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Isophorone on Au/MgO/Ag(001): Physisorption with Electrostatic Site Selection

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Abstract

We report a computational study of isophorone $C_9H_{14}O$ adsorption on an Ag(001) supported ultra-thin MgO film with Au adatoms and clusters employing density functional theory (DFT) calculations. The calculations show that the keto form of isophorone is more stable than the enol tautomers both in gas-phase and on the MgO/Ag(001)surface. The interaction between the keto isophorone and step and terrace sites of MgO/Ag(001) displays long interaction distances, relatively weakly exothermic adsorption energies, lack of charge transfer, and minor changes in the density of states (DOS), all of which indicate that the molecule merely physisorbs on the surface. The step sites are energetically preferred adsorption sites due to attractive electrostatic interaction between more exposed Mg^{2+} cations and the polar O=C bond in isophorone. The adsorption on the step sites is 0.6 to 0.8 eV more exothermic compared to terrace sites. The calculations suggest that isophorone can chemisorb on MgO/Ag(001) surface but that requires the presence of O vacancy. The interaction between an Au atom and isophorone was studied both in vacuum and on the MgO/Ag(001) terrace. In vacuum calculations, we did not find chemical bonding between an anionic, cationic or neutral Au atom and the keto species. On the MgO/Ag(001) surface, a negatively charged Au adatom repels the keto isophorone while electrostatic attraction is observed with the enol form. The calculations employing an Au stripe supported by MgO/Ag(001) to mimic the edge of the 2D Au nanoisland show that keto isophorone physisorbs at the edge and on-top of an Au stripe. The enol isophorone demonstrates adsorption site selectivity to the edge of the stripe due to electrostatic attraction between the negatively charged cluster edge and the positive end of the polar H-O bond which makes physisorption on the Au edge energetically preferred.

Introduction

Metal supported oxide thin films form a versatile class of materials with multiple applications in different fields including microelectronics, gas sensors, protective coatings, and heterogeneous catalysis.¹⁻⁶ The oxide thin films can be grown with their thickness controlled to an atomic precision by evaporating the cation metal on the carrier metal in an oxygen background.⁷ The great advancement of the thin film arrangement compared to bulk is that surface science techniques such as scanning tunneling microscopy (STM) are applicable to intrinsically insulating oxides. The tunneling current can pass trough the oxide thin film⁸ enabling the study of local properties of adsorbates on the oxide. The prototypical thin film model systems include MgO films either on an Ag(001) or Mo(001) surface where the lattice mismatch between the oxide and the support metal is small. The MgO films grow into large islands with step sites along the island edges that can be active e.g., towards adsorption and dissociation of water.⁹

Both experimental and theoretical studies demonstrate that the adsorption characterictis of molecules and small Au clusters differ on thin MgO films compared to bulk oxide surfaces^{10–18} but some species exhibit smaller sensitivity towards the film thickness.^{9,19,20} Au atoms bind strongly to MgO oxide thin films and are negatively charged whereas they have less exothermic adsorption energies and remain neutral on the bulk MgO.^{21,22} The film thickness also affects the charge state and morphology of Au clusters on the surface: Au grows as 2D islands on MgO thin films while Au clusters exhibit 3D geometry on bulk oxides.^{23,24} The 2D Au islands have typically a quasi hexagonal shape and quantum well (QW) like states as indicated by DFT calculations and STM measurements.^{25–28} It has also been suggested that the properties of these states can be modified by changing the film thickness which could be used to optimize their catalytic activity.²⁹

Recently, STM methods were applied to study the adsorption of isophorone on a MgO thin film grown on an Ag(001) support with quasi hexagonal 2D Au clusters.³⁰ Isophorone, $C_9H_{14}O$, is a α,β -unsaturated ketone with O-C and C-C double bonds which make an attractive model molecule for selective hydrogenation. Isophorone exhibits keto-enol tautomerism where in addition to a C-C double bond in all tautomers the keto form has a O-C double bond while the enol species have an OH group. The enol forms differ by the position of H atoms in the molecule, while the C atoms have same positions as in the keto form. Isophorone can change rapidly from an enol to the keto tautomer in the gas-phase. The STM experiments demonstrated that the isophorone molecules adsorb at the edges of the Au islands with a molecular spacing close to 1 nm corresponding to the apparent molecular size but the interior of the clusters remained empty.³⁰ Moreover, the molecules could be removed by a voltage pulse which enabled the study of the same cluster with and without adsorbates and shows that the molecules have relatively low binding energies. Comparison of the QW states with and without the attached isophorone demonstrated a systematic modification to the QW states of the cluster. The change in the QW states of the cluster will impact its chemical properties. In our most recent combined DFT and STM study, we suggested that the enol form of isophorone was observed in the experiment to attach to the gold on MgO/Ag(001). This implies that the keto-enol tautomerization is kinetically possible at room temperature on that support.³¹

The adsorption and dehydrogenation of isophorone have also been studied experimentally on a Pd(111) surface using multiple methods, such as infrared spectroscopy and temperatureprogrammed desorption.^{32,33} The results were compared with DFT calculations and the inclusion of a van der Waals interaction to the computational energies was found to be important for obtaining the experimentally observed binding strength since the PBE functional

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underestimates the isophorone adsorption energies on Pd(111). The molecule was found to adsorb in a planar geometry with the vdW interactions giving a significant contribution to the binding energy.

In this work, we address the adsorption of keto and two different enol isophorones on a MgO/Ag(001) surface together with Au adatoms and clusters employing different surface models. These models include different defect sites such as steps and O vacancies as well as the flat terrace sites. All surface calculations are performed using an exchange-correlation functional with a van der Waals correction to get a more realistic picture of the binding especially in the case of physisorption. We find that isophorone weakly physisorbs on the Ag(001) and MgO/Ag(001) surfaces. The adsorbed molecule is further stabilized on the edge sites of the MgO film due to attractive electrostatic interaction between Mg²⁺ cations and a polar O-C bond. Calculations demonstrate that keto species interacts weakly with an Au atom in a vacuum and physisorbs on larger Au clusters supported over a MgO/Ag(001) surface. The extended and vinylogous enols, however, physisorb closer an Au adatom and at the edge of Au island than the keto tautomer while being energetically slightly less favorable. In the presence of an O vacancy in the MgO/Ag(001) terrace, the molecule chemisorbs into the vacancy.

Computational methods and systems

The DFT calculations are performed in the real space grid implementation of the PAW formalism using the GPAW code.^{34,35} The slab models and the gas-phase references for the adsorbed molecules are performed as spin-polarized using real space grids with 0.2 Å grid spacing and the van der Waals corrected BEEF exchange-correlation functional.³⁶ Calculations for the Kohn-Sham orbitals shown in Figure 1 and the Au-isophorone interaction

shown in Figure 3 are done with the PBE^{37} functional in the LCAO mode. The neutral Au-isophorone system is calculated as spin-polarized while the orbitals and charged systems are treated as spin-compensated. In all the calculations at least a 5 Å thick vacuum region separates the atoms from the non-periodic unit cell edges. A three-layers thick slab is used to model an Ag(001) support with a previously calculated lattice constant of 4.17 Å.⁹ The anions in the MgO films are aligned with the Ag atoms at the interface.³⁸ The experimental MgO/Ag(001) surface has multiple different sites including a bare Ag(001) terrace and step sites between MgO layers. To reduce the computational cost, we construct seven slab systems each modeling a particular adsorption site. The model systems include three terrace sites (Figure 2 and Figure 4), three step sites (Figure 2 and Figure 5), and an oxygen vacancy (Figure 6). The bare Ag(001) is modeled with a 2×2 cell and an Ag(001) supported one monolayer (ML)-thick MgO film with 2×2 and 3×3 unit cells. A step site is considered between bare Ag(001) and a MgO monolayer, one and two layers-thick MgO on Ag(001), and an Au stripe and MgO/Ag(001), all of these systems are modeled with a 4×2 unit cell. The O vacancy on MgO(1ML)/Ag(001) is considered in a 3×3 unit cell. $(4\times4\times1)$, $(3\times5\times1)$, and $(3\times3\times1)$ Monkhorst-Pack k-point samplings are used for the 2×2 , 4×2 , and 3×3 unit cells, respectively.^{39,40} The structures are relaxed until residual forces are below 0.05 eV/Å with two bottom Ag layers frozen to the bulk positions. The adsorption energies are calculated as

$$E_{ads} = E_{adsorbate/surface} - E_{surface} - E_{adsorbate}, \tag{1}$$

where the energies of a bare surface E_{surface} and the adsorbate in a vacuum $E_{\text{adsorbate}}$ are subtracted from the energy of the system, where the adsorbate is on the surface $E_{\text{adsorbate/surface}}$. The charges of the atoms are estimated using the Bader charge analysis⁴¹ where the total

electron density is split between the atoms using zero-flux surfaces.

Results and Discussion

Isophorone in vacuum

To begin with, we consider isophorone in gas-phase and in particular focus on keto, extended enol, and vinylogous enol tautomers. While the keto isophorone has all the H atoms bound to the C atoms, an enol form has one H atom attached to the carbonyl oxygen instead of a C atom. The optimized atomic structures are shown in Figure 1 together with the numbering of C atoms in the ring. Calculations show that C-C double bonds are clearly shorter than single C-C bonds. For example, we obtain 1.35 Å for a C2-C3 bond length in keto isophorone and the rest of the C-C bonds range from 1.47 to 1.54 Å. Different enol forms are obtained depending from which C atom the hydrogen is transferred. In the extended enol, a H atom from C6 has been transferred to the O atom. This leads to a formation of a double bond between C6 and C1 with a bond length of 1.35 Å to preserve the coordination of these C atoms. The second double bond between C2 and C3 remains intact with a bond length of 1.35 Å, while the longer single bonds from 1.46 to 1.55 Å are found between other carbon atoms. In the vinylogous enol, the methyl group attached to C3 converts to a methylene group by transferring a H atom to the carbonyl oxygen. Again, this enol form has two double bonds with the same bond length of 1.35 Å: one between atoms C1 and C2 and another one between C3 and the methylene group. The remaining C-C bonds vary from 1.45 to 1.55 Å. In a vacuum, the keto form is the most stable tautomer while the extended (vinylogous) enol is 0.64 (0.5) eV higher in energy.

Table 1 summarizes Bader charges for most relevant atoms in isophorone and demon-





Figure 1: **a**) The optimized gas-phase structures for the studied keto, extended enol, and vinylogous enol forms of isophorone. The keto form is 0.64 (0.5) eV lower in energy than the extended (vinylogous) enol. The carbon atoms in the ring are numbered and the double bonds are shown with two sticks. The color coding is as follows: C atoms are shown in dark grey while H atoms are white, and O atoms are displayed in red. **b**) Selected molecular orbitals and orbital energies of the keto isophorone with the zero energy between HOMO and LUMO energies.

strates internal polarization of an overall neutral molecule. In a carbonyl group, C1 loses electron density to more electronegative oxygen. In the case of enol, oxygen gains electron density from both C1 and H attached to oxygen. Thus, the keto form has a polar O-C1 double bond and the enol forms have two polar H-O and O-C1 bonds. The negatively charged end of the O-C1 bond points away from the molecule and thus a steric hindrance may prevent the attractive electrostatic interaction between negatively charged species and the negatively

Table 1: Bader charges of O, C1, and the H atom in the OH group for keto and enol forms in |e|. The last column gives the maximum absolute charge of all the other atoms in the molecule.

	q(C1)	q(O)	q(H)	-q(rest)-
m keto	0.95	-1.10		0.08
extended enol	0.46	-1.10	0.56	0.09
vinylogous enol	0.47	-1.08	0.55	0.11

charged carbonyl oxygen. For enol, the situation is different since the H in the OH group is slightly positively charged and can therefore be attracted to the negatively charged species. This difference can impact the adsorption behavior of the keto and enol forms. To explore the electronic structure of the gas-phase isophorone, we analyzed KS orbitals together with their corresponding energies. Figure 1b) shows the HOMO-1, HOMO, and LUMO orbitals of the ketone species. The HOMO orbital is localized at the O=C1 bond while the HOMO-1 is mainly centered at the C2-C3 double bond in agreement with previous calculations.³³ The orbital energies show that keto isophorone has a Kohn-Sham HOMO-LUMO gap close to 3 eV.

Isophorone on Ag(001) and MgO/Ag(001)

First, we address and compare the adsorption of isophorone at different possible sites on bare Ag(001) and MgO/Ag(001) employing both terrace and stepped surface models depending on what kind of site we are interested in. Figure 2 summarizes the most favorable adsorption geometries and studied surface models. The corresponding adsorption energies together with the Bader charges are given in Table 2. The adsorption energies range from -0.5 on Ag(001) to -1.4 eV on stepped MgO(2ML)/Ag(001) and the molecule remains neutral upon adsorption. On the Ag(001), the molecule floats above the surface with the minimum H-Ag distance of approximately 3 Å. This together with mildly exothermic adsorption energy of -0.5 eV and tiny Bader charge indicates that the molecule does not bond covalently to the surface but merely physisorbs. Furthermore, the density of states (DOS) analysis (not shown) does not find hybridization between the isophorone and surface states. This fully agrees with the physisorption picture since the states of the molecule and the surface are only slightly perturbed due to molecule-surface interaction.

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Table 2: The adsorption energies (eV) and total Bader charges (|e|) of keto isophorone on different surfaces.

	E_{ads}	$q(C_9H_{14}O)$
Ag(001)	-0.53	-0.06
MgO/Ag	-0.69	-0.20
MgO(1ML step)/Ag	-1.21	-0.14
MgO(2ML step)/Ag	-1.37	-0.26



Figure 2: Optimized geometries for isophorone on MgO/Ag(001). The Ag atoms are light gray, Mg atoms are green and the rest as in Figure 1. The top (side) view is shown in the upper (lower) row. The Ag bonds are omitted in the top view to avoid clutter.

Interestingly, on the MgO/Ag(001) terrace the carbonyl group points towards the Mg²⁺ cation, while the rest of the molecule reside above the surface. The distance between the carbonyl oxygen and the closest Mg cation is 2.2 Å with the Mg cation being pulled away from the surface by 0.4 Å due to attractive interaction between a positive cation and negative carbonyl oxygen. This renders adsorption on MgO/Ag(001) slightly more exothermic compared to Ag(001). The electrostatic stabilization is even more pronounced at the MgO-Ag interface where the cations at the step edge are more exposed and the cyclohexenone ring can have favorable vdW interaction with the silver surface. The carbonyl bond orients towards the cation with the O-Mg distance of 2.1 Å and the carbon ring lies parallel to the Ag substrate with a minimum H-Ag distance again close to 3 Å. The orientation of the molecule is qualitatively similar on a MgO step at a 2ML thick film with the O-Mg distance

of 2.2 Å and most exothermic adsorption energy among the all studied structure models.

The variation of adsorption energy from one model to the other can be understood in terms of an attractive electrostatic interaction between surface cations and the polar O-C1 bond with negatively charged oxygen. In the case of the pristine Ag(001) surface, there is no electrostatic interaction and exothermic adsorption energy is due to physisorption. On the MgO/Ag(001), there is some electrostatic stabilization but less than on the step sites where the orientation of the O-C1 dipole is more directly towards the adjacent Mg cation. More exothermic adsorption on a step site between two MgO layers results from two adjacent Mg cations close to carbonyl oxygen, while on the MgO-Ag(001) step there is only one cation.

Au-isophorone interaction in vacuum

As a first step to address the interaction between isophorone and Au, we study their interaction in vacuum, which excludes the potential attractive or repulsive contribution of the surface. This is done by screening multiple Au-isophorone geometries and varying the charge state of the Au atom from neutral to cationic and anionic Au. To reduce the degrees of freedom, Au and isophorone are fixed to a plane, modeling their coadsorption geometry on a MgO/Ag(001) surface. Energies are then calculated for frozen geometries, where the Au atom moves a full circle around the molecule in this plane. These geometries are described by a rotation angle indicating the orientation of the molecule with respect to the Au atom and the distance between the Au atom and its nearest atom in the isophorone.

The results from the screening of Au-isophorone interaction are collected into Figure 3. In the case of the neutral Au atom, the variation of the energy is at most ~ 0.4 eV for all calculated angles and distances. This indicates a lack of chemical bonding between species, since we anticipate the formation of a covalent bond to be manifested by a large



Figure 3: Isophorone interaction with a neutral (Au), anionic (Au⁻), and cationic (Au⁺) Au atom in vacuum. Nine angles and three Au-isophorone distances are displayed. The zero energy is set to the most stable geometry in each case. The Au atom is yellow and the rest as in Figure 1. Angle is given in radians

variation in energy as a function of a Au-isophorone distance while only small fluctuation are seen herein. For Au^{-1} , a clear repulsion is observed between the anion and the carbonyl group at angles between zero and one radian which corresponds to the shortest Au-oxygen distance. This is in line with the computed Bader charges which indicate that the carbonyl O is negatively charged. Energetically the most favorable structure is obtained when the anion is close to the methyl group next to C5 (the angle around 4 radians) and far away from the carbonyl group. For cationic Au, we find the attractive interaction at the short Au^+-O distances, which again highlights the negative charge of the carbonyl oxygen. For both charged systems, we do not find chemical bonding between the species. The attractive interaction is due the electrostatic stabilization between a point charge and the negative end of the dipole. The charge state of the Au atom is verified with the Bader charge analysis for the most stable anionic, neutral, and cationic system. The charges are -0.81, -0.07, and 0.59 |e| for Au⁻, Au, and Au⁺, respectively.

Au and isophorone on MgO/Ag(001)

This section focuses the coadsorption of isophorone with a single Au atom on the MgO/Ag(001) terrace. An Au atom preferably adsorbs on a hollow site with the adsorption energy of -1.59 eV and Bader charge of -0.77 |e| in line with the previous computational results.^{20–22} For the keto isophorone, we initially place the Au atom close the carbonyl oxygen. This geometry leads to a repulsive interaction between Au and isophorone and we find that the total energy follows a $1/d^2$ relation where d is the Au-O distance (not shown). This agrees with the expected behavior of interaction energy between a dipole and a point charge which in this case are a carbonyl group and a negatively charged Au, respectively. Figure 4 gives the energetically most favorable geometries for keto and both enol species on Au/MgO/Ag(001).

For the keto form, the optimized Au-O distance is 3.7 Å and the Au adatom is located on a Mg-top site. For the extended (vinylogous) enol, the most stable adsorption geometry has an Au-H(O) distance of 2.27 (2.45) Å and an O-Mg distance of 2.2 (2.4) Å. We tentatively ascribe the longer O(H)-Mg distance in vinylogous enol to increase in steric repulsion between the molecule and the surface, which originates from the two H atoms in C6. In an extended enol, both C2 and C6 have only one H atom leaving the OH group more exposed compared to the vinylogous enol, which enables better binding to a surface cation.

The adsorption energy of the keto isophorone on in the presence of adsorbed Au is -0.58 eV, which is comparable to the adsorption energy of -0.69 eV without the Au adatom.³¹ The adsorption of an extended (vinylogous) enol is 0.18 (0.47) eV is less stable than the adsorption of keto isophorone, which is dictated by larger instability of gas-phase enols in spite of that both enols display electrostatic attraction to cationic Au indicated by relatively short Au-H(O) distances. The difference in adsorption energies between enols originates from an additional stabilization experienced by an extended enol due the shorter Mg-O(H) distance and reduced steric hindrance. We note that no charge transfer from Au into isophorone was observed as expected.

Next, we estimate the mutual interaction strength between adsorbed Au and isophorone. For that we define the interaction energy as follows $E_{Au-I} = E_{Au\&I/S} + E_S - (E_{Au/S} + E_{I/S})$, where $E_{Au\&I/S}$ stands for the energy of Au and isophorone on MgO/Ag(001) in the same computational cell, E_S is the energy of the bare surface, and $E_{Au/S}$ and $E_{I/S}$ are the energies of Au and isophorone on MgO/Ag(001) in separate computational cells. Note that, negative (positive) E_{Au-I} indicates attraction (repulsion) between species. The computed interaction strength is +0.1 eV between Au and keto isophorone and -0.3 eV between Au and extended enol. This indicates the thermodynamic driving force towards the formation of Au-extended

enol pairs while no driving force exists for the formation of Au-keto pairs.



Figure 4: Optimized adsorption geometries for keto and enol isophorone and their relative stabilities on Au/MgO/Ag(001). The keto isophorone is the most stable while enol forms are higher in energy. The top (side) view is shown in the upper (lower) row. Colors are as in Figures 2 and 3.

Isophorone interaction with an Au stripe on MgO/Ag(001)

To investigate the adsorption of isophorone on a larger supported Au cluster, we employ an Au stripe model shown in Figure 5 to mimic the edge of a 2D Au cluster. The Au stripe has a fcc(111) structure with the average Au-Au distance of 2.78 Å along the edge of the stripe. The model exhibits a comparable charging behavior to the large 2D Au clusters with excess charge at the edges²⁷ having the average Bader charge of -0.26 |e| for edge atoms and -0.10 |e| for center atoms. Two possible adsorptions sites are considered: one at the edge of the stripe.

The adsorption energy of a keto species is almost isoenergetic on the top and edge sites of the Au stripe and close to the value on a pristine MgO/Ag(001) terrace. The lack of site dependence and weakly exothermic adsorption energy indicates physisorption. For the





Figure 5: The optimized adsorption geometries and relative stabilities for isophorone on the edge and top of an Au stripe on MgO/Ag(001). The keto isophorone on top of the stripe is the most stable geometry and selected for a reference. Colors are as in Figure 4.

extended (vinylogous) enol, the edge site is about 0.5 (0.3) eV more stable than the top site which again is due to an electrostatic stabilization between the negatively charged Au edge and the polar OH group but without explicit charge transfer from the Au stripe to the molecule as indicated by the Bader charge. Figure 5 shows how a keto isophorone floats above an Au stripe with a minimum Au-H distance more than 3 Å and without any preference to a particular adsorption site. The enol forms also float when placed directly above the Au stripe. In that case, the minimum Au-H distance is over 2.7 Å. However,on the Au edge, both enol forms interact with the Au/MgO interface and show shorter Au-H distances, which are 2.58 and 2.73 Å for the extended and vinylogous enol, respectively. Again, the extended enol lies closer to the surface with the O-Mg distance of 2.28 Å while the vinylogous enol demonstrates the longer O-Mg distance of 3.4 Å.

The experimentally observed decoration of the edges of Au clusters with isophorone and the empty cluster interior has been tentatively explained by enol tautomers³¹ which according to our recent DFT calculation can kinetically form in the presence of anionic Au. Yet, thermodynamically the most stable form of isophorone is the keto tautomer on top of the Au stripe, which is 0.14 (0.3) eV more stable than the extended (vinylogous) enol at the edge of the Au stripe.

Au and Isophorone on MgO/Ag(001) with an O vacancy

Finally, we consider the adsorption of keto isophorone on MgO(1ML)/Ag(001) in the presence of an oxygen vacancy without or with an Au adatom⁴² in a vacancy. The oxygen vacancies are known to be active sites towards adsorption of atoms and molecules and they could facilitate chemical interaction between a molecule and an oxide surface. However, in the supported thin films the vacancy concentration is low; it is estimated to be about 0.1 %.⁴³ The experimental evidence from STM measurements indicates that the vacancies prefer the step edges to the terraces^{44–46} which will make the experimental observation of an isophorone adsorbed into an O vacancy challenging. Three different adsorption geometries for keto isophorone are calculated. First, the adsorption is considered into the O vacancy without Au. In this geometry, the carbonyl oxygen points towards the vacancy and the molecule adopts a more perpendicular orientation to the surface than on the ideal surface as seen from Figure 6. While the adsorption energies on a step site and an O vacancy are comparable (see Table 3) the binding mechanisms differ. On the step sites, there is no charge transfer from the surface to isophorone and the molecular structure remains intact. However, in an O vacancy the O-C1 bond elongates from 1.23 Å in a vacuum to 1.38 Å in a vacancy, which indicates a conversion of a double bond to a single bond. Furthermore, the molecule gains one electron from the vacancy since the total charge of isophorone is -0.93 |e|. The analysis of C-C distances indicates two adjacent double bonds between C1 and C3 while the rest of the C-C bond lengths imply single bonds.



Figure 6: optimized adsorption geometries for isophorone on $Mg_1O_{1-x}/Ag(001)$. C2 is shown in blue when it has a double bond with both C1 and C3. The rest of the colors are as in Figure 4.

Table 3: The C1-C2 and C2-C3 distances in Å, adsorption energies in eV for keto isophorone with respect to $Mg_1O_{1-x}/Ag(001)$ or $Au/Mg_1O_{1-x}/Ag(001)$, and the Bader charges of O and C1 in |e|. The $\mu(tot)$ is the total magnetic moment of the system in μ_B .

	\mathbf{d}_{C1-C2}	d_{C2-C3}	$E_{ads}(C_9H_{14}O)$	q(O)	q(C1)	$\mu(tot)$
$C_9H_{14}O/Mg_1O_{1-X}/Ag$	1.40	1.39	-1.17	-1.41	0.45	0.92
$\mathrm{AuC_9H_{14}O/Mg_1O_{1-X}/Ag}$	1.48	1.35	-0.31	-1.38	0.46	0.0
${\rm AuC_9H_{14}/MgO/Ag}$	1.40	1.39	-0.72	-1.60	-0.12	0.83

Next, an Au atom is added to the surface near the isophorone occupied vacancy. Upon structural relaxation, Au binds to the C1 atom with the Au-C1 distance of 2.18 Å. The Au adatom also impacts the minimum surface cation and carbonyl oxygen distance, which decreases to 2.26 Å while the O-C1 distance increases to 1.43 Å. The double bond between C1 and C2 relaxes to a single bond with the C1-C2 distance increasing from 1.4 to 1.48 Å. There is still a double bond between C2 and C3 while the remaining C-C bonds are single bonds. In the third considered case, the O vacancy is closed by a dissociation of the O-C1 bond. The forming radical species remains attached to the Au adatom and lies parallel to the surface. The distances between the C atoms in the ring indicate the presence of two double bonds between C1-C2 and C2.C3 while the rest of the C-C distances support single bonds and the Au-C1 distance is 2.04 Å.

Figure 7 presents a potential energy surface for isophorone adsorption at an Au covered O vacancy followed by a dissociation of the O-C1 bond. Both the adsorption and dissociation of the keto isophorone are exothermic. This shows that the presence of an O vacancy makes AuC_9H_{14} thermodynamically the most stable species on MgO/Ag(001). While there is a thermodynamic driving force towards isophorone dissociation, we did not calculate the reaction barrier, since the experimentally observed sparseness of O vacancies probably leaves this process unusable in catalytic applications.⁴³ Before the C-O bond breaking, the $AuC_9H_{14}O$

species with the carbonyl oxygen in an oxygen vacancy has a total charge of -0.89 |e|. The isophorone adsorption decreases the Bader charge of Au from -0.95 to -0.24 |e| suggesting the formation of the covalent bonding between Au and C1. Closing of the O vacancy with the carbonyl oxygen and breaking of the O-C1 bond form the neutral AuC₉H₁₄ species. Furthermore, we note that both isophorone in the O vacancy and the AuC₉H₁₄ on the pristine surface have a nonzero total magnetic moment while in all the other studied systems the total magnetic moment has been zero. We interpret that magnetization results from the over coordination of C2. To compensate O-C1 bond elongation, C1 forms a double bond with C2, which already binds to one H and forms a double bond with C3. This leads to the formal coordination of five for C2.



Figure 7: The potential energy surface for isophorone adsorption on $Au/Mg_1O_{1-x}/Ag(001)$.

Conclusions

The coadsorption of Au and isophorone $(C_9H_{14}O)$ on a MgO/Ag(001) thin film surface was studied with DFT calculations. Isophorone interacts weakly with MgO/Ag(001) utilizing dispersion forces and electrostatic interaction to attach to the surface. The adsorption site

selectivity relies on an electrostatic stabilization arising from the interaction between a polar O=C bond in the molecule and the surface cations. The more exposed Mg cations on the step sites enable a more exothermic binding compared to the terrace sites. Calculations with different angles and distances between isophorone and a neutral, cationic and anionic Au atom in a vacuum do not show chemical bonding between these twp species. In line with gas-phase calculation, surface calculations show a repulsive interaction between an Au anion and the negative carbonyl O with the energy closely following an inverse square relation with respect to the Au-carbonyl O distance. The interesting adsorption site selectivity observed in experiments³⁰ can be tentatively ascribed to by the presence of enol isophorone at the edges of 2D Au clusters due the attractive Au^{$\delta-$}-H^{$\delta+$} interaction between the edge Au and hydroxyl H, which makes adsorption more favorable at the cluster perimeter while the interaction to the cluster interior is dominated by van der Waals forces. The presence of an O vacancy can make the MgO/Ag(001) surface reactive towards chemical interaction with isophorone. The dissociative adsorption of isophorone on vacancy-bound Au and interchanging of the positions of Au and O is thermodynamically preferred compared to the associative adsorption of isophorone into an oxygen vacancy and formation of an $AuC_9H_{14}O$ species. However, we have not attempted to estimate activation energies for this process.

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