Density Functional Study of the Adsorption of Propene on Mixed Gold-Silver Clusters, AunAgm: Propensity Rules for Binding

Steeve Chrétien
University of California - Santa Barbara

Mark S. Gordon
Iowa State University, mgordon@iastate.edu

Horia Metiu
University of California - Santa Barbara

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs

Part of the Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/437. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Density Functional Study of the Adsorption of Propene on Mixed Gold-Silver Clusters, AunAgm: Propensity Rules for Binding

Abstract
We use density functional theory to investigate the binding of propene to small mixed Au–Ag clusters, in the gas phase. We have found that the rules proposed by us for propene binding to Au and Ag clusters, also work for binding to mixed Au–Ag clusters. The rules state that propene binds to those sites on the edge of the cluster where the equal density plots of the LUMO of the naked cluster protrude into the vacuum. Furthermore, the desorption energy of propene correlate with the LUMO energy: the lower the LUMO energy, the stronger the propene bond. We have also found an additional rule that is specific to mixed clusters. We call active the atoms on which the LUMO of the naked cluster protrude in the vacuum, and inactive those for which such protrusions do not exist. To define the rules we use the following notation: A is an active site to which propene is bound B is another active site, and C is an inactive site. If the atom in C(Ag or Au) is replaced with another atom (Au or Ag) propene desorption energy changes very little. If we replace the atom B with a more electronegative atom (i.e., we replace Ag by Au) the propene bond to A becomes stronger. If we replace the atom B with a less electronegative atom (i.e., we replace Au by Ag) the propene bond to A becomes weaker.

Keywords
Gold, Chemical bonds, Density functional theory, Desorption, Adsorption

Disciplines
Chemistry

Comments
The following article appeared in Journal of Chemical Physics 121 (2004): 9931, and may be found at doi:10.1063/1.1809601.

Rights
Copyright 2004 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

This article is available at Iowa State University Digital Repository: http://lib.dr.iastate.edu/chem_pubs/437
Density functional study of the adsorption of propene on mixed gold-silver clusters, \( \text{Au}_n \text{Ag}_m \): Propensity rules for binding

Steeve Chrétien, Mark S. Gordon, and Horia Metiu

Citation: The Journal of Chemical Physics 121, 9931 (2004); doi: 10.1063/1.1809601

View online: http://dx.doi.org/10.1063/1.1809601

View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/121/20?ver=pdfcov

Published by the AIP Publishing

Articles you may be interested in
Density functional study of the interaction between small Au clusters, \( \text{Au}_n \) (\( n = 1 \sim 7 \)) and the rutile \( \text{TiO}_2 \) surface. II. Adsorption on a partially reduced surface

CO adsorption on pure and binary-alloy gold clusters: A quantum chemical study

Characterization of methoxy adsorption on some transition metals: A first principles density functional theory study

Density functional study of the adsorption of propene on silver clusters, \( \text{Ag}_m \) \( q = 0, +1 \)

Binding of propene on small gold clusters and on Au(111): Simple rules for binding sites and relative binding energies

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 129.186.176.217 On: Wed, 02 Dec 2015 15:55:33
Density functional study of the adsorption of propene on mixed gold-silver clusters, $\text{Au}_n\text{Ag}_m$: Propensity rules for binding

Steeve Chrétien
Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106

Mark S. Gordon
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Horia Metiu a)
Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106

(Received 28 July 2004; accepted 2 September 2004)

We use density functional theory to investigate the binding of propene to small mixed Au–Ag clusters, in the gas phase. We have found that the rules proposed by us for propene binding to Au and Ag clusters, also work for binding to mixed Au–Ag clusters. The rules state that propene binds to those sites on the edge of the cluster where the equal density plots of the LUMO of the naked cluster protrude into the vacuum. Furthermore, the desorption energy of propene correlate with the LUMO energy: the lower the LUMO energy, the stronger the propene bond. We have also found an additional rule that is specific to mixed clusters. We call active the atoms on which the LUMO of the naked cluster protrude in the vacuum, and inactive those for which such protrusions do not exist.

To define the rules we use the following notation: $A$ is an active site to which propene is bound, $B$ is another active site, and $C$ is an inactive site. If the atom in $C$ (Ag or Au) is replaced with another atom (Au or Ag) propene desorption energy changes very little. If we replace the atom $B$ with a more electronegative atom (i.e., we replace Ag by Au) the propene bond to $A$ becomes stronger. If we replace the atom $B$ with a less electronegative atom (i.e., we replace Au by Ag) the propene bond to $A$ becomes weaker. © 2004 American Institute of Physics. [DOI: 10.1063/1.1809601]

I. INTRODUCTION

In two previous papers 1,2 we have studied the adsorption of propene on small Au and Ag clusters. We have found there a number of “empirical” rules that allow us to guess the relative desorption energy and the binding site of the propene, from the shape and the energy of the lowest unoccupied molecular orbital (LUMO) of the “naked” metal cluster. In this paper we extend this work by examining the binding of propene to mixed Au and Ag clusters.

Small Au and Ag clusters (2 nm < diameter < 4 nm) catalyze propene epoxidation 3-18 even though large gold clusters are inert, and large Ag clusters burn propene to $\text{CO}_2$ and $\text{H}_2\text{O}$. We are particularly interested in exploring whether clusters with a few atoms can be use to catalyze these (or other) reactions. Numerous examples from homogeneous catalysis shows that many reactions are catalyzed by one or a few metal atoms. There is no fundamental reason why this could not happen in heterogeneous catalysis. Besides saving expensive metals, very small clusters may be advantageous because their catalytic properties are very sensitive to the number of atoms in the cluster, its environment (support or ligands), and its composition (alloying); more parameters are available for optimizing their catalytic activity.

The latter possibility is one of the reasons prompting us to examine the Au–Ag alloys, and determine to what extent their ability to bind propene is modified by alloying. Since both metals catalyze propene epoxidation, it may be that the alloy has useful properties.

In this paper we show that the rules proposed earlier, for propene binding to Au or Ag clusters, 1,2 also work for mixed clusters: propene bond strength and binding sites are controlled by the properties of the LUMO of the naked cluster. Propene binds preferentially to sites where the LUMO protrudes most into the vacuum, and the desorption energy correlates with the LUMO energy; the lower the LUMO energy, the stronger the bond.

In the previous work we pointed out that propene binding to a Au or Ag cluster is an electron donor. One therefore expects that the electronegativity of the metal atoms should play a role in determining the ability of an alloy to bind propene. Since Au is more electronegative than Ag, a gold atom in a mixed Au–Ag cluster will gain some electronic charge density at the expense of Ag. This should lower the ability of the Au atoms to bind propene and make the Ag atom more active towards propene binding.

This simple rule works in some, but not all, cases. We find that there are many alloyed clusters for which the substitution of some of the Au atoms with Ag (or vice versa) has no effect on propene binding. This can be rationalized as follows. To characterize the shape of the LUMOs, we plot the surface on which the orbital wave function squared, $[\varphi_i]^2$, has a fixed value. We call this a LUMO density plot or a LUMO plot. The LUMO plots of Au or Ag clusters having the same number of atoms and similar structure have very similar shapes. This is why the binding of propene on these
clusters is so similar. By using such a plot we divide the atoms in a cluster into two classes: active atoms (which have a high LUMO density located on or very near them) and inactive atoms (which have very little LUMO density on them). For example, atoms 1 and 3 in the LUMO plots shown in Fig. 1 are active, and atoms 2 and 4 are inactive. The rules we have previously found tell us the propene binds most strongly to the active atoms.

In the work presented here we have found that replacing one inactive Au atom with Ag (or vice versa) has a negligible effect on the desorption energy of the propene. Changes in desorption energy occur only if we exchange an active atom. For example, if propene is bound to atom 1 (of the Ag₄ cluster at the top of Fig. 1), then replacing Ag atoms 2 or 4 with a Au atom causes practically no change in propene desorption energy; on the other hand, replacing a Ag atom located at site 3 with a Au atom, increases the propene desorption energy; the active Au atom at site 3 takes electron density from the active Ag atom located at site 1. This makes atom 1 more active towards propene binding since propene binds by donating electrons. Only the electronegativity of the active atoms affects propene binding.

The density functional theory (DFT) results supporting these statements are given in the following section. As in the previous papers we emphasize again that we are quite aware that total energy is not simply related to the orbital energy, and that it is difficult to find a convincing theoretical justification for the rules proposed here. They should be viewed as “empirical” rules, which systematize the results obtained by the DFT calculations.

II. COMPUTATIONAL DETAILS

The methodology used for the DFT calculations is the same as that used in our previous work. All the calculations have been performed with the VASP program (version 4.5.5) using the revised Perdew–Burke–Erzerhoff (r-PBE) functional of Hammer, Hansen, and Nørskov and the projector augmented-wave pseudopotentials optimized for the PBE functional.

III. ADSORPTION OF PROPENE ON AuₙAgₘ (n+m≤4)

Our results for the structures of the naked mixed Au–Ag clusters, AuₙAgₘ (n = 1–3, m = 1–3, and n + m ≤ 4), are the same as the ones reported in Ref. 26 using the 19e-RECP BP86. However, we have found that the bent structures (θ = 135° for the Au₂Ag and Au₄Ag₂ clusters and θ = 129° for Au₄Ag₃) are more stable than the linear ones. These structures were probably not considered in Refs. 26 and 27.

A. The lowest energy compounds for each composition

In Figs. 2 and 3 we give the results of our calculations for compounds having the formula AuₙAgₘ(C₃H₆) with n + m ≤ 4. We studied a very large number of isomers, but we show here the most stable ones (for each composition), together with the metastable isomers whose energy does not exceed that of the most stable compound with the same composition by more than 0.35 eV. The calculations were performed with the r-PBE functional.

FIG. 1. LUMO orbital density plots (|ψ|²) for two Ag₄ clusters. The plots show equal density surface of 0.025e/Å³.

FIG. 2. Desorption energies ΔE of propene (in eV) from the compounds AuₙAgₘ(C₃H₆) (n = 1–2, m = 1–2, n + m ≤ 3) calculated with Eq. (1). We give only the results for those isomers whose energy does not exceed that of the most stable compound with the same composition by more than 0.35 eV. ΔE is the energy difference between a given compound and the most stable compound with the same composition. By definition, the most stable isomer has ΔE = 0. The calculations were performed with the r-PBE functional.
The figures give the desorption energy $D_e$ of propene, calculated with the formula

$$D_e = E[Au_{n}Ag_{m}] + E[C_3H_6] - E[Au_{n}Ag_{m}(C_3H_6)].$$

(1)

Here $E[Au_{n}Ag_{m}]$ is the energy of the naked $Au_{n}Ag_{m}$ cluster having the same shape as in the $Au_{n}Ag_{m}(C_3H_6)$ compound, but relaxed to its equilibrium structure. For example, for the compound 2 in Fig. 2 the $Au_{2}Ag$ cluster has a bent structure and the energy $E[Au_{2}Ag_{m}]$, used to calculate $D_e$ for this system is the minimum energy of the naked cluster with a bent structure in which the terminal positions are occupied by Ag atoms.

We make no correction for the zero-point energy; this is the difference between the zero-point energy of the “products” and that of the “reactants,” and it is small compared to $D_e$. For example, this correction is 0.04 eV for the $[Ag(C_3H_6)]^+$ complex.28

The rules stated in our previous papers,1,2 on propene adsorption on one-component clusters, work as well for mixed clusters. We find that the LUMOs of the mixed Au–Ag clusters have the same shape as those of the Au or Ag clusters with the same structure. As in the previous cases, propene binds to the sites on the cluster where the LUMO of the naked cluster protrudes into the vacuum, and the desorption energy correlates with the LUMO energy.

The shapes of the LUMOs are such that propene binds to the edge of the cluster and does not bind to its flat sides. We

found this behavior to be general: oxygen,29–32 hydrogen,33 CO,34 NO,35 propene oxide, or acetone36 also bind only to the edge of the cluster.

On the edges, propene prefers to bind to the low coordination sites (the corners). The bonding is such that the double bond of the propene is in contact with one atom in the cluster; a bond in which the two carbon atoms involved in the double bond make contact with two atoms in the cluster is rare.

The geometry of a propene molecule bound to a mixed cluster is very close to that of the gas phase molecule. This is very different from the case of oxygen, which binds by accepting electronic charge in the antibonding $2\pi^*$ orbital, which causes a substantial increase of the O–O bond.

As in the case of binding to a one-metal cluster, propene rotates almost freely around an axis that (roughly) goes through the metal atom to which the molecule is bound and the middle of the propene double bond. This happens because the LUMO is almost symmetric around such an axis and the overlap of the $\pi$ orbital of propene with LUMO is similar at all angles.

Metal clusters with an adsorbate on them have a remarkable ability to form many low energy isomers. For example, there are seven $Au_{3}Ag(C_3H_6)$ isomers whose energy exceeds by less than 0.28 eV than that of the most stable compound with the same chemical formula. If the cluster is in equilibrium with a propene gas these compounds are present at concentrations proportional to the appropriate Boltzmann factor. Moreover, an individual cluster will cycle through these structures in the course of time, spending a long time in the low energy structures and a shorter time in the higher energy ones. This may have an influence on the kinetics of the reactions undergone by a $Au_{3}Ag(C_3H_6)$ cluster.

Consider, for example, the compounds 3A and 3G in Fig. 3. The desorption energy of propene in compound 3A is 0.84 eV, while in 3G it is 0.61 eV. However, the energy of 3G is higher than that of 3A by 0.28 eV. The energy required to desorb propene from the more stable compound 3A by isomerization to 3G followed by desorption is the same (within the accuracy of DFT) as that required for direct desorption from 3A. This means that propene will desorb by direct desorption from 3A, but it will also desorb from the intermediate 3G. A kinetic mechanism for desorption will have to take into account all the relevant parallel processes.

Furthermore, imagine that the cluster 3B in Fig. 3 absorbs $O_2$ much faster than cluster 3A. Then, it would be possible that cluster 3B is more important than cluster 3A in propene oxidation, even though 3A is present in the system in a larger amount. These possibilities should be kept in mind when examining reaction mechanisms.

Our previous work has shown that the propene desorption energy grows initially with the number of atoms in the cluster and then starts to decrease. This is true for the neutral Au and Ag clusters. To see if there is any pattern in the dependence of propene desorption energy on the number of atoms and the composition of the Au–Ag cluster, we have collected in Table I the desorption energies of propene in the most stable $Au_{n}Ag_{m}(C_3H_6)$ compounds.

At first sight, it is very difficult to distinguish a pattern.
We know that propene binds by donating electron density to the cluster and that the electronic affinity of the Au clusters is larger than that of the Ag clusters.\cite{27,28} For this reason propene binds more strongly to a Au cluster than to Ag cluster with the same number of atoms and the same shape. We also know that Au is more electronegative than Ag. We expect that, due to its higher electronegativity, Au in a mixed cluster will take electron density from Ag. This should make the Ag atoms more reactive with propene and the Au ones less reactive. This conjecture works for all but two cases in Table I. For example, adding Au to Ag Ò increases the desorption energy of propene from a Ag atom in the cluster go from 0.47 eV (for Ag3), to 0.54 eV (for Au2Ag), and to 0.71 eV (for Au3Ag). Obviously, substituting a Ag atom with Au increases the desorption energy of propene from a Ag atom in the cluster. Similarly, the desorption energy from a Au atom in a cluster with three atoms goes from 1.27 eV (for Au3) to 0.72 eV (for Au2Ag). The exceptions are AuAg3 and Au2Ag2 where the desorption energy of propene from a Ag atom in the cluster (0.49 eV) is less than the desorption energy to a Ag4 cluster (0.52 eV); the addition of one or two Au atoms does not induce the Ag to bind the propene stronger, as the rule suggests. The electronegativity based rule works in some cases but not in others, which means that unless we modify it to make it more predictive, it is not useful.

As we show below, as we examine more isomers, we find that the rule based on electronegativity alone, fails rather often; there are many cases when the replacement of a Ag atom with a Au atom, or an exchange in position between a Ag and a Au atom in a cluster, does not affect the desorption energy of propene. In other cases such modifications have a large effect. Fortunately, it is possible to modify the rule to account for all these cases.

**B. Propene binding to mixed Au–Ag dimers**

The electronegativity based rule works well for propene binding to two-atom clusters. The LUMO density plots of the Au2, AuAg, and Ag2 clusters have large lobes at the ends of the clusters and practically no density in the center. As a result, propene binds to the ends of these clusters. When we compare Ag5(C3H6) with AuAg(C3H6) (structures 4A and 4B in Fig. 4) we see that replacing with Au the Ag atom that is not bound to propene, increases the propene desorption energy from 0.24 to 0.55 eV. The Au atom, which is more electronegative than Ag, will drain some electron density from Ag. This makes it easier for propene to donate electron density to the Ag atom, making it more active for propene adsorption. When we compare AuAg(C3H6) with Au2(C3H6) (structures 4C and 4D in Fig. 4) we see that propene binds less strongly to the gold end of the AuAg cluster than to Au2. Replacing Au with a Ag increases the electron density of the remaining Au atom making it less capable to bind propene. Mixing Au and Ag to form a AuAg cluster activates Ag towards propene adsorption and makes Au less active. In the case of the AuAg cluster propene binds more strongly to the Ag end (0.55 eV) than to the Au end (0.42 eV), even though the bond to Ag2 is 0.24 eV and that to Au2 is 1.01 eV; alloying makes Ag more active than Au and Ag behave more like Au, and Au more like Ag.

![Propene binds to Ag](image)

![Propene binds to Au](image)

**C. Propene binding to mixed Au–Ag tetramers**

In Fig. 5 we show the structure, the desorption energy, and the LUMO energy of the naked cluster, for a few compounds with four metal atoms. The results included were selected to illustrate a rule, for mixed clusters, which has no analog when all the metal atoms in the cluster are of one kind.

Let us look at the results shown for the first three compounds in the left column of Fig. 5. As we go from Ag4(C3H6), to AuAg5(C3H6), and to Au2Ag2(C3H6) we see practically no change in propene desorption energy. In all these compounds propene is bound to a Ag atom, and we replace successively the Ag atoms that are not bound to propene, with Au atoms. In spite of the fact that Au is more electronegative than Ag, this replacement has practically no effect on propene desorption energy. The fourth complex in the first column acts differently: replacing with Au the Ag atom opposite to the one to which propene is bound, increases the desorption energy of propene. The electronegativity rule seems to work in this case but not on the previous two examples.

A look at the picture of the LUMO of the Ag4 cluster shown at the top of Fig. 1 suggest an explanation for this behavior. The LUMO has large lobes protruding from atoms 1 and 3, but it has little density on atoms 2 and 4. This means that replacing a Ag atom at 2 or 4 with a Au atom has a small

---

**TABLE I. Comparison of the desorption energies (in eV) of propene from the most stable AuAg4(C3H6) compounds with n = 0–4, m = 0–4, and m + n ≤ 4.**

<table>
<thead>
<tr>
<th>n + m</th>
<th>Bound to</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Ag2</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Au1Ag1</td>
<td>0.55</td>
<td>0.42</td>
</tr>
<tr>
<td>2</td>
<td>Au2</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ag3</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Au1Ag2</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Au2Ag1</td>
<td>0.71</td>
<td>0.72</td>
</tr>
<tr>
<td>3</td>
<td>Au3</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ag4</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Au1Ag3</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Au2Ag2</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Au3Ag1</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Au4</td>
<td>1.20</td>
<td></td>
</tr>
</tbody>
</table>
Propene binds to Ag

Propene binds to Au

Effect on LUMO energy $\varepsilon$ of the naked cluster (see Fig. 5). Since, according to our rules, the desorption energy tracks the orbital energy, no change in $\varepsilon$, means no change in $D_e$. Indeed, this is what we see: the LUMO orbital energies of the naked clusters in the top three compounds in the left column of Fig. 5 are $-3.3$, $-3.4$, and $-3.4$ eV, and the desorption energies are 0.52, 0.49, and 0.49 eV, respectively. However, if we replace the Ag atom in position 4 with a Au atom, the orbital energy drops to $-3.8$ eV and the desorption energy increases to 0.67 eV.

This observation suggests a useful nomenclature: we call the atoms on which the LUMO of the naked cluster has a high density active, and the ones with low or no density, passive. In Fig. 1 the atoms 1 and 3 are active and 2 and 4 are passive. We can now formulate the following rule: replacing a passive atom with another atom (Ag with Ag or Ag with Au) has a very small effect on the LUMO of the naked cluster and on the desorption energy of propene to an active atom. The substitution of an active atom causes a substantial change in the LUMO energy of the naked cluster and in the desorption energy of propene to another active atom.

One can easily see that this rule covers all the compounds shown in the left column of Fig. 5, as well as the compounds in the right-hand column. We can now reformulate the rule concerning the electronegativities of the atoms participating in the substitution. If an active atom is replaced by an atom with higher electronegativity, the desorption energy of propene to another active atom is increased and the energy of the LUMO of the naked cluster is decreased. You can see this happen when going from the structure 5A to structure 5D, where we replace an active Ag atom with a Au atom. If the replacing atom has a lower electronegativity, the desorption energy of propene is decreased. An example is seen while going from structure 5E to structure 5H by replacing a Au atom with a Ag one.

In summary, only the electronegativity of the active atoms matters.

In Fig. 5 we have looked at what happens when we start with Ag$_4$ and replace the Ag atoms, one by one, with Au (or start with Au$_4$ and replace the Au atoms, one by one, with Ag). Next we show that the rule derived in that analysis applies to all isomers of Au$_3$Ag and all isomers of Au$_2$Ag$_2$. These isomers are obtained by rearranging the positions of the Ag and Au atoms in a given compound.

In the left column of Fig. 6 we show all isomers of Au$_3$Ag(C$_3$H$_6$) in which propene binds to an active Au atom located in position 1 (see the numbering of atoms in Fig. 1). In complexes 6A and 6B the active site 3 is occupied by a Ag atom. The Au atom in position 1 (to which propene is bound) draws some charge from the active Ag atom in position 3 and this should weaken the propene-Au bond. Indeed, the desorption energy of propene to the clusters 6A and 6B in Fig. 5 is 0.84 and 0.61 eV, while the desorption energy to position 1 of a Au$_4$ cluster with a rhombus structure is 1.16 and 1.20 eV when the Au$_4$ cluster has a T-shaped structure such as in 6A. Replacing an active Au atom in position 3 of Au$_4$ with a Ag atom, decreases substantially the desorption energy of propene to the Au atom in 1.

Let us look now at the complexes 6B, 6C, and 6D in Fig. 6. These compounds are isomers of Au$_3$Ag(C$_3$H$_6$) in which the active sites 1 and 3 are occupied by Au and propene binds to the atom 1. The remaining Ag and Au atoms are placed in the inactive sites 2 and 4. No matter how we place these two atoms in the inactive sites, their location does not affect propene desorption energies, which are 1.23, 1.19, and 1.18 eV. A similar behavior is seen in the right-hand column in Fig. 6, where we show data for the isomers of Au$_3$Ag$_2$(C$_3$H$_6$), where propene is bound to an active Au atom: two Au atoms in the two active sites lead to a large desorption energy of propene; the desorption energy is small if the other active atom is Ag: it does not matter whether the inactive sites are occupied by Au or Ag.

We have performed calculations with all possible four atom clusters containing Au and Ag, including many high energy isomers. The rule proposed in this section works in all cases. Furthermore, in all cases, the LUMO energy of the naked cluster correlates with the desorption energy of propene.
pene, as specified by the rules proposed in our previous work.\textsuperscript{1,2}

D. Propene binding to mixed Au–Ag trimers

Some of the results of the calculations for propene adsorption on three metal-atom clusters are shown in Fig. 7. All three metal atoms in these compounds are active. If propene is bound to a Ag atom, replacing another Ag atom with Au, always increases the propene desorption energy. The higher electronegativity of Au depletes the bonded Ag atom of electronic charge, making it more receptive to electron donation by propene. The opposite trend is observed for clusters in which propene is bound to Au. The desorption energy in AuAg\textsubscript{2}(C\textsubscript{3}H\textsubscript{6}) is the lowest, because the Au atoms gain electron density at the expense of the two Ag atoms. As Ag is replaced with Au, to form Au\textsubscript{2}Ag(C\textsubscript{3}H\textsubscript{6}) and AuAg\textsubscript{2}(C\textsubscript{3}H\textsubscript{6}), the desorption energy of propene increases.

IV. SUMMARY AND CONCLUSIONS

In our previous work\textsuperscript{1,2} we have shown that propene bonding to small Au or Ag clusters follows simple rules based on the shape and the energy of the LUMO of the naked cluster. Propene prefers to bind to those sites, at the edge of the cluster, where the LUMO density of the naked clusters protrudes in the vacuum. The desorption energy correlates with the LUMOs energy: the lower the energy of the LUMO, the higher the desorption energy of the propene.

The work presented here shows that these rules also work well for propene binding to mixed Au–Ag clusters. In studying propene binding to mixed clusters a new problem arises: how does the desorption energy depend on the composition of the cluster (the number of Ag and of Au atoms)? For clusters of fixed composition, how does propene binding depend on the manner in which the Au and Ag atoms are distributed over various sites in the cluster? To answer these questions we found it useful to divide the atoms in a naked cluster into active or inactive: LUMO density of a naked cluster protrudes in the vacuum near or at the location of the active atoms and no such protrusion exists near the passive atoms. With this nomenclature we can formulate the following rules. Let us assume that propene is bound to an active atom \(A\) and the cluster has another active site \(B\). If an atom at \(B\) is replaced with a more electronegative atom, the desorption energy of propene to \(A\) increases. The opposite is true if the replacing atom is less electronegative. Replacing an atom at an inactive site has a negligible effect on the desorption energy of propene.

It is not difficult to rationalize these findings. Propene bonding is controlled by the need to transfer electron density to the naked cluster. This is why we expect that the LUMO
of the cluster will be heavily involved. The surprise is that examining the shape and the energy of the LUMO alone has so much predictive power.

Given the importance of LUMO shape and energy, the existence of active and inactive atoms in the cluster is understandable. If an atom does not participate in forming the LUMO, we expect that replacing it with a similar atom (i.e., Ag with Au or vice versa) will not affect the LUMO much; hence, it will not affect propene binding.

On the other hand, exchanging one of the atoms that participate in LUMO formation should cause modifications. If the new atom is more electronegative than the one it replaces, the substitution will cause some electron density drain from the atom to which propene is bonded. This will strengthen the propene-metal bond.

It is possible that these rules work only because the atoms involved are fairly similar (Au and Ag). It will not surprise us if the rules will work for Cu, Ag, and Au. However, it is not clear whether they will be successful when Ag is replaced with a very different atom.

These rules are intellectually satisfying because they simplify considerably our view of bonding, and allow us to predict trends. For example, if a small metal cluster is bound to an oxygen vacancy at the surface of an oxide support (e.g., TiO$_2$), electron density is transferred to the cluster and propene binding is weakened. If the bond with the vacancy site involves an active atom in the cluster, this effect is stronger than if an inactive atom is involved.

The rules are also useful when performing calculations. By examining the shape of the LUMO of the naked cluster, we can determine, with a high probability of success, the binding site of the propene, the site where a substitution of a metal atom is most effective, and the direction in which this substitution affects the propene bond. This a priori knowledge can save a substantial number of computations.

Finally, we note again the propensity of these systems to form many low energy isomers. Because of this it may not be possible to think that, in a catalytic system, chemistry takes place on a cluster of a given shape. The shape of the cluster is changing all the time and cluster shapes with a shorter lifetime (of lesser stability) may contribute substantially to catalytic chemistry.

ACKNOWLEDGMENTS

Financial support from the Air Force Office of Scientific Research (AFOSR) through a Defense University Research Initiative on Nanotechnology (DURINT) grant is gratefully acknowledged. We are grateful to Greg Mills for helpful discussions.

11M. Haruta, Cattech 6, 102 (2002).
28M. J. Manard, P. R. Kemper, and M. T. Bowers (private communication).