First-Principles Study of Alkoxides Adsorbed on Au(111) and Au(110) Surfaces: Assessing the Roles of Noncovalent Interactions and Molecular Structures in Catalysis

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ABSTRACT: Microscopic understanding of molecular adsorption on catalytic surfaces is crucial for controlling the activity and selectivity of chemical reactions. However, for complex molecules, the adsorption process is very system-specific and there is a clear need to elaborate systematic understanding of important factors that determine catalytic functionality. Here, we investigate the binding of eight molecules, including seven alkoxides and one carboxylate, on the Au(111) and Au(110) surfaces. Our density-functional theory calculations including long-range van der Waals interactions demonstrate the significant role of these "weak" noncovalent forces on the adsorption structures, energetics, and relative adsorbate stabilities. Interestingly, the binding energy trends are insensitive to the surface structure. Instead, the adsorption stability depends strongly on the structural and chemical characteristics of the molecules: linear vs branching configurations, number of unsaturated C−C bonds, bidentate adsorption, and the presence of electronegative atoms. Our calculations help establish the influence of individual and collective chemical factors that determine the catalytic selectivity of alkoxides.
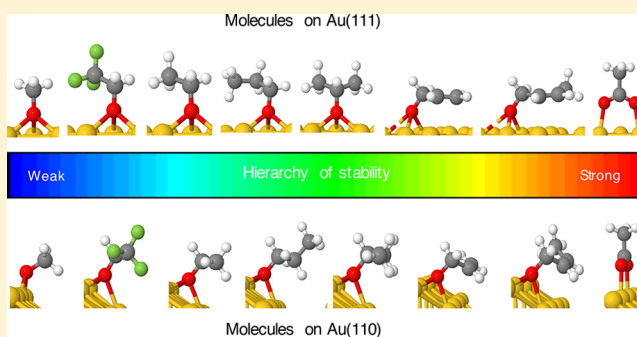
I. INTRODUCTION

One of the key contemporary challenges in heterogeneous catalysis is to understand the adsorption and desorption mechanisms of complex molecules on catalytic surfaces, which ultimately determine the activity and selectivity of chemical reactions. First-principles calculations in the framework of density-functional theory (DFT) have been extensively used to investigate the surface adsorption of molecules. The analyses of these calculations have led to important advances in the understanding of catalytic reactions, as evidenced, for example, by powerful models for reactivity of small molecules on surfaces and scaling relations for stability and reactivity.[1−4] During the past decades, remarkable progress has been made in the fundamental understanding of the adsorption behavior of atoms and small molecules on metal substrates.[5−7] However, catalytic reactions of larger molecules remain poorly understood, since many additional factors could contribute to their adsorption behavior, compared to the case of atoms and small molecules.

For example, when studying catalytic reactions of large molecules, long-range van der Waals (vdW) interactions can become the dominant effect that determines the relative stability of reaction intermediates.[8−10] Reliable modeling of complex molecule/metal interfaces became possible only recently due to advances in the development of vdW-inclusive methods that incorporate the strong screening effects within inorganic substrates.[10−13] This has led to a general recognition of the importance of vdW interactions for a variety of systems.[14,15] In particular, our recent studies of alkoxide adsorption on Au and Cu surfaces, using a combination of experiment and theory, have demonstrated the critical role of vdW interactions, even for molecules that form covalent bonds with the surface.[8,9,16] Compared to previous work, the aim of this paper is to present a more extensive analysis on the structural and energetic properties of seven alkoxides and one carboxylate on Au(111) and Au(110) surfaces, as obtained from first-principles calculations, with and without the inclusion of screened vdW interactions.

Detailed knowledge about the hierarchy of relative stabilities of adsorbed molecules may be quite useful for achieving desired product selectivity in certain catalytic reactions. Therefore, it is important to understand the determining factors that dictate

binding between different molecules on a variety of surfaces. This information can be subsequently utilized to tailor the adsorption and relative concentration of molecules, and to predict molecular adsorption behavior on substrates with different surface structures. A widely used method to predict the binding strength hierarchy is to use the molecular gas-phase acidity, where the stability of the intermediate on a surface exhibits correspondence with the gas-phase acidity of the respective parent molecule. The relative stability of a range of alkoxides on Au(111),[8,9] with respect to the oxygen-assisted displacement reaction, was shown to roughly follow their trend in gas-phase acidities. However, there are several molecules showing exception to this trend, including fluorinated species and molecules containing phenyl rings. This highlights the need for an examination of the structural and energetic properties in the adsorption systems beyond the gas-phase acidity model, which ignores the interaction between molecules and substrates.

Our previous studies provide evidence that the vdW interaction is a critical factor to consider for the correct description of complex catalytic systems. For example, the surface stability hierarchy determines the competition of reactants for binding at the available adsorption sites on the surface, thereby providing information for understanding how to control selectivity in complex catalytic reactions, which generally can only be accurately predicted by vdW-inclusive calculations.[8,9] Building on our previous work, here we present a comprehensive study of eight molecules adsorbed on Au(111) and Au(110) surfaces, using DFT calculations with screened vdW interactions. First, the effects of vdW interactions on the structure and energetics of each adsorbate-surface system are investigated, demonstrating that the magnitude of stabilizing vdW interactions is highly specific to the molecular structure. The different molecular features, such as branched alkyl chains, number of unsaturated C−C bonds, bidentate adsorption, and the presence of electronegative atoms, all strongly affect the surface binding strength of the molecules to the surface. Second, a close comparison between the two surface facets is performed, which demonstrates the lack of sensitivity of the relative binding hierarchy of adsorbates to the surface facet, even though the absolute binding energy is sensitive to the surface structure. The work described here provides detailed insights into the factors that control the binding strength of molecules on Au surfaces, which could also facilitate the prediction of the catalytic activity and selectivity of reaction intermediates on other metallic surfaces and on nanoporous catalysts.

II. METHOD

Accurate prediction of the surface binding energy is a fundamental prerequisite for characterizing the molecular adsorption on catalytic surfaces. In past years, several methods emerged to include the key contribution of vdW interactions in the DFT framework.[11,17−19] While some pairwise methods (vdW-DF, DFT-D3, exchange-hole dipole moment, Tkatchenko−Scheffler) capture the local polarization effects partially and can be successful for relatively symmetric systems, the true nature of dielectric screening in systems with arbitrary geometries can only be captured by going beyond the pairwise-additive approximation.[12] Recently the Tkatchenko−Scheffler vdW^{surf} method[12] has been developed, resulting in quantitative improvements in the predictive capabilities of vdW-inclusive DFT calculations to describe molecular

adsorption on surfaces.[20−23] It combines the DFT+vdW^{TS} method[11] for intermolecular interactions with the Lifshitz−Zaremba−Kohn (LZK) theory[24,25] for describing the collective substrate response in the vdW energy. This method leads to a good agreement in the adsorption distances and interaction energies compared to available experimental data for a wide range of systems including atoms, small and large molecules, and nanostructures adsorbed on different metallic surfaces.[12,26−28] However, the many-body vdW effects beyond dielectric screening are not included in the vdW^{surf} method; instead, a more advanced many-body approach is generally more efficient to capture these many-body effects, which can be pronounced in extended heterogeneous systems.[29] For a detailed classification of vdW-inclusive methods according to the treatment of microscopic polarizability and interaction potential, and discussions on the reliable description of vdW interactions in different materials, we refer the reader to ref 30.

In this work, we employ the DFT+vdW^{surf} method,[12] which is accurate and efficient for modeling molecular adsorption on metal surfaces. We use two different DFT codes: FHI-aims[31] and VASP,[32] to calculate various adsorbates on the Au(111) and Au(110) surfaces, respectively. The two codes were shown to agree very well in a recent benchmark study.[33] In addition, our benchmark calculations of methoxy adsorbed on Au(111)[8] show that the two codes agree quantitatively in the computed binding energies and optimized geometries (see detailed comparison in section III). Such good agreement demonstrates that the two codes (VASP and FHI-aims) can be used interchangeably for studying adsorption of molecules on surfaces, provided that converged settings are employed in both codes.

Calculation Details for Au(111) Surface. We used the all-electron/full-potential electronic-structure code FHI-aims.[32] The PBE[34] exchange-correlation (XC) functional and tight settings are used for the calculations. Convergence criteria include 10^{-5} electrons for the electron density, 10^{-6} eV for the total energy, and 0.01 eV/Å for the maximum final force in geometry relaxations. Relativistic effects were included via the atomic scalar zeroth-order regular approximation.[35] The system consisted of a single molecule adsorbed on the Au(111) surface modeled with six metallic layers. The surface slab was modeled with a 5 × 5 supercell and a vacuum of enough thickness (40 Å), to make the interactions between periodic images negligible. We used a Monkhorst−Pack grid of 3 × 3 × 1 k-points. During structural relaxation, the molecule and the Au atoms in the topmost two layers were allowed to relax.

Calculation Details for Au(110) Surface. We used the plane-wave code VASP,[32] with projector-augmented wave (PAW) potentials.[36] We used PBE[34] for the XC functional and 400 eV for the energy cutoff of the plane-wave basis sets. The missing-row reconstructed Au(110)-(1×2) surface containing five atomic layers was employed, with a vacuum region of more than 12 Å along the z-direction. The bottom two layers of Au were fixed in their bulk positions, and all the other atoms in the slab were relaxed to obtain the ground-state structure. We used a 4 × 5 × 1 k-point mesh[37] for the 2 × 4 supercell of the Au(110)-(1×2) surface.

The vdW effects on adsorption geometries and binding energies were investigated for a series of adsorbates, including methoxy, ethoxy, 1-propoxy, 2-propoxy, allyloxy, methallyloxy, acetate, and trifluoroethoxy, bound to the Au(111) and Au(110) surfaces. The relative stability between two

intermediates X_{ads} and X'_{ads} on the surface is experimentally established by displacement reactions[38]

$$X_{ads} + X'H_{gas} \rightarrow XH_{gas} + X'_{ads} \tag{1}$$
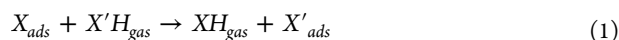
Here, we calculate the adsorption energy (E_{ads}) of each adsorbate X_{ads} with respect to the oxidation reaction of alcohol (XH_{gas})

$$2XH_{gas} + O_{ads} \rightarrow 2X_{ads} + H_2O_{gas} \tag{2}$$
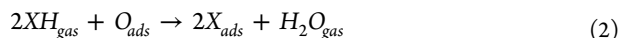
so that

$$E_{ads} = 1/2[E(H_2O_{gas}) + 2E(X_{ads}) - E(O_{ads}) - E(Au) - 2E(XH_{gas})] \tag{3}$$

The adsorption of each intermediate was calculated with and without vdW interactions. The negative values of E_{ads} indicate attractive adsorbate−surface interactions.

III. BENCHMARK OF ELECTRONIC STRUCTURE CODES (FHI-AIMS AND VASP)

The binding energy differences between competing reaction intermediates are generally rather small, on the order of tens of meV.[8,9] Therefore, it is imperative to obtain tightly converged adsorption energies. Using different DFT codes could sometimes result in energy differences of up to 0.1−0.2 eV.[33] Here, we demonstrate a more detailed comparison of the two different codes initially studied in ref 8, to assess the reproducibility of electronic structure calculations for the adsorption energies of complex molecule/surface systems.[33] Namely, we use an all-electron FHI-aims code and a plane-wave pseudopotential VASP code, both yielding an excellent agreement (6 meV for the PBE+vdW^{surf} method) in the adsorption energy of methoxy on Au(111), providing evidence for the tight convergence of our calculations; see Table 1.

Table 1. Adsorption Energies of Methoxy on Au(111) Computed with and without vdW Corrections Using FHI-aims and VASP

code	PBE (eV)	PBE+vdW^{surf} (eV)
FHI-aims	−0.133	−0.277
VASP	−0.136	−0.283

By comparing the results from the two codes, we find that the optimized geometries are also in excellent agreement (Table 2). Methoxy is found to be adsorbed on the *fcc* site of the Au(111) surface (Figure 1). The vertical distances from the

Table 2. Structural Parameters of Methoxy Adsorbed on Au(111) Surface (Figure 1), Calculated by the PBE+vdW^{surf} Method

optimized geometry details		FHI-aims	VASP
vertical distances	O−Au	1.30 Å	1.30 Å
	C−Au	2.73 Å	2.73 Å
	C−O	1.43 Å	1.43 Å
nearest Au atom distances	O−Au$_1$	2.31 Å	2.31 Å
	O−Au$_2$	2.30 Å	2.30 Å
	O−Au$_3$	2.30 Å	2.30 Å
nearest Au atom angles	∠C−O−Au$_1$	125.7°	125.5°
	∠C−O−Au$_2$	124.9°	124.8°
	∠C−O−Au$_3$	124.9°	124.8°
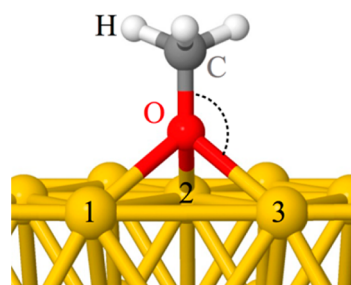
Figure 1. Optimized geometry of methoxy adsorbed on Au(111) surface, calculated using the PBE+vdW^{surf} method. The nearest Au atoms (1, 2, and 3 of the *fcc* site) to the adsorbed O atoms and C−O−Au$_3$ angle are marked.

Au surface (O−Au and C−Au) and the distance between the adsorbed oxygen atom and the Au atoms on the *fcc* site (O−Au$_1$, O−Au$_2$, and O−Au$_3$) are very similar from both codes. All angles agree to 0.2°. In agreement with previous studies,[33] our benchmark calculation of methoxy adsorbed on Au(111) confirms the reproducibility of optimized geometries and binding energies between an all-electron and a pseudopotential code.

Furthermore, we compare our calculations of binding energies with calorimetry measurements. Although we do not have such measurements on Au to compare with, we perform calculations of methoxy and formate adsorption on Pt(111), with the VASP code using the same method as described above. The binding energies are found to be 1.84 and 2.63 eV, respectively, in good agreement with the calorimetry measurements (1.928 ± 0.114 eV and 2.633 ± 0.135 eV, respectively) conducted by Campbell et al.[39,40]

IV. COVERAGE EFFECTS

The coverage dependence of adsorption structures and energies may profoundly affect the catalytic reactivity on a surface. A weakly bound adsorbate may be more reactive by changing the reaction conditions, such as temperature and/or pressures. However, electronic structure calculations typically rely on a supercell representation of the real system, which could be too large to be treated explicitly at the full atomistic level, and is approximated using a periodic system built up from a relatively small unit cell. Hence, the convergence of the results and the coverage effects should be analyzed to avoid unphysical results.

The coverage effects on the binding energies were investigated for 2-propoxy adsorbed on the Au(111) surface with different slab sizes. The system consisted of a single molecule adsorbed on the Au(111) surface with three metallic layers. The surface slabs were modeled with 3 × 3, 4 × 4, 5 × 5, 6 × 6, and 7 × 7 supercells, using the PBE+vdW^{surf} optimized lattice parameter of 4.163 Å.[41] During structural relaxation, the molecule and the Au atoms in the topmost two layers were allowed to relax. Calculations were performed with commensurate scaling of *k*-point density for different supercells (see Table 3; a maximum spacing of 0.07 Å^{-1} was used for the Monkhorst−Pack grid). The dense *k*-point meshes allow the adsorption energies to be converged to within 8 meV/system.

The binding energies for 2-propoxy adsorbed on different surface slabs as a function of surface coverage is presented in Table 3. For the smallest supercell (3 × 3 Au slab), the binding energy is weaker due to lateral interactions between the adsorbates. For the other slabs, the binding energies are well converged and the coverage effects become insignificant.

Table 3. Coverage Effects: Adsorption Energies of 2-Propoxy Adsorbed on Au(111) Slabs of Different Sizes

| supercell size	k-point sampling	binding energies of 2-propoxy on Au(111) in eV	
		PBE	PBE+vdW^{surf}
3 × 3	10 × 10 × 1	0.04	−0.48
4 × 4	8 × 8 × 1	−0.06	−0.56
5 × 5	6 × 6 × 1	−0.05	−0.53
6 × 6	5 × 5 × 1	−0.08	−0.55
7 × 7	5 × 5 × 1	−0.09	−0.56

V. RESULTS AND DISCUSSION

The present work is motivated by previous studies that illustrate the effect of competitive binding in catalytic reactions, which is correctly predicted only when using vdW-inclusive DFT calculations.[8,9] While the effect of vdW interactions is clearly established for predicting the binding strength of various intermediates on Au surfaces, key questions to be answered include to what extent the noncovalent interactions affect the stable geometries and relative surface stabilities of intermediates, and which structural factors determine the binding strength. Therefore, here we examine the optimized structures and binding energies for seven alkoxides and one carboxylate bound to Au surfaces with and without vdW interactions included. Some of the key factors affecting the stability of intermediates are addressed on Au(111) and Au(110) surfaces, including the effects of branching of the alkyl chain, unsaturated C=C bond, bidentate adsorption, and substitution of an electronegative atom.

Here, we assume a very low coverage or isolated molecule limit for the molecular adsorption. Finite molecular coverage of the surface and the ensuing intermolecular interactions can have a significant role on the surface structure and stability. For example, finite coverage can drive surface reconstruction for acetate adsorption on the Au(110) surface.[15]

Before proceeding to analyze the results of our calculations, we first comment on previous experimental studies that firmly established the stability hierarchy for seven alkoxides studied in this work adsorbed on Au catalysts.

i. Previous Experimental Studies on Hierarchy for Surface-Stability of Intermediates. A key factor determining the catalytic reaction is competition for reactive sites among reactants and reaction intermediates on the surface.[8,9] To
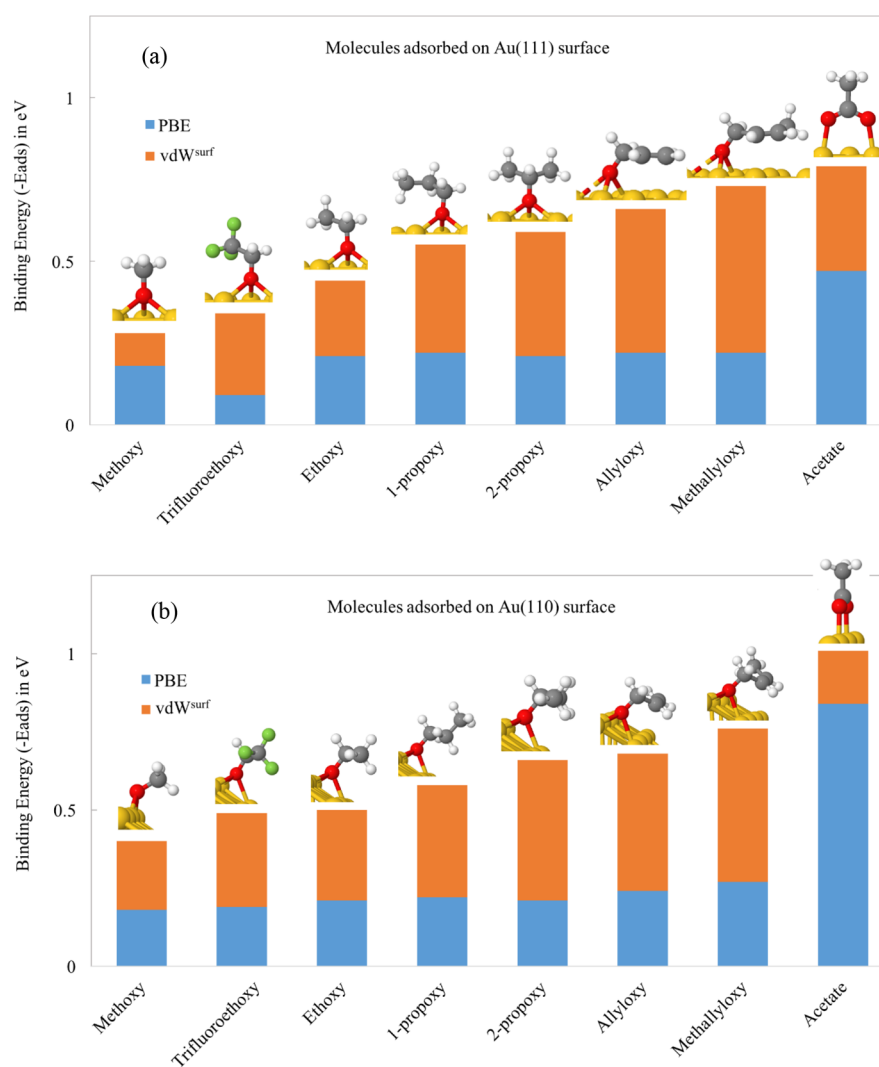
Figure 2. Hierarchy of stability of eight adsorbates (a) on Au(111) surface and (b) on Au(110) surface. The binding energies are obtained from PBE (in blue) and PBE+vdW^{surf} (binding enhancement due to vdW in orange) methods.

Table 4. Optimized Structural Details of Adsorbates on Au(111) Surface Studied Using PBE+vdW^{surf} and PBE Methods[a]

adsorbates	method	reaction energies (eV)	vertical distances (Å)				angle C$_1$OAu
			O−Au	C$_1$−Au	C$_2$−Au	C$_3$−Au	
1-propoxy	PBE+vdW^{surf}	−0.55	1.33	2.76	3.40	3.38	130.0
	PBE	−0.22	1.26	2.70	3.42	3.48	127.5
2-propoxy	PBE+vdW^{surf}	−0.59	1.28	2.72	3.18	3.20	125.5
	PBE	−0.21	1.25	2.70	3.20	3.33	123.0
allyloxy	PBE+vdW^{surf}	−0.66	1.62	2.77	2.63	2.51	121.5
	PBE	−0.22	1.23	2.67	3.11	3.68	120.3
methallyloxy	PBE+vdW^{surf}	−0.73	1.62	2.78	2.67	2.72	121.6
	PBE	−0.22	1.23	2.67	3.11	3.63	119.5
methoxy	PBE+vdW^{surf}	−0.28	1.33	2.76			124.9
	PBE	−0.18	1.23	2.66			121.6
acetate	PBE+vdW^{surf}	−0.79	2.22	2.77	4.29		124.7
	PBE	−0.47	2.24	2.80	4.32		125.1
ethoxy	PBE+vdW^{surf}	−0.44	1.30	2.73	3.20		123.2
	PBE	−0.21	1.23	2.67	3.26		122.2
trifluoroethoxy	PBE+vdW^{surf}	−0.34	1.37	2.78	3.42		126.9
	PBE	−0.09	1.33	2.73	3.51		124.1

[a]The vertical distances are measured with respect to the top Au plane.

Table 5. Optimized Structural Details of Adsorbates on Au(110)-(1×2) Surface Studied Using PBE+vdW^{surf} and PBE Methods[a]

adsorbates	method	reaction energies (eV)	vertical distances (Å)				angle C$_1$OAu
			O−Au	C$_1$−Au	C$_2$−Au	C$_3$−Au	
1-propoxy	PBE+vdW^{surf}	−0.58	0.73	1.82	1.64	2.79	132.7
	PBE	−0.22	0.76	2.01	2.18	3.51	123.5
2-propoxy	PBE+vdW^{surf}	−0.66	0.71	1.83	1.78	1.79	129.6
	PBE	−0.21	0.81	2.11	2.26	2.28	124.5
allyloxy	PBE+vdW^{surf}	−0.68	0.74	1.80	1.27	1.44	140.4
	PBE	−0.24	0.74	1.96	1.85	2.58	127.5
methallyloxy	PBE+vdW^{surf}	−0.76	0.74	1.78	1.25	1.48	140.5
	PBE	−0.27	0.73	1.93	1.76	2.31	128.4
methoxy	PBE+vdW^{surf}	−0.40	1.57	2.31			118.4
	PBE	−0.18	1.52	2.44			119.6
acetate	PBE+vdW^{surf}	−1.01	2.17	2.74	4.25		124.4
	PBE	−0.84	2.18	2.74	4.25		124.6
ethoxy	PBE+vdW^{surf}	−0.50	0.73	1.87	1.77		131.1
	PBE	−0.21	0.78	2.05	2.26		123.5
trifluoroethoxy	PBE+vdW^{surf}	−0.49	0.87	2.09	2.28		127.3
	PBE	−0.19	0.88	2.14	2.43		123.1

[a]The vertical distances are measured with respect to the Au atoms on the top row of the slab.

achieve high selectivity for heterogeneous catalytic reactions, the relative concentrations of the reactive intermediates on the surface must be optimized. When species compete for available binding sites, the relative surface binding strengths determine their concentrations on the surface. This competition for active sites can be dramatically affected by small differences between the binding energies (few tens of meV) of the competing intermediates to the surface. The selectivity of oxygen-assisted cross-coupling reaction of intermediates was previously studied for a range of alkoxides. The experimental measurements were done at an initial low coverage of O of 0.05 ML. These coverages are well controlled by calibrated doses of ozone. More details of the experiments can be found in ref 8. The qualitative hierarchy of binding on Au surfaces determined experimentally demonstrates the stability of intermediates: methoxy < trifluoroethoxy < ethoxy < 1-propoxy < 2-propoxy < allyloxy < methallyloxy. The same trend was observed experimentally on both Au(111) and Au(110) surfaces. It was also shown that a theoretical framework is necessary for predicting the factors controlling the relative stability and thus selectivity of intermediates involved in oxygen-assisted reactions on metallic gold, which has broad relevance in heterogeneous catalysis.

ii. The Role of vdW Interactions on the Calculated Stability Hierarchy. The relative binding energies for various molecules on Au surfaces show that inclusion of vdW interactions is necessary to predict the trends in relative surface binding for alkoxides and carboxylate with different molecular structures. We found that, without inclusion of vdW interactions, the calculated binding energies are essentially the same for all the adsorbates studied on both Au(111) and Au(110) surfaces (see PBE adsorption energy in Figure 2a,b). Moreover, the surface stabilities calculated using the standard PBE functional are inconsistent with experimental observations. For example, the binding energies of 1-propoxy and 2-propoxy computed with PBE are quite close; however, the experimental data show that 2-propoxy displaces 1-propoxy on Au surfaces. Once the noncovalent vdW forces are included, 2-propoxy is

found to be more stable than 1-propoxy on both (111) and (110) surfaces of Au, in accordance with the experimental measurements.[8]

In general, for the eight studied molecules, the relative binding strength calculated with DFT+vdW^{surf} is in excellent agreement with the qualitative hierarchy obtained from experiment:[8,9] methoxy < trifluoroethoxy < ethoxy < 1-propoxy < 2-propoxy < allyloxy < methallyloxy < acetate (Figure 2). The exposed surface facet is usually another important factor to consider in controlling the binding strength of molecules on surfaces. By close comparison between the binding energies of adsorbates on (111) and (110) surfaces of Au, we found that the relative binding strength of intermediates is insensitive to the surface facet (see the hierarchy in Figure 2a,b). For example, the binding energies of methoxy on Au(111) and Au(110) surfaces are essentially the same (−0.18 eV) when the PBE functional is used, even if the molecule is adsorbed at a different site on a surface and has a different overall adsorption structure (Tables 4 and 5). After including vdW interactions, the total binding energies change to −0.28 and −0.40 eV on Au(111) and Au(110) surfaces, respectively. Even though now the absolute binding energies are not the same, the binding energy hierarchy on both surfaces is equal and in agreement with experimental observations.

The different structures and chemistry of the molecules strongly affect their stability on Au surfaces. We analyzed and compared the geometries and binding energies of each adsorbate-surface system on Au(111) and Au(110) surfaces in order to determine the structural factors, which contribute to the stability of adsorbates in chemical reactions. We observed that, irrespective of the surface structure, there are several common factors that stabilize adsorbed molecules, due to a significant vdW interaction between the adsorbate and the substrate: (i) presence of branched chain configurations of the alkyl group, (ii) C=C unsaturated bonds, and (iii) bidentate adsorption. However, because of their repulsive interaction with the metal substrate, the presence of electronegative atoms decreases the stability of fluorine-containing molecules on both Au surfaces. Quantitatively, the presence of a C=C bond or a CH$_3$ group adds an extra stability of 0.1 ± 0.01 eV per C=C bond and 0.1 ± 0.06 eV per CH$_3$ group to the binding energy.

The dependence of vdW interactions on linear and branched chain configurations can be observed by comparing 1-propoxy with 2-propoxy. The binding energies show that the adsorbates with branched chain configurations are more stable than the linear chains by 0.04 and 0.08 eV on Au(111) and Au(110) surfaces, respectively (see Tables 4 and 5). In PBE calculations, adsorbates with linear chains are slightly more stable than those with branched configurations; however, the stronger vdW interactions significantly stabilize branched configurations on both surfaces. The presence of unsaturated C=C bonds adds extra stability to the adsorption of allyloxy and methallyloxy.[42] Allyloxy contains the same number of C atoms as 1-propoxy in the carbon skeleton; however, allyloxy is more stable by 0.11 and 0.10 eV than 1-propoxy on (111) and (110) surfaces, respectively. The extra stability of allyloxy and methallyloxy resulting from the vdW contributions (66.7% and 70.5% of the total binding energies, respectively) can be correlated with their molecular structures containing conjugated C=C bonds. As mentioned above, the addition of a C=C bond stabilizes allyloxy and methallyloxy by ∼0.1 eV; in addition, an extra methyl group in methallyloxy yields 0.07 eV stabilization relative to allyloxy.

The effect of bidentate adsorption on surface stability is studied for acetate by comparing it with methoxy. It was predicted that the vdW interactions between the surface and the alkyl group affect the surface stability of the carboxylates, making them more stable on the surface than similar alkoxides.[9] Our study reveals that acetate is more stable than all the alkoxides we considered (Figure 2), which indicates that the carboxylate−Au interactions are stronger than alkoxide−Au interactions. However, in this case, the extra stability of acetate comes from the PBE functional, contrary to all the other systems we have considered here. This stems from the bidentate adsorption, whereby two oxygen−Au bonds are established with the metal surface, instead of a single bond as in the case of monodentate adsorption.

Finally, the substitution of a hydrogen atom by an electronegative atom, such as fluorine, leads to a noticeable change in the energetics and stability of the adsorbates, due to the repulsion between the electron-rich CF$_3$ group and the Au surface. Trifluoroethoxy is bound more weakly to Au(111) than ethoxy by 0.1 eV at the PBE level, and slightly stronger polarizability of fluorine is unable to compensate for the increased repulsion. However, on the Au(110) surface, the surface binding strength is observed to be insensitive to the presence of an electronegative atom; ethoxy and its fluorine substituted derivative, trifluoroethoxy, have essentially the same PBE and vdW energies. We attribute this difference between Au(111) and Au(110) to the larger distance between the CF$_3$ group and the surface in the latter case.

iii. The Role of vdW Interactions on the Adsorption Structures. The inclusion of vdW interactions has a pronounced effect on the structures of all studied molecules adsorbed on Au(111) and (110) surfaces. The qualitative effect is similar for all molecules; however, the magnitude of structural changes is molecule dependent. First of all, the vdW interactions change the oxygen vertical adsorption distances for all adsorbates on the Au(111) surface. For example, in the case of allyloxy, the O−Au distance is increased from 1.23 to 1.62 Å when the vdW interactions are considered (Figure 3). However, the adsorption distances are found to be unaffected on the Au(110) surface (Figure 4), except in the case of the branched configuration (2-propoxy), where an increase of 0.1 Å is observed (see Tables 4 and 5). It is interesting to note that, on both surfaces, the Au−O bond length decreases slightly for the bidentate adsorption of acetate after the inclusion of vdW interactions; however, in the case of monodentate adsorption of methoxy, the Au−O bond length elongates (Figures 5 and 6). It is worth noting that, irrespective of the surface structures, the Au−O−C$_1$ bond angle generally increases, and the alkyl chain of the intermediate is tilted toward the surface upon inclusion of the vdW interactions in the calculations, which is also reflected in the reduced vertical distances. For example, in the case of allyloxy, the vdW interaction increases the Au−O−C$_1$ bond angle from 120.3° to 121.5° on the Au(111) surface and from 127.5° to 140.4° on the Au(110) surface. Correspondingly, the distance between C$_3$ atom in the alkyl chain and the Au surface is decreased by 1.17 and 1.14 Å on Au(111) and (110) surfaces, respectively, indicating the attractive interaction between the alkyl chain and the Au surface. Such strong bending of the CH$_3$ group leads to higher stability of methoxy on the Au(110) surface compared to the Au(111) surface (see Figures 5 and 6).

The inclusion of vdW interactions does not alter the structure of the C=C bonds appreciably (see Figures 3 and
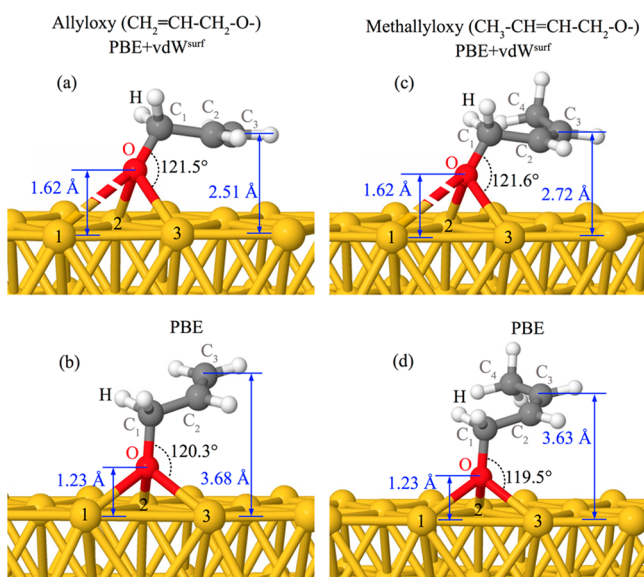
Figure 3. Optimized structures of allyloxy (left) and methallyloxy (right) on the Au(111) surface, calculated with (top panel, (a) and (c)) and without (bottom panel, (b) and (d)) vdW interactions. After the inclusion of vdW interactions, both allyloxy and methallyloxy are adsorbed on the *fcc-bridge* site.
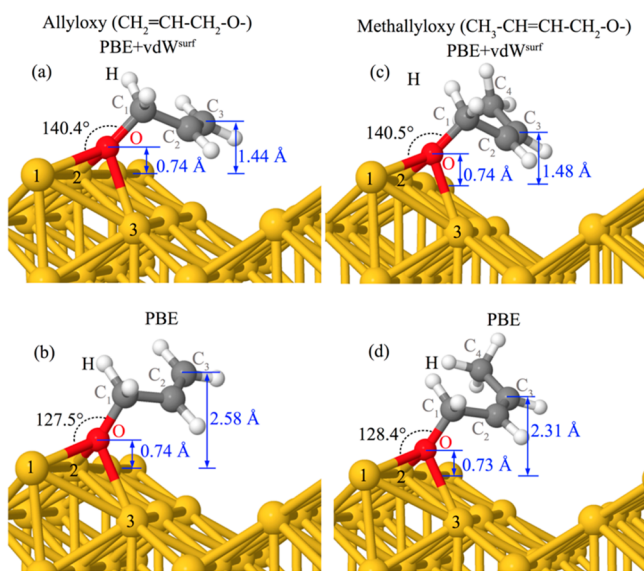

Figure 4. Optimized structures of allyloxy (left) and methallyloxy (right) on the Au(110)-(1×2) surface, calculated with (top panel, (a) and (c)) and without (bottom panel, (b) and (d)) vdW interactions. The key parameters such as vertical distances and angles are marked.

4). On the Au(111) surface, the C=C bond lengths are increased by 0.03 and 0.02 Å for allyloxy and methallyloxy, respectively, and on the Au(110) surface, the change is merely 0.01 Å for both adsorbates. We find that both molecules bind on *fcc* sites (with PBE functional) on the Au(111) surface, shifting toward the *fcc-bridge* site (see Figure 3) with an increase in the adsorption distance (O−Au) by 0.38 Å when using PBE +vdW^{surf}. There is also a significant increase shown in the vertical distance between the Au surface and the C_1 atom (C_1−Au). The elongation presumably reflects an optimization of the interactions between the Au surface and the unsaturated C=C bonds, and such a large change in bond distance leads to
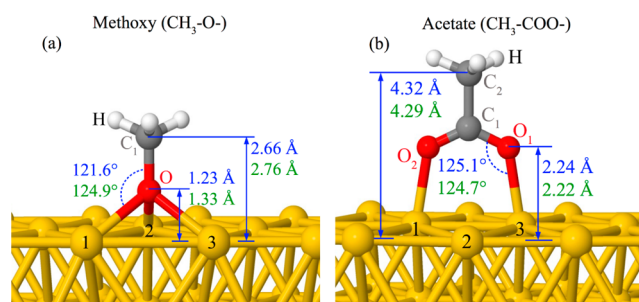
Figure 5. Optimized structures of methoxy (a) and acetate (b) on the Au(111) surface. The important structural parameters obtained with (green) and without (blue) vdW interactions are marked.
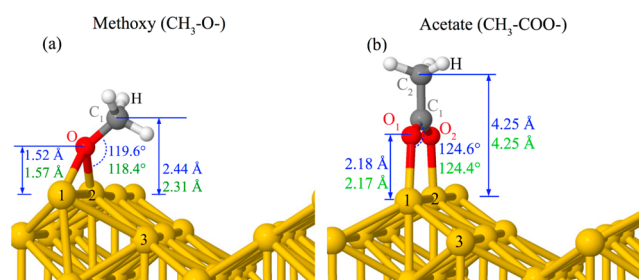

Figure 6. Optimized structures of methoxy (a) and acetate (b) on the Au(110)-(1×2) surface. The important structural parameters obtained with (green) and without (blue) vdW interactions are marked.

enhancement of the relatively weak vdW interactions between the O atom and the Au surface. After accounting for vdW interactions, we found that the C=C bond is tilted and moved parallel to the Au surface. As a result of the alkyl tail tilting, the Au−O−C_3 bond angle increases from 120.3° and 119.5° to 121.5° and 121.6° for allyloxy and methallyloxy, respectively, in the presence of vdW interactions. The unsaturated C=C bonds move toward the Au top atom position of the slab due to the strong interaction between the Au surface and C=C π-bond, which makes the intermediates more stable on the surface. However, on the Au(110) surface, allyloxy and methallyloxy are adsorbed on a pseudo-threefold site (when using either PBE or PBE+vdW^{surf}) and the adsorption distances are unaffected by the vdW interactions (Figure 4). The tilting of the alkyl group toward the Au surface is clearly visible from the C_3−Au distances, which decrease from 2.58 and 2.31 Å (PBE only) to 1.44 and 1.48 Å (PBE+vdW^{surf}) for allyloxy and methallyloxy, respectively.

The adsorption site is an important factor that determines the adsorption distance. We observed that all the molecules are adsorbed on the threefold site except methoxy on (110), acetate on both surfaces, allyloxy on (111), and methallyloxy on (111). On the Au(110) surface, the most stable geometry of methoxy is found to be the bridge site (PBE and PBE+vdW^{surf} optimization, Figure 6), which is more stable than the *fcc* site by 0.05 eV. This can be attributed to the strong Coulomb repulsion of H atoms of methoxy with the surface, while, in larger molecules, the carbon chains can adjust the bond angles to minimize the repulsion. Due to the bidentate adsorption structure, acetate is adsorbed on the top site on both Au surfaces (Figures 5 and 6). On the Au(111) surface, allyloxy and methallyloxy move from *fcc* to *fcc-bridge* position after including vdW interaction (Figures 3 and 4); this is due to the strong vdW attraction between the π bonds and the Au
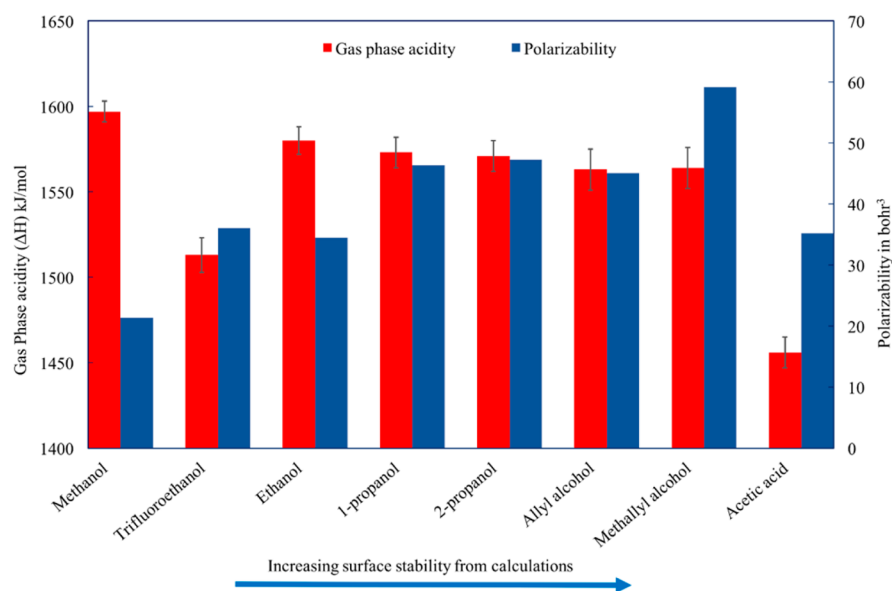
Figure 7. Polarizability computed from DFT+vdW calculations and the gas-phase acidities with error bars (taken from NIST database) of the parent gas phase molecules XH_{gas}.[44]

substrate, which pulls the carbon skeleton toward the surface, with the C=C bond moving toward the top site to yield a more stable geometry.

iv. DFT+vdW^{surf} Calculations vs Gas-Phase Acidity for Predicting the Surface Stability Hierarchy. The gas-phase acidities have been used before to provide guidance into the on-surface stabilities of reaction intermediates.[38,43] The trend in reactivity and stability hierarchy of intermediates can be formulated on the basis of their relative gas-phase acidities, which is known for a wide range of molecules. Generally, the gas phase acidity is defined as the enthalpy (ΔH) of the gas phase reaction

$$XH_{gas} \rightarrow X^-_{gas} + H^+_{gas} \quad \Delta H_{acid} \text{ (kJ/mol)}$$
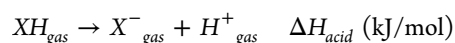
The lower values of ΔH indicate stronger gas-phase acidities and the reaction is endothermic. The relative gas-phase acidities are useful to infer whether the intermediate X_{ads} dominates X'_{ads} in competition for binding sites on a catalytic surface. In Figure 7, we show the gas-phase acidities and the computed polarizabilities of the molecules we have considered. For most studied molecules, the gas-phase acidity correlates well with the stability hierarchy established above. This is presumably due to the fact that the gas-phase acidity is related to the polarizability of the molecule. Larger polarizability implies stronger vdW interaction (all other things being equal); hence, the gas-phase acidity seems to be able to capture the overall trend in the stability of intermediates. Among the eight molecules we have considered, methanol, ethanol, and acetic acid show weaker polarizability (Figure 7) and their alkoxy intermediates show less significant vdW interactions with the surface (Figure 2) compared with other molecules.

However, trifluoroethoxy and allyloxy break this trend; both adsorbates do not bind as strongly as anticipated from their gas-phase acidities. For example, the gas phase acidity of trifluoroethanol is higher than ethanol but ethoxy is found to interact stronger with the surface than trifluoroethoxy. In addition, both calculations and experiments reveal that methallyloxy is more stable than allyloxy; however, allyl alcohol

and methallyl alcohol have similar gas-phase acidities and their binding stabilities cannot be inferred from their acidity.

From these results, we conclude that the relative stabilities of the adsorbed intermediates cannot be fully predicted by the gas-phase acidities of their parent molecules. The heat of adsorption of intermediates in some cases may be sufficiently different to alter the order of surface stability predicted by the gas-phase acidities.

VI. CONCLUSION

We investigated different factors that determine the adsorption strength of molecules on Au surfaces and the importance of considering the vdW interactions for the correct description of surface stabilities. Our studies demonstrate that the structural characteristics of the adsorbed molecule play an important role in determining the strength of vdW interactions and hence the energetics of catalytic intermediates. In particular, from our comparative study, we found that branched carbon-chain configurations, unsaturated bonds, and bidentate adsorption all contribute to increase the intermediate stability on Au surfaces. At the same time, molecules with electronegative atoms close to the surface are destabilized. Overall, the inclusion of vdW interactions in first-principles calculations yields a significant improvement in vertical adsorption heights, tilting angles, and stabilities of adsorbed molecules on both (111) and (110) Au surfaces. Interestingly, we observed that the adsorption stability for the studied molecules is insensitive toward the surface facet [(111) or (110)]. The present work provides insight into the factors controlling the reactivity on gold catalysts, by addressing the structural and chemical effects of molecular adsorbates. This particular approach can be extended to other molecular structures and metallic surfaces.

To enhance the catalytic activity, Au catalysts are often fabricated into nanoporous structures, in which several facets inevitably coexist. The binding strength of reaction intermediates is an important quantity that is intimately related to the reactivity. Our present study of alcohols on two dominant facets suggests that the reactivity depends on the molecular structures of the intermediates much more heavily than on the

underlying surface facet. Therefore, in fabricating nanoporous gold catalysts, it is likely more important to maximize the surface area than to control the surface facet distribution, if the two factors could not be optimized simultaneously.

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Notes

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