FIRST PRINCIPLE ANALYSIS OF THE CATALYTIC REACTION PATHWAYS IN THE SYNTHESIS OF VINYL ACETATE

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Abstract—Acetoxylation of ethylene over supported palladium and palladium/gold is a well established commercial route for the formation of vinyl acetate. While the overall reaction chemistry for the synthesis of vinyl acetate was uncovered some thirty years ago (Eur. Chem. News 1967; World Pet. Cong. Proc. 1968, U.S. Patent 1967 & 1977), the active catalytic surface ensembles, key reaction intermediates, and mechanism are still poorly understood. Issues such as the oxidation state of the active centers (Pd 0 vs Pd 2+), particle ensemble size (small clusters versus large particles), rate-determining elementary steps, secondary decomposition routes, and the structural and/or electronic role of Au, have yet to be resolved. Herein, we employ first-principle quantum chemical techniques to model a series of proposed elementary steps representative of vinyl acetate synthesis. Calculations using palladium and oxidized palladium particles of varying size provide a fundamental understanding of the elementary physicochemical steps in the oxidative coupling of ethylene and acetic acid in route to the formation of vinyl acetate.

BACKGROUND
In the commercial process, ethylene, acetic acid, and oxygen are reacted over supported Pd-Au particles to form vinyl acetate and water (U.S. Patents 1967 & 1977).

\[
\begin{align*}
\text{O}_2 & + \frac{1}{2} \text{O}_2 + \text{CH}_2 = \text{CH}_2 & \rightarrow & \text{O} \rightarrow \text{CH}_3 \text{CH}_2 \text{CO} \text{OH} + \text{H}_2 \text{O} \\
& & & \text{(VA)}
\end{align*}
\]

The reaction proceeds with selectivities as high as 96%. Optimization of a mature process along with tighter market competition provides a strong incentive for a more rigorous understanding of the elementary steps which comprise the underlying mechanism. While the chemistry is carried out in a fixed bed reactor, it is still debated as to whether or not the chemistry occurs on the catalyst surface or whether small discrete palladium acetate particles form in the liquid phase and subsequently carry out the chemistry. The two competing mechanisms organize along the lines of Pd(0) and Pd(2+) centers (Moiseev et al. 1966 & 2). Mosieev et al. (1991) have championed the idea that Pd(0) centers make up the active site and proposed a rate-limiting step which involves the activation of the C-H bond of ethylene. Subsequent reaction of the vinyl intermediate with acetic acid is rapid and goes on to form the product, vinyl acetate. The alternative mechanism proposed in various forms by Mosieev et al. (1978), (1991) involves a Wacker-like process over Pd(2+). The key steps here are the initial adsorption of ethylene and acetic acid, ethylene insertion into surface acetate, C-H bond activation of the ethyl acetate intermediate, and desorption of the vinyl acetate product. Both ethylene insertion and C-H bond activation have been suggested as rate-limiting. While this mechanism was originally established for reactions carried out on homogeneous palladium acetate clusters, oxidized palladium surfaces were thought to undergo similar chemistry.

While evidence for both mechanisms exists, it has yet to be definitively established which is predominant. In addition, little is known about subsequent secondary decomposition routes which lead to the combustion of acetate and ethylene. Herein, we present initial quantum chemical results toward modelling the overall elementary steps for the proposed catalytic pathways. As a first approximation, we...
examined the primary oxidation route to vinyl acetate over small Pd(2+) homogeneous palladium clusters while secondary decomposition paths were modelled over larger palladium metal clusters.

METHODS
First principle density functional theory (DFT) was used to probe the effects of electronic and geometric structure on binding of reactants, intermediates, and products in vinyl acetate synthesis and the secondary acetate decomposition reaction pathways. Density functional quantum chemical calculations have rapidly become the standard for reliably predicting the electronic structure of complex transition metal systems. DFT, which formally scales as $N^3$ (where $N$ is the number of basis functions) provides essentially the same level of accuracy as advanced ab initio correlation methods which scale as $N^5-N^7$. This enables one to examine much more complex structures with reliable quantitative structural and energetic results. For organometallic systems, DFT methods typically provide bond lengths to within 0.01-0.05 Å, bond angles to within 3°, binding energies to within 2-5 kcal/mol, and infrared and Raman shifts to within 5% of the experimental values (Ziegler, 1991).

The DGauss program from Cray Research Inc. was used to perform all calculations described herein (DGauss 1993; and Andzelm and Wimmer 1991). DGauss employs DFT-optimized Gaussian basis sets (Godbout et al. 1992) and self-consistently solves a series of single-particle Kohn Sham equations. The Vosko-Wilk-Nusair (1980) exchange-correlation potential was used to compute the local spin density. Nonlocal gradient corrections to the exchange and correlation energies were determined in-situ to the self-consistent-field SCF calculation using the functionals developed by Becke (1988 1 & 2) and Perdew (1986) respectively. Energy gradients were computed analytically subsequent to convergence of each SCF cycle. Second derivatives and force constants were computed numerically and used to verify the stability of all ground state structures. Relativistic corrections were treated through the use of pseudo-potential basis sets for the core orbitals of palladium. All adsorbates were treated with DGauss optimized DZVP basis sets. SCF calculations were converged to within 1x10^-6 a.u. on the energy, whereas geometry optimizations were converged to within 1.0x10^-3 a.u..

CLUSTER MODELS
We examine adsorption and chemistry on the Pd$_3$O$_3$ and Pd$_{18}$ cluster models depicted in Fig. 1. These systems were chosen to mimic homogeneous oxidation by palladium acetate clusters and the secondary acetate decomposition over heterogeneous palladium particles, respectfully. Palladium acetate is known to form the stable trimer Pd$_3$OAC$_6$ structure (Skapski and Smart 1970). The large number of atoms and electrons in this system limits a rigorous first-principles analysis. The Pd$_3$O$_3$ model enables us to retain the basic trimeric form, as well as, the formal Pd(2+) oxidation state.

![Figure 1](image-url)  

Model palladium clusters analyzed. A) Pd$_3$O$_3$ and B) Pd$_{18}$ are used to model Pd(2+) and Pd(0) catalyzed chemistry.

The Pd$_{18}$ model was chosen as a balance between accuracy of the surface electronic structure and computational expenditures. Pd$_{18}$ enables all first-order interactions to be accounted for including 1-, 2-, and 3-fold binding sites. The surface is also large enough to accommodate intermediates which adsorb parallel to the surface, such as CH$_2$=COO(-).

Pd$_3$O$_3$ and Pd$_{18}$ cluster models were also included in a series of calculations which were originally performed to establish the effects of cluster size on the prediction of properties (Neurock et al. 1996). This is the subject of a future communication. Briefly, relativistic corrections were found to be important
for accurately predicting the properties of all of the clusters studied. For the case of Pd$_2$, relativistic effects, included through use of pseudo-potentials, result in a lowering of the 5s derived molecular orbital energy below that of the 4d$_{z^2}$ orbital (Nakao et al. 1993). This leads to lengthening of the bond, and formation of a triplet ground-state. Relativistic effects were found to be important for the larger Pd clusters as well. Results indicate that closed-packed "spherical" arrangements are the favored conformation for all cluster-sizes examined, in agreement with the FCC crystal structure of large Pd particles. Bond lengths increase from 2.58 Å for the dimer and converge near the bulk value of 2.75 Å as cluster size is increased. Binding energies also increased with cluster size.

While ab initio methods have required the implementation of bond preparation techniques to obtain reasonable adsorption energies (Siegbahn and Wahlgren 1991), our DFT results for the adsorption of atomic and molecular adsorbates on small to moderate clusters indicate that energies are within 5 kcal/mol of the experimental systems. Table 1 summarizes this information for several adsorbates on various transition metals.

Table 1. Comparison of DFT cluster binding energies (in kJ/mole) with experimental binding energies on a variety of transition metals.

<table>
<thead>
<tr>
<th>Atomic Adsorbates</th>
<th>Exp</th>
<th>DFT</th>
</tr>
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<tbody>
<tr>
<td>Oxygen on Cu (111)</td>
<td>431</td>
<td>449</td>
</tr>
<tr>
<td>Oxygen on Ni (111)</td>
<td>469</td>
<td>441</td>
</tr>
<tr>
<td>Oxygen on Pd (111)</td>
<td>364</td>
<td>349</td>
</tr>
<tr>
<td>Hydrogen on Pd (111)</td>
<td>259</td>
<td>251</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecular Adsorbates</th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ on Pd (111)</td>
<td>25-50</td>
<td>30</td>
</tr>
<tr>
<td>CO on Cu (111)</td>
<td>66</td>
<td>63</td>
</tr>
<tr>
<td>NH$_3$ on Cu (111)</td>
<td>~50</td>
<td>40</td>
</tr>
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Figure 2 depicts the cluster size dependence on the predicted adsorption energy for oxygen bound to different Pd$_x$ clusters. This figure nicely illustrates the well-known fact that the adsorption energy oscillates with cluster size although not as strongly as for most ab initio calculations (Neurock et al. 1996). The interesting feature here is that the amplitude of these oscillations is found to be small (+/- 40 kJ/mol for Pd$_x$ where $x > 2$) and centered about the experimental value for atomic oxygen on palladium, 360 kJ/mol. The computed Pd-O vibrational frequencies for these clusters also agreed well with known experimental spectra. For example, three characteristic Pd-O stretches for Pd$_6$O (491, 529 and 650 cm$^{-1}$), matched known experimental data for oxygen on palladium (475, 510 and 675 cm$^{-1}$) (Banse and Koel 1990). The general result here is that with a diligent accounting of appropriate spin states, optimal cluster morphologies, relativistic corrections, and explicit optimization of cluster/adsorbate geometries accurate structural, energetic, and spectroscopic information can be determined for transition metal cluster systems.

**Palladium Oxide Clusters**

The Pd$_3$ cluster was used to study the role of increasing cluster oxygen coverage on bare palladium clusters. This cluster was used as the base model due to its simplicity and its relationship to the known
Pd$_3$OAc$_6$ homogenous cluster. The results in Fig. 3 examine both the structural and the energetic changes which occur upon the addition of oxygen atoms to the bare Pd$_3$ cluster. The structures found here were quite similar to those found in an earlier study on Ni$_3$S$_x$ ensembles (Neurock and van Santen 1994). The bare Pd$_3$ cluster has two three-fold binding sites. Atomic oxygen prefers these higher-fold coordination sites. Therefore, the first two oxygen atoms add at these sites, however, subsequent addition of a third oxygen induces a significant change in the cluster morphology. This change in morphology is driven by the strong repulsive interactions of the oxygen atoms. The cluster reconstructs to accommodate all three oxygens and repulsive interactions force the oxygens into bridging positions. As might be expected, the overall energies for the addition of oxygen are highly exothermic and decrease with the cluster oxygen content (i.e., the charge on the Pd centers) as is shown in Fig. 4. The structural changes also include a bond length increase as the amount of atomic oxygen is progressively increased. The Pd-Pd distances for bare Pd$_3$ cluster are 2.56 Å and 2.66 Å, whereas the Pd-Pd bonds for Pd$_3$O$_3$ are on average 2.80 Å.

![Image](image_url)

Figure 3. DFT-optimized structure and energetics for Pd$_3$O$_x$ cluster series.

**CATALYTIC REACTION PATH ANALYSIS**

A set of elementary steps were proposed to describe reaction (1), and each was examined to determine its relevance. Adsorption energies for all proposed intermediates were computed by allowing both the cluster as well as the surface-bound adsorbates to optimize simultaneously.

**Vinyl acetate monomer synthesis over palladium oxide clusters**

The Pd$_3$O$_2$ and Pd$_3$O$_3$ clusters described were used as models for examining the elementary steps involved in the homogeneous synthesis of vinyl acetate over small palladium-oxide particles. As discussed earlier, the suggested mechanism for this route is similar to the Wacker oxidation mechanism. Two similar routes have been proposed in the literature, the inner-sphere and the outer-sphere mechanisms (Henry and Pandey 1973). In the inner-sphere mechanism, the ethylene and acetate are both bound to the surface and the reaction proceeds via the insertion of ethylene into the PdOAc bond. In the
outer-sphere mechanism, however, ethylene is bound to the surface and attacked by acetate. We concentrate our efforts herein on the inner-sphere approach.

We have chosen seven basic steps for describing the catalytic cycle representative of vinyl acetate synthesis: 1) the oxidation of Pd\(_3\)O\(_2\), 2) the dissociative adsorption of acetic acid, 3) the coadsorption of ethylene, 4) insertion of ethylene to form ethyl acetate 5) \(\beta\)-C-H scission, 6) desorption of vinyl acetate and 7) the associative removal of water. Each of these steps were analyzed in detail to determine the optimal adsorbate-cluster structures and energies. The results are depicted in Fig. 4 and 5. The optimized clusters at each stage in the catalytic cycle are presented in Fig. 4, whereas the overall energy diagram for each step of the cycle is given in Fig. 5. The overall energy of reaction for VAM synthesis is predicted from the calculations to be exothermic at -142 kJ/mol (depicted as the final energy in diagram of Fig. 5). This is very good agreement with the experimental value of -138 kJ/mol depicted by the dotted line in Fig. 5.

![Diagram of catalytic reaction pathways](image)

**Figure 4.** DFT optimized reactant, intermediate, and product structures for an inner-sphere Wacker-like catalytic reaction path for the synthesis of vinyl acetate over Pd\(_3\)O\(_3\).
Fig. 5. DFT predicted energies for the steps involved in the inner-sphere mechanism depicted in Fig. 4.

The proposed cycle is initiated by oxidizing the Pd₃O₂ cluster to Pd₃O₃. The structure and energetics for both of these complexes were discussed earlier. The energies reported earlier correspond to the binding energy of atomic oxygen (-290 kJ/mol), whereas the energy reported in step 1 of the cycle in Fig. 5 (-5 kJ/mol) refers to the overall reaction energy for the addition of a half of a mole of oxygen to Pd₃O₂ to form Pd₃O₃. The difference between the two is the energy required to break the oxygen-oxygen bond. This relatively small reaction energy for this step, -5 kJ/mol, reflects a balance between the Pd-O and O-O bond strengths for this Pd(2+) cluster.

In the next step, acetic acid dissociatively adsorbs to form acetate and hydroxyl intermediates. The high surface concentrations of oxygen enhanced the heterolytic dissociation to form the bound acetate and hydroxyl intermediates. A similar result was found experimentally for oxygen covered palladium surfaces (Davis and Barteau 1991), where oxygen disrupted catemer binding networks for acetic acid and helped to promote the surface stability of acetate. Surface oxygen was subsequently desorbed as water. As derived from the calculations, the energy required to break the O-H bond of acetic acid was more than compensated for by the formation of two acetate Pd-O bonds and a new O-H bond. The reaction is highly exothermic (-260 kJ/mol). This is consistent with stability of acetate on oxygen covered palladium metals (Davis and Barteau 1991).

Ethylene, which is known to bind in both π- as well as in di-σ modes on bare palladium (Stuve and Madix 1985, 1), was found to adsorb here on the oxidized Pd₂O₃ cluster only in a π-bonding configuration. In fact, even when ethylene is initially bound di-σ, it optimizes to a π-bonding mode. This is consistent with experimental information that at low surface coverages ethylene binds to the metal primarily through di-σ bonding, but easily converts to π-bonding as the surface coverage of oxygen (or ad-species) is increased (Stuve and Madix 1985, 1 & 2; Yagasaki et al. 1990). The adsorption energy here is rather small (-5 kJ/mol). The optimal arrangement is one in which one of the Pd-O cluster acetate bonds and ethylene share a single palladium atom center.

The coupling reaction involves the insertion of ethylene into the local Pd-OAC bond. The overall reaction energy for this path is endothermic and requires about +18 kJ/mol to form the ethyl-acetate intermediate. The ethyl-acetate then assumed to react via a β C-H bond scission to form vinyl acetate. Overall, the insertion and scission steps are highly endothermic (+131 kJ/mol) and specific to the formation of a palladium hydride intermediate. The resulting optimized cluster shown in Fig. 4 between steps 5 and 6 clearly depicts the formation of the bound vinyl acetate product. Vinyl acetate behaves similar to ethylene and π-bonds to a single palladium center.

The remaining steps in the cycle, 6 and 7, involve the desorption of vinyl acetate and the subsequent recombinative desorption of water. Vinyl acetate desorption was endothermic requiring +9 kJ/mol. This...
Catalytic reaction pathways in the synthesis of vinyl acetate

is consistent with the same low adsorption energy predicted for ethylene on Pd3O3 (-5 kJ/mol). The recombinative desorption of water is exothermic at -31 kJ/mol. Upon the removal of water, the cluster returns to its original Pd3O2 morphology. The insertion and scission steps were the most highly endothermic steps in the overall cycle. To a rough approximation, we might consider these steps as candidates for the rate-limiting step. This qualitatively agrees with the literature on homogeneous VAM synthesis (van Helden et al. 1968, Henry and Pandey 1973; Samanos et al. 1971). Complete transition state searches, however, are required in order to quantitatively discern which steps in the cycle are rate-limiting.

Closer examination of Fig. 4 indicates that the chosen reaction path depicted involves the formation of a palladium hydride intermediate. At higher oxygen coverages, a second route also exists, whereby the C-H bond dissociates to form a proton which attacks a neighboring oxygen to form a stable hydroxyl group. Calculations indicate that the thermodynamics for this path is more favorable than the previous path. This is related to the fact that the O-H bond is substantially stronger than the Pd-H bond. By including the oxygen-assisted bond activation path, the β C-H bond scission step is reduced in energy from +131 kJ/mole to -10 kJ/mole making the thermodynamics of this step much more favorable. Subsequent analysis of the activation barrier, however, is required to determine whether or not oxygen plays a direct role in the β C-H activation. A simple analysis of the thermodynamics suggest that ethylene insertion may become rate limiting.

Secondary Decomposition of Acetic Acid

In addition to the primary selective oxidation route, there are a number of paths which lead to the over-oxidation of acetic acid to form CO and CO2. We examined the overall path for the secondary decomposition of acetate to CO2 and surface CHx species. Preliminary experimental studies indicate that this route occurs most prevalently over palladium metal rather than Pd(2+) (Provine et al. 1996). Therefore, we probed the adsorption of relevant intermediates on bare palladium clusters. We focus primarily on the interaction of acetate on Pd. The Pd18 cluster presented above was chosen because it provides a large surface for reliable energetic information for the binding of acetate with coadsorbates and parallel bound intermediates.

A series of initial scouting calculations indicated that the most energetically favorable interaction for acetate on Pd(111) came from di-σ bonding. Acetate sits nearly perpendicular to the surface and binds through two equivalent Pd-O bonds. The optimized structure is depicted in Fig. 6A. The 2.17 Å Pd-O bond lengths are consistent with surface hydroxyl, and alkoxy intermediates as well as with the known Pd3OAc6 structure (Skapsik et al. 1970). The computed C-O bonds are 1.29 Å which places them between the 1.22 Å C=O bond and the 1.37 Å C-OH bonds for gas phase acetate. This is indicative of a relatively strong Pd-O surface interaction. The C-C bond (1.517 Å) is then 0.1 Å shorter than the gas phase C-C bond.

The influence of surface relaxation was modelled by allowing the three local Pd neighbors to simultaneously optimize along with the surface acetate. The results indicate that the Pd-Pd bond of the bidente PdOAc structure is essentially held fixed while all subsequent bonds to these atoms are elongated. The energy required to open the O-C-O angle may effectively be restricting the Pd-Pd bond from elongating. The binding energy for acetate was found to be -240 kJ/mol which is nearly 40 kJ/mol greater than the that predicted for the frozen Pd18 cluster.

The decomposition of acetate to the CO2 and surface CHx fragments was thought to be controlled by the C-H bond activation of the terminal CH3 group. We analyzed the structure of the resulting CH2=CO2(-) surface intermediate. As the C-H bond is broken the acetate intermediate begins to approach the surface. Upon the complete dissociation, the CH2=CO2(-) product binds parallel to surface through the two Pd-O bonds and through a π interaction with the C=O bond that is formed. The resulting structure is depicted in Fig. 6B. The CH2=CO2(-) species positions itself so as to enhance the interaction of the CO2 carbon over the three-fold hollow site and the interaction between the tail carbon and the central palladium atom. These direct surface interactions result in rehybridization of the sp2 orbitals to an sp3 arrangement and elongation of the C-C bond (1.491 Å). This is similar to the binding of ethylene on Pd (Ibach and Lehwald 1978; Steininger et al. 1982; Winham et al. 1988). The overall decomposition step in Fig. 6 is endothermic (+69 kJ/mol).

INFLUENCE OF COADSORBED OXYGEN

Bartean and Davis (1991) found that the coadsorption of oxygen with acetate essentially eliminated the formation of acetic acid catenmers on the Pd. In addition, surface oxygen was found to stabilize acetate binding and inhibit acetate decomposition kinetics. In order to examine this, we added a single oxygen atom to our model Pd18 cluster. Bond order conservation principles suggest that the most favorable
interaction between surface oxygen and acetate would be one in which the two adsorbates are one surface palladium-palladium bond removed from one-another. This corresponds to the structure depicted in Fig. 7A whereby the two Pd-Pd bonds separating the adsorbates are weakened. In theory, this should give rise to enhanced acetate adsorption. DFT cluster optimizations indicate little change in acetate binding geometry and an increase in the adsorption energy by 12 kJ/mol. This modest increase in the adsorption energy is consistent with the small increase in the temperature of acetate desorption reported by Barteau and Davis (1991).

Repulsive through-surface and through-space interactions between the CH$_2$=CO$_2$(-) and the OH product surface species require that the two species be separated. As the acetate bends toward the surface, repulsion forces the adsorbed oxygen intermediate to move away toward an adjacent three-fold site. This proves to be an interesting reaction coordinate, whereby the oxygen species needs to accept the transferring proton yet maintain its distance from the approaching acetate. The repulsion and related requirement for vacant neighboring surface sites is consistent with results of Barteau and Davis (1991), in that the acetate decomposition is inhibited due to the presence of oxygen. The optimized final surface structure for CH$_2$=CH$_2$O(-) and OH is depicted in Fig. 7B. The overall energy for this route which is +60 kJ/mol, is slightly less endothermic than the route over bare Pd.

Fig. 6. The binding (A) and C–H bond activation (B) of acetate on a model Pd(111) cluster.

Fig. 7. The influence of coadsorbed oxygen on the binding (A) and C–H activation (B) of acetate on a model Pd(111) cluster.
SUMMARY AND CONCLUSIONS
First-principle theoretical calculations were used to provide relevant fundamental information on adsorbate-surface interactions on palladium clusters and surfaces. The results were used to predict overall catalytic reaction cycles for vinyl acetate synthesis. For well-defined transition metal systems, density functional methods provide very good predictions of structure (to within 0.05 Å) and reliable energetic predictions (within 5 kcal/mol). The addition of oxygen to small Pd₃ particles is highly exothermic. In the inner-sphere mechanism for vinyl acetate synthesis, ethylene insertion and ¹³ C-H bond activation are the most highly endothermic paths. ¹³-C-H scission, however, is much more favorable in the presence of adjacent oxygen species which will readily accept the proton. While thermodynamically favorable, this path may still be rate-limiting, especially if the reaction coordinate involves a palladium insertion into the C-H bond.

DFT calculations studying the energetics of acetate on Pd₁₈ revealed that coordinates perpendicularly to a palladium (111) model through a di-σ bonding. The initial C-H activation results in the parallel bond CH₂=CO₂(-) surface intermediate. The presence of oxygen enhances the acetate stability by 12 kJ/mole and provides a Bronsted base site which readily accepts the dissociated proton. The repulsion between the approaching CH₃ group and the O surface species, however, forces the surface oxygen to move to a neighboring three-fold site.

REFERENCES
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