Au/TiO_2 nanocatalysts toward the oxidation of methanol originate from the presence of active sites at the interface between the gold nanoparticle and the reduced titania surface. Our calculations suggest that the activation of molecular oxygen at the interface occurs via charge transfer from the Au/TiO_2 system, which is subject to significant “Metal–Support Interaction” effects. This leads to the formation of chemically active $\text{O}^{\delta-}$ peroxide species close to the gold/titania interface. This O_2 preadsorption and activation step is followed by the formation of an intermediate $\text{CH}_3\text{OH}-\text{O}_2$ complex. The newly formed intermediate undergoes oxidative dehydrogenation, which yields formaldehyde and water. The key step in the proposed catalytic cycle is the activation of molecular O_2 at the interface that opens a low-lying and thus low-temperature reaction channel for the oxidation of methanol to formaldehyde and water. Reference calculations without preadsorbed O_2 being present clearly demonstrate that the very first oxidation step, leading from

methanol to methoxy, is actually an unfavorable one in that case and, furthermore, that it cannot be achieved by Au/TiO_2 alone. Comparison of this scenario to the one obtained by involving preadsorbed and activated O_2 at the level of the underlying electronic structure furthermore demonstrates the key role of positively charged Au sites in the immediate vicinity of the peroxide species, which stabilizes highly active $\text{O}_2^{\delta-}-\text{Au}^{\delta+}$ complex species.

It thus appears that oxidation of alcohols at O_2 -activated gold/titania nanocatalyst models in contact with the gas phase is fairly well understood by now in terms of molecular mechanism and electronic structure changes. In contrast, when it comes to the selective oxidation of alcohols in the realm of liquid-phase heterogeneous catalysis, no such detailed picture is yet available. Most interesting in the context of the unveiled crucial charge transfer processes, positively charged gold sites, and dioxygen activation involving them are previous observations^{43,44} that report on significant solvent-induced charge rearrangements at such supported metal nanoparticles due to the presence of bulk water. In particular, water has been shown to stabilize $\text{Au}^{\delta+}$ charge states different from those found in the gas phase as a result of structure-specific charge transfer from/to the solvent, thus altering the surface reactivity of Au/TiO_2 systems due to solvation. It will be highly interesting to compare in future investigations the present gas-phase mechanism for alcohol oxidation to what happens at such fully solvated Au/TiO_2 nanocatalysts, i.e. at water/gold/titania interfaces.

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