Gold-Palladium Nanocluster Catalysts for Homocoupling: Electronic Structure and Interface Dynamics

by

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Gold-Palladium Nanocluster Catalysts for Homocoupling: Electronic Structure and Interface Dynamics

Masahiro Ehara*[^a,b] and U. Deva Priyakumar[^c]

Abstract: The gold-palladium (Au–Pd) bimetallic nanocluster (NC) catalyst in colloidal phase performs the homocoupling reaction of various aryl chlorides (Ar–Cl) under ambient conditions. We have systematically investigated various aspects of the Au–Pd NC catalysts with respect to this homocoupling reaction by using density functional theory (DFT) calculations, genetic algorithm (GA) approaches, and molecular dynamics (MD) simulations. Our findings include the geometric and electronic structures of the Au–Pd NC, the reactive Pd sites on the NC surface, the electron-donating effects of surrounding polymer matrix, the reaction mechanism of homocoupling reaction and rate-determining step, the inverse halogen dependence of the reaction, and the solvation dynamics at interface region between NC and polymer matrix in aqueous solution.

Keywords: Au–Pd nanocluster catalysts, Ullmann coupling, DFT calculations, MD simulations, Genetic algorithm

1. Introduction

Nanocluster (NC) catalyst performs unique chemical reactions which bulk surface of the same metal does not show owing to the geometric effects like surface-atom arrangement and low-coordinated atoms, and the electronic effects like perturbation from support and quantum size effects. The NC catalysts not only offer the possibility of unique reactions, but also provide the advantages of high efficiency and good recyclability, and allow “ligand-free” synthesis. In the past three decades, various NC catalysts have been extensively developed since the pioneering works of Haruta et al. for gold (Au) NC catalysts.[^1–5] Generally, these NC catalysts are supported or stabilized by metal oxides[^1] or polymer matrix.[^6–8] These metal oxide support and polymer matrix not only stabilize the NC, but also activate the NC electronically. By introducing the bimetallic NC, the activity of NC catalysts can be enhanced and even new reactions can be achieved that are not possible in the monometallic counterparts.[^7–9] Among these bimetallic NC catalysts, the various catalytic reactions have been developed with Au–Pd NC catalysts,[^10–12] in which the monomeric Pd sites are utilized.[^10,11] Characteristic effect of atomic Pd was also reported; single Pd atom doping in Au NC drastically enhances the catalytic activity for aerobic oxidation of alcohols.[^13]

Among the methods available for synthesizing symmetrical biaryls, Ullmann coupling reaction is one of the most useful strategies. The reaction was originally developed for synthesizing biaryls from aryl iodides using copper catalysts at high temperature.[^14–16] More recently, reactions using aryl bromides or chlorides were introduced in the presence of a co-reductants under mild conditions based on homogeneous and heterogeneous catalysts.[^17–20] Unfortunately, the Ullmann coupling reaction of aryl chlorides has been limited until recently.[^19,21] This is because the activation of C–Cl bond is...
more difficult than the activation of C–Br and C–I bonds; bond energies are C–Cl (96) > C–Br (81) > Cl–I (65) in kcal mol\(^{-1}\). Generally, aryl chlorides are more cost effective than bromides or iodides, and therefore the reaction using aryl chlorides is desirable. In view of coupling reaction using NC catalysts, there are several difficulties, for example, the oxidative addition needs to occur twice within a single catalytic cycle with all C–M intermediates resisting hydrogenation by co-reductants.\(^{[22]}\)

In 2012, it was found that the Au–Pd bimetallic NC performs Ullmann coupling reaction using aryl chlorides under the ambient condition.\(^{[23,24]}\) The Au–Pd NCs are stabilized by the hydrophilic polymer, for example, poly-N-vinylpyrrolidone (PVP) in colloidal liquid media.\(^{[6,25–27]}\) Interestingly, this reaction does not proceed in monomeric Au or Pd NC and their physical mixture, but only Au–Pd alloy NC conducts this reaction as shown in Table 1. The reaction proceeds in the basic condition, namely in KOH or K\(_2\)CO\(_3\) and in the presence of dimethylformamide (DMF) in water. The reaction is general for various substrates of aryl compounds with various substituents at some positions.

Table 1. Reaction condition and observed yield for Ullmann coupling reaction of ArCl on Au–Pd NC catalysis.\(^{[23]}\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Base</th>
<th>T/C</th>
<th>t/h</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au:PVP</td>
<td>K(_2)CO(_3)</td>
<td>45</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>Pd:PVP</td>
<td>K(_2)CO(_3)</td>
<td>45</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>Au(<em>{0.5})Pd(</em>{0.5})</td>
<td>K(_2)CO(_3)</td>
<td>45</td>
<td>24</td>
<td>30</td>
</tr>
<tr>
<td>Au(<em>{0.5})Pd(</em>{0.5})</td>
<td>KOH</td>
<td>27</td>
<td>24</td>
<td>98</td>
</tr>
<tr>
<td>Au(<em>{0.5})Pd(</em>{0.5})</td>
<td>KOH</td>
<td>27</td>
<td>24</td>
<td>98</td>
</tr>
</tbody>
</table>

Although the reaction proceeds for aryl chloride (ArCl) in high yield over 90% for various substrates, the reaction yield is drastically reduced for aryl bromide (ArBr) and the reaction does not even proceed for aryl iodide (ArI); namely, the inverse halogen dependence was observed in this system.\(^{[28,29]}\)

Later, an efficient and durable Au–Pd NC catalyst has been developed using ion-exchange resin support.\(^{[30]}\) The Au–Pd NC catalyst also has other various potentials with appropriate metal oxide support depending on the substrates and reactions; for example, the Au-Pd supported on Nb\(_2\)O\(_5\) (Au–Pd/Nb\(_2\)O\(_5\)) performs selective hydrosilylation in high yield,\(^{[31]}\) while Au–Pd/TiO\(_2\) catalyzes cycloaddition of alkynes.\(^{[32]}\)

Theoretically, we have extensively investigated the NC catalysts both in colloidal phase stabilized by polymer matrix and supported on metal oxides. For the colloidal phase Au NC catalysts stabilized by PVP, we clarified the mechanism of some catalytic reactions using DFT calculations; for example aerobic oxidation of alcohols,\(^{[33,34]}\) homocoupling of phenylboronic acid,\(^{[35]}\) and intramolecular hydroamination by a primary amine of an unactivated alkene.\(^{[36]}\) We have also worked on the mechanistic crossover in the CO oxidation on nucleobases tagged Au NC.\(^{[37]}\) In these theoretical works, the systems of NC catalysts with multi-step reactions are large in size and complicated and therefore, reliable calculation as well as high-throughput computation is required. Therefore, we carried out the benchmarks\(^{[38,39]}\) regarding the DFT functionals and basis sets with the reference of highly-accurate \textit{ab initio} calculations including completely renormalized coupled

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cluster singles, doubles and noniterative triples (CR-CC(2,3)) approach.\textsuperscript{[40]} We also worked on the synergetic alloy effects and metal-support interaction of metal NC catalysts. For the alloy effect, we have intensively investigated the colloidal phase Au–Pd bimetallic NC catalysts for homocoupling of ArCl.\textsuperscript{[23,28,41–43]} For the metal-support interaction, we have investigated the selective hydrogenation on Ag NC/Al₂O₃ and CO oxidation on M₄/Al₂O₃ etc.\textsuperscript{[44,45]} In these works, we demonstrated that the reactivity is controlled in delicate energetics and by some predominant factors. For example, the reactivity is correlated to the d-band center of each metal atom and the perimeter site, i.e. interface between NC and support, is relevant as the catalytic center.\textsuperscript{[44,46]} We also systematically investigated the geometric structure and bond activation of bimetallic Cu–M (M: group 8–11 metals) NCs,\textsuperscript{[47]} in particular, the catalytic activity of Cu–Rh NC.\textsuperscript{[48]} Through these systematic studies on NC catalysts, we have clarified some important aspects of the NC catalysts.

PVP has not only been shown to stabilize NCs in solution but also has been shown to actively take part in the catalytic process by altering the electronic distribution and hence enhancing the catalytic activity of the NCs.\textsuperscript{[41,49,50]} The concentration and length of PVP and stabilizers in general also has a significant effect on the size and shape of nanoparticles synthesized. The structures and dynamics of polymer dispersed NCs are poorly understood and NC catalyzed reaction modeling is usually carried out on pristine clusters. Similar to PVP, metal nanoparticles dispersed in peptides have also been shown to determine their size/shape and catalytic properties related to Stille coupling reactions.\textsuperscript{[51,52]} Modeling a system with explicit presence of PVP structures adsorbed to NCs in presence of water using DFT approaches is not practical and hence MD simulations based on force fields are used to investigate this phenomenon.\textsuperscript{[53,54]} Previously, MD simulations have been used to obtain atomistic level details of NCs adsorbed to proteins, DNA, lipids and dendrimers.\textsuperscript{[55–61]} Most of these studies used Lennard-Jones (LJ) potentials for the metal NCs, and this methodology was shown to reasonably reproduce the energetics and geometric features obtained using DFT methods.\textsuperscript{[45]} Recently, Heinz and coworkers have developed a method based on the combination of LJ potential, harmonic bond stretch potential and a Coulomb electrostatic term to include the polarization effects. They demonstrated that the density, surface tension and mechanical properties for Au surfaces calculated using this method are in excellent agreement with experiments and that this models performs better than some DFT methods.\textsuperscript{[62,63]}

In the series of works, we have theoretically investigated the origin of the catalytic activity of the Au–Pd NC catalysts using the DFT calculations, GA approaches, and MD simulations with respect to (1) the geometric and electronic/
2.2. MD Simulations

Au–Pd alloys of five different sizes (Au$_x$Pd$_{1-x}$; $x$ = 10, 19, 28, 40 and 50) were chosen as model systems to study the PVP interactions with NCs. The initial structures of these NCs were obtained using the GA method as explained in the previous section. Monomeric moiety, N-ethylpyrrolidone (EP) was used as the model for PVP to enable proper equilibration. MD simulations were performed using the LJ parameters from Heinz et al. for the NCs[73] and CHARMM general force field[74,75] for EP along with TIP3P water model. All the five NC model systems were simulated in up to eleven different concentrations of aqueous EP (0 to ~13.5 % EP in water). The protocol followed an initial energy minimization followed by 1 ns equilibrium simulation with harmonic restraints on the NC and the non-hydrogen atoms of EP and finally 100 ns production simulation in the NPT ensemble without any constraints. The structural and energetic factors were analyzed using thermodynamic free energy calculations, interaction energy calculations, local mole fraction enhancement, radial distribution function and adsorption isotherm analyses. Initial the ability of the force field used here to model these systems correctly was validated by comparing the structures and adsorption energies obtained using M06-L method.[43]

3. Results and Discussion

3.1. Geometric and Electronic Structures of Au–Pd NC

The structure and phase of bimetallic NCs are relevant for their catalytic activity. Possible NC structures are phase-separated, fused-alloy, and core-shell structures, which depend on various factors like combination, composition, or ratio of binary metals and the preparation procedure. The structure of the bimetallic NC affects the catalytic activity because of their geometric and electronic structures, charge polarization, and spin states. Various theoretical works have been performed to predict the NC structures. Recently, the structure of Cu–M (M = group 8–11 metals) binary NC has been systematically investigated using M06 NC.[47] It was found that the segregation energy, that is the energy difference between the core and shell position of metal-doping, correlates well with the d-population change of the doped metal. For group 8 and 9 elements, Cu–M binary NC shows core-shell structure with M in core position, and for group 10 and 11 elements, the fused-alloy structure is preferred. In the case of Au–Pd NC, the GA and DFT calculations showed that the small Au–Pd NC has fused-alloy structure with both Au and Pd atoms existing on NC surface as explained below.[41,43]

For calculating the entire reaction energy profile, small Au–Pd NC was selected for the computational model. Figure 1 shows some of the low-lying stable structures for the Au$_{10}$Pd$_{10}$ NC. Many stable geometric structures in singlet to quintet spin states exist for this size of Au–Pd NCs. Generally, Pd atom prefers to be located in the core-position, while Au atom tends to at shell-position.[41] Relatively small-size Au–Pd NCs with the ratio of 1:1 like Au$_x$Pd$_{1-x}$ NC is stable in fused-alloy structure. This trend was also observed in larger NC as seen in Section 3.6.[43]

![Figure 1](image-url)  
(a) Stable structures of Au$_{10}$Pd$_{10}$ NC and (b) energy profile (kcal mol$^{-1}$) for the oxidative addition of ArCl on Au$_x$Pd$_{1-x}$ NC in some structures and spin states. Only the active-center Pd site of NC is shown.[41]  
1A state in C$_1$ symmetry is abbreviated as 1C$_1$ state.
oxidative addition step, \(^{1}\)A state in \(\text{C}_1\) symmetry abbreviated as \(^{0}\)C\(_1\) state has low energy barrier, although it is located slightly higher in energy at bare NC. The trends of the results were similar among the DFT calculations with different functionals; B3LYP, M06-L, and TPSS were examined for the adsorption energy, energy barrier and reaction energy.\(^{[41]}\) The energy barriers obtained using pure functionals (M06-L,\(^{[64]}\) TPSS\(^{[76]}\)) are lower than those using hybrid functional (B3LYP\(^{[77]}\)).

### 3.2. Effects of Surrounding PVP

In colloidal phase NC catalyst, the Au–Pd NC is stabilized by polymer matrix like PVP. Beside the role of stabilization of NC, the PVP matrix plays an important role in activating the surface of the Au–Pd NC,\(^{[41]}\) or more precisely, the Pd atoms surrounded by Au atoms as seen in Section 3.3. Calculations on the model system of Au\(_{10}\)Pd\(_{10}\) NC adsorbed by four ethylpyrrolidone (EP) molecules, which is the unit of PVP, (Au\(_{10}\)Pd\(_{10}\):4EP) indicated that PVP domain donates electron density to the Au–Pd NC and has the effect of reducing the energy barrier of the oxidative addition. The energy barriers of the Au\(_{10}\)Pd\(_{10}\) (neutral), Au\(_{10}\)Pd\(_{10}\)\(^{−}\) (anion), and Au\(_{10}\)Pd\(_{10}\):4EP model systems are compared in Table 2. Coordination of four EP molecules reduces the activation energy barrier by 3.1 kcal mol\(^{−1}\) at Pd site compared to the values of Au\(_{10}\)Pd\(_{10}\) (neutral, \(^{0}\)C\(_1\)) and Au\(_{10}\)Pd\(_{10}\):4EP (\(^{0}\)C\(_1\)). The activation barrier obtained using Au\(_{10}\)Pd\(_{10}\)\(^{−}\) (anion) (7.2 kcal mol\(^{−1}\)) is similar to that by using Au\(_{10}\)Pd\(_{10}\):4EP (7.9 kcal mol\(^{−1}\)). The electron-donation of PVP was experimentally observed by XPS and the electron donation was also confirmed in the Au–PVP system by theoretical calculations.\(^{[33,49]}\)

<table>
<thead>
<tr>
<th>Model</th>
<th>(E_a), kcal mol(^{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(<em>{10})Pd(</em>{10}) (neutral)</td>
<td>11.0</td>
</tr>
<tr>
<td>Au(<em>{10})Pd(</em>{10}):4 EP</td>
<td>7.9</td>
</tr>
<tr>
<td>Au(<em>{10})Pd(</em>{10}) (anion)</td>
<td>7.2</td>
</tr>
</tbody>
</table>

In the real system, some PVP segments of polymers coordinate and stabilize the Au–Pd NC, and the ArCl undergoes oxidative addition at the vacant sites of Au–Pd NC or PVP desorbed sites. The solvation dynamics at interface and surface coverage will be explained in Section 3.6.

### 3.3. Active Sites

The catalytic center of the Au–Pd NC would consist of low-coordinated Pd atom(s) at the corner or edge sites. The present Au–Pd NC:PVP catalytic system shows high activity in the alloy ratio of Au\(_{10}\)Pd\(_{10}\) and therefore it is expected that both Au and Pd atoms exist on the NC surface, which is also supported by GA calculations for large Au\(_{18}\)Pd\(_{2}\) NCs (n = 19–50), although Pd atom prefers to be in core position.\(^{[43]}\)

For elucidating the reaction center, the Pd, Pd–Pd, and Au sites in Au\(_{18}\)Pd\(_{10}\) NC, and Au sites in Au\(_{18}\)Pd\(_{6}\) and Au\(_{20}\) NCs were examined for oxidative addition. Note that the Au\(_{18}\)Pd\(_{2}\) NC has a core-shell structure, although it is a small NC model system. The results of the energy barrier are summarized in Table 3. The DFT calculations showed that the energy barrier of oxidative addition is generally high at Au sites, namely higher than 27.5 kcal mol\(^{−1}\) in Au\(_{10}\)Pd\(_{18}\) NC, while it is significantly low at the Pd and Pd–Pd sites, at around 11.0 and 8.2 kcal mol\(^{−1}\), respectively. The Au\(_{18}\)Pd\(_{2}\) NC model shows that the coordination of core Pd atoms to shell (surface) Au atoms reduces the activation barrier (32.3 kcal mol\(^{−1}\)) compared to Au\(_{10}\) NC case (40.4 kcal mol\(^{−1}\)), but still not enough to allow C–Cl bond activation at room temperature. In these examinations, we compared the energy barrier for the lowest spin state of each NC and the trend of energy barrier is similar in other spin states. Therefore, in the Au–Pd system for the reaction with Ar–Cl bond activation, it was suggested that the reaction center is the Pd and Pd–Pd sites on the surface of NC.\(^{[41]}\)

**Table 3. Energy barrier (\(E_a\), in kcal mol\(^{−1}\)) of the oxidative addition for various sites of Au–Pd and Au NCs.**\(^{[41]}\)

<table>
<thead>
<tr>
<th>Model (site)</th>
<th>(E_a), kcal mol(^{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(<em>{10})Pd(</em>{10}) (Pd site)</td>
<td>11.0</td>
</tr>
<tr>
<td>Au(<em>{10})Pd(</em>{10}) (Pd–Pd site)</td>
<td>8.2</td>
</tr>
<tr>
<td>Au(<em>{10})Pd(</em>{10}) (Au site)</td>
<td>27.5</td>
</tr>
<tr>
<td>Au(<em>{18})Pd(</em>{2}) (core-shell, Au site)</td>
<td>32.3</td>
</tr>
<tr>
<td>Au(_{20}) (Au site)</td>
<td>40.4</td>
</tr>
</tbody>
</table>

### 3.4. Entire Reaction Mechanism

The entire reaction mechanism of Ullmann coupling was elucidated based on experimental evidences and theoretical calculations.\(^{[42]}\) The difficult issue in the present catalytic reaction is that the oxidative addition of substrate (ArCl) occurs at least twice and the coupling reaction proceeds without hydrogenation to generate benzene. The reaction systems consist of DMF and base (KO\(_H\) or K\(_2\)CO\(_3\)) besides the NC catalysts and substrate (ArCl) as noted in introduction. From the isotope labeling experiment, the hydrogen transfer from DMF to the NC surface was found to be the
rate-determining step. Based on the experimental facts, the possible catalytic cycle of the present Ullmann coupling reaction of \( \text{ArCl} \) as well as its competitive reaction, benzene formation, was examined by the DFT calculations. The proposed catalytic cycle is shown in Scheme 1. There are two possible pathways, that is (1) the \( \text{ArCl} \) oxidative addition followed by the Cl abstraction from the NC surface occurs twice stepwise (outer blue cycle) and (2) the successive oxidative addition of two \( \text{ArCl} \) proceeds before the Cl abstraction (inner red cycle).

The energy profiles for these pathways were computed by DFT calculations using the model cluster of \( \text{Au}_{10}\text{Pd}_{10} \) NC. The solvent effect was considered by the SMD method of aqueous solution. The geometry optimizations were conducted without any restriction of the internal coordinates. In pathway I, the Cl atom is abstracted by DMF and KOH before the second \( \text{ArCl} \) oxidative addition occurs. The energy profile of the first half of the reaction is shown in Figure 2. The rate-determining step was the proton transfer from DMF to \( \text{Au}–\text{Pd} \) NC surface, which agrees well with the deuterium labeling experiment. The energy barrier of this step (18.8 kcal mol\(^{-1}\)) was considerably reduced by the assistance of water molecule; namely, it was reduced via the proton shuttle by about 10 kcal mol\(^{-1}\). After the desorption of \( \text{Me}_2\text{NH} \) and \( \text{CO}_2 \) from NC surface, the Ar–X–H species is generated where X denotes Au–Pd NC.

The second \( \text{ArCl} \) dissociative adsorption follows this step and the homo-coupling reaction proceeds without the reduction to benzene. The activation energy barriers of these steps are significantly low except for the reductive elimination of biphenyl; the energy profile is smooth and slightly exothermic as shown in Figure 3. The generation of benzene is prohibited by the relatively high energy barrier (~15.0 kcal mol\(^{-1}\)). From these computational results, it was found that the present coupling reaction is controlled by the delicate energetics.

The energy profile of pathway II is also smooth without large energy barriers, which is referred to the original article.[42] The DFT calculations have clarified the entire reaction mechanism of the homo-coupling reaction of \( \text{ArCl} \) on \( \text{Au}–\text{Pd} \) alloy NC. The multi-step reaction occurs in exothermic pathways. The entire reaction is controlled by some relevant factors consisting of the colloidal phase NC catalyst, namely, the electron donation from surrounding polymer media and the abstraction of the resultant Cl atoms by solvent or base.[42] The mechanism and energetics of entire reaction obtained by theoretical calculations would be useful for further developing the NC catalysts for related reactions.

### 3.5. Inverse Halogen Dependence

As noted in introduction, the yield of the present reaction on \( \text{Au}–\text{Pd} \) NC catalyst drastically reduces for other hydrides which are usually used in coupling reactions. For example, yield was 48% for ArBr in the same reaction condition and even the reaction never proceeded in the case of ArI; namely, the inverse halogen dependence was observed.[28,29] To elucidate the origin of this dependence, the oxidative addition of ArBr on \( \text{Au}_{10}\text{Pd}_{10} \) NC was examined in the presence of aqueous solution by the DFT calculations.[28] As shown in Figure 4, the energetics of the oxidative addition of ArBr on the \( \text{Au}_{20} \) and \( \text{Au}_{10}\text{Pd}_{10} \) NCs is almost the same as the \( \text{ArCl} \) case. For \( \text{Au}_{20} \) NC, both direct and indirect dissociations of Ar–Br bond are possible. Although the energy barriers of ArBr are lower than those of \( \text{ArCl} \) case, the calculated energy barriers are too high (29.6 and 27.6 kcal mol\(^{-1}\)) in the case of \( \text{Au}_{20} \) NC. On the other hand, the energy barriers are significantly reduced on \( \text{Au}_{10}\text{Pd}_{10} \) NC to 10.0 and 7.0 kcal mol\(^{-1}\) for the direct and indirect dissociation, respectively. Thus, the C–Br bond activation is energetically feasible to proceed on \( \text{Au}_{10}\text{Pd}_{10} \) NC at least. The reaction starts from the adsorption of Ar–\( \text{Br} \) forming a \( \pi \)-complex on the facet site of \( \text{Au}_{20} \) NC or on the Pd–Pd bridge site of \( \text{Au}_{10}\text{Pd}_{10} \) NC, respectively. Again, the direct coordination effect of the Pd atom plays an important role in this step.

Another relevant factor is the leaching of surface Pd atoms from \( \text{Au}–\text{Pd} \) NC generating the Pd complex with aryl halides (ArX), which might also be possible after the ArX adsorption; for example, in the case of \( \text{Au}_{20}–\text{Pd}_{8} \) NC the oxidative addition at a single Pd atom affords Pd(II) complex as,
ArX + 2H₂O + Au₀₂₋ₐPdnₐ →

ArPd ((H₂O)ₓX + Au₀₂₋ₐPdn₋₁ (X=Cl, Br).

To examine this possibility, the free energy changes (ΔΔG₂₉₈) of the leaching process for both ArBr and ArCl were calculated for some Au–Pd NCs with different Pd ratios; namely, Auₓ₋ₐPdnₐ NCs (n = 0, 1, 4, 10, 20). The solvation free energy change in each Au–Pd NC is shown in Figure 5 for ArCl and ArBr cases. In Equation (1), the energy of Auₓ₋ₐPdn₋₁ NC is dependent on a defect site of Auₓ₋ₐPdn₋₁ NC due to the leaching of Pd complex and therefore, the calculated free energy changes have some range as shown by error bars in Figure 5. Negative energy means the leaching process is preferred.

The free energy changes show that the leaching of surface Pd atoms from Au–Pd NC could occur in the case of ArBr after oxidative addition. The surrounding PVP domain may prevent the desorption of the Pd(II) complex, while this process is unlikely in the case of ArCl. The leaching of Pd(II) complex was also experimentally observed. As shown in Ref., the catalytic reaction via the C–Br bond activation towards Ullmann coupling occurs on the Au–Pd NC via the formation of Br spillover intermediate (heterogeneous path). Formation of such intermediate was assumed to be a crucial factor for the coupling reaction. This process was also validated by the experiments. However, the leaching of Pd(II) complex from Auₓ₋ₐPdn₋₁ to generate Auₓ₋ₐPdn₋₁ and ArPd(H₂O)ₓBr is also energetically favorable (homogeneous path). Consequently, this pathway prohibits the coupling reaction. The exothermicity in the case of ArBr increases as the ratio of Pd in Au–Pd NC increases, while it is endothermic for ArCl except for Pd-rich Au–Pd NC. This is consistent with the experimental observation that leaching of Pd occurs in Pd-rich Au–Pd catalyst.
3.6. Dynamics of the PVP Dispersed NCs

In colloidal NC catalyst, the effects of surrounding polymer matrix are crucial, for example, the polymer length affects the catalytic activity and also the morphology, which is attributed to the coverage of the metal NC by polymer matrix.
Therefore, the adsorption dynamics at interface is relevant for the catalytic activity as seen in the preceding sections. In this regard, we investigated the solvation and adsorption dynamics at the interface region of the Au–Pd NC with EP in aqueous solution by using the MD simulations.\(^\text{[43]}\) MD simulations on the metal NC systems in organic solvent is not so straightforward, in particular, with respect to the force field parameters of metals and their interaction with organic molecules. We used a LJ energy function to model a rather complicated problem and hence examining the quality of the energy function and the parameters is crucial.\(^\text{[73]}\) Thus, for the MD simulation of metal NC in aqueous EP solution, the force filed parameters were assessed by comparing the structures and the adsorption energies of the Au–Pd NC-EP systems using the DFT calculations. The structures of the NCs used here are shown in Figure 6(a). As discussed in Section 3.1, Pd atoms prefers core position, while Au atoms prefers shell position. In the modeling of Au\(_{10}\)Pd\(_{10}\) system, the mixed alloy structures were obtained as the most stable structure by the GA calculations. On the NC surface, both Pd and Au atoms exist although the ratio of Pd is much less than that of Au. As discussed in Sec. 3.3, the Pd atom is suitable for the active site in view of activation energy barrier.

Figure 6(b) shows the comparison of the EP-adsorption structures optimized by the MM and DFT-M06-L (QM) calculations for Au\(_{10}\)Pd\(_{10}\)-EP\(_m\) (\(m = 2, 8, \text{and } 14\)): other adsorption structures with different number of EP molecules were also examined in the original article.\(^\text{[43]}\) Regardless of the number of EP molecules adsorbed, the MM and QM calculations provided nearly the same structures as seen in Figure 6(b). Comparison of the adsorption energies of the NC-EP obtained from the QM and MM methods indicate very good agreement although there is a minor quantitative deviation. Adsorption energies per EP molecule varies in 20–25 kcal mol\(^{-1}\) with the value decreasing as the number of EP molecules increases. Such good agreement in adsorption structures and energies supports the validity of the present force field of Heinz et al.\(^\text{[73]}\) used for the MD simulation.

MD simulations were performed for the five different sized Au\(_n\)Pd\(_n\) NCs in aqueous EP solution with various concentration of EP. The production simulations were performed for 100 ns for each system totaling about 5 \(\mu\)s and the mean interaction energies were calculated over the last 80 ns of each of the simulation. The interaction energy increases as the EP concentration increases and converges at around 2% EP in aqueous solution to the value in the range of \(-800--200\) kcal mol\(^{-1}\), which depends on the size of Au–Pd NC.\(^\text{[43]}\) The interaction energy was calculated between the NC and rest of the solvent box using the LJ energy term. The two-dimensional (2D) probability distributions of the interaction energies from NC-water and NC-EP are shown in Figure 7(a) in the case of Au\(_{50}\)Pd\(_{50}\). The trend of the interaction energies was almost the same for other size of Au\(_n\)Pd\(_n\) NCs.\(^\text{[64]}\) As the concentration of aqueous EP solution increases, the NC-EP interaction becomes more favorable, while NC-water interaction less favorable. This is because the adsorption energy of EP molecule on NC surface is much larger than that of water molecule. Free energy calculations also confirmed this effect. In the simulations, it was noted that water is mostly excluded from the surface of the NC within the first few nanoseconds of the simulation and the

![Figure 6](image_url)

**Figure 6.** (a) The stable structures of the Au\(_n\)Pd\(_n\) (\(n = 10, 19, 28, 40, \text{and } 50\)) obtained by the GA calculations and (b) the optimized geometries of Au\(_{10}\)Pd\(_{10}\)-EP\(_m\) (\(m = 2, 8 \text{ and } 14\)) systems obtained by MM and DFT(M06-L) methods that are shown in red and gray color, respectively.\(^\text{[43]}\)

![Figure 7](image_url)

**Figure 7.** (a) The 2D probability plot of the interaction energies of Au\(_{50}\)Pd\(_{50}\) NC with EP and water molecules for different concentration of aqueous EP. (b) The 2D plot of the number of EP and water molecules.\(^\text{[43]}\)
NC is mostly covered by EP molecules. This effect was more pronounced in the lower concentrations of aqueous EP and no significant change was observed at higher concentration above 1.5% because the NC surface area are saturated. This trend was also seen in the 2D plot of the numbers of EP and water molecules adsorbed on Au–Pd NC surface, which is shown in Figure 7(b). Due to structural constraints from the covalent bonds connecting the monomeric units in PVP, more such vacant sites on the NCs are expected to be occupied by water molecules. These sites possibly will facilitate adsorption of reactant molecules for the reaction to proceed on the NC surface. The number of molecules adsorbed on NC surface was defined as the number of molecules within the distance of 4.5 Å from the surface based on the radial distribution functions of EP molecules. For details, see original article. Both the number of molecules adsorbed and interaction energies converge at around 2% concentration possibly indicating full coverage of the NC by EP molecules.

The adsorption site and dynamics of EP molecule are both crucial for the catalytic reaction. The radial distribution function (RDF) of EP molecules to NC surface was analyzed. It was found that the EP molecules are equally adsorbed at the Au and Pd atoms on the NC surface based on the analysis of Au-OEP and Pd-OEP RDF. The RDF has a minimum at around 4.5 Å and therefore, this distance was regarded as the cutoff distance for discriminating whether a molecule is adsorbed on the NC surface or not in the following analysis.

The concentration of EP molecules enhances in the vicinity of Au–Pd NC. To evaluate this enhancement, the local mole fraction enhancement (LMFE) of EP molecules around NC were calculated for all the Au–Pd NC system by

$$L_{\text{EP}}(r) = \frac{1}{x_{\text{EP}}} \left( \frac{N_{\text{EP}}(r)}{N_{\text{EP}}(r) + N_{\text{water}}(r)} \right)$$

where is the mole fraction of EP and is the number integral or the number of molecules within the distance of from the NC surface. The calculated LMFE with respect to %EP is shown in Figure 8. LMFE gives a measure of difference in the concentration of EP molecule around the NC compared to its concentration in the bulk aqueous solution. The LMFE $= 1$ means that the concentration of EP near the NC and the bulk solvent are the same. Regardless of the concentration of aqueous EP solution and the NC size, the LMFE values are significantly larger than 1, which indicates strong preference of EP over water molecules to the NC. Lower concentrations of aqueous EP exhibit large values of LMFE because all the EP molecules are adsorbed on the NC leaving only water in the bulk. The LMFE values converge to a constant value LMFE $\sim 10$ at %EP $= 10$ and are independent of the NC size. All these parameters such as the number of molecules adsorbed, interaction energies, free energies, RDFs and LMFE values indicate strong preference of EP by the NCs compared to water.

The 2D plot of probability of number of EP and water molecules (Figure 7(a)) demonstrates that fewer water molecules adsorbed on the Au–Pd NC surface. The radial distribution functions calculated for the Au-O$_{\text{water}}$ and Pd-O$_{\text{water}}$ are shown in Figure 9. At lower concentrations of aqueous EP, the distribution functions show clear peaks corresponding to the first layer of adsorbed water and second solvation shell. These peaks show the hydrogen-bonded networks in the low concentration. However, these peaks gradually disappear in the high concentration of aqueous EP.
This means that isolated water molecules present in the first adsorption layer are at a higher energy state. These high-energy water molecules may participate in the reactions which occurs on the NC, or may be displaced by incoming reactant molecules. It was demonstrated in Section 3.4 that water molecule can assist the double proton transfer from DMF to Au–Pd NC, that is the rate-determining step of the coupling reaction.

The surface area of NCs covered by EP molecules were calculated. Figure 10 shows the percentages of the surface area of NCs covered by EP molecules plotted to the numbers of EPs that are adsorbed on the NCs. Irrespective of the concentration of the aqueous EP, the surface of the NC is not completely covered by EP molecules. In all cases, the residual surface of the NCs is not covered by EP because of the structure of EP adsorption; namely, 10% surface area is remain uncovered. Also the data from this analysis can be well fit to the Langmuir-Freundlich adsorption isotherm:

\[
\text{SA} = \frac{\text{K} \times \text{N}_{EP}^n}{1 + \text{N}_{EP}^n} \times 100
\]

where SA is the surface area of NP covered by EP molecules, \(N_{EP}\) is the number of EP molecules adsorbed at the NP surface, and K and n are fitting parameters.

The reaction occurs at the uncovered area of the NPs or the area where the EP/PVP are detached from the NC surface.

4. Summary

Nanocluster (NC) catalysts perform various kinds of chemical reactions under mild condition. Recently, Au–Pd alloy NC catalysts have been developed to catalyze the Ullmann coupling reaction with various aryl chlorides at low temperature. We have worked on the geometric and electronic structures of Au–Pd NC and analyzed the reaction mechanism of this NC catalysis. We also investigate the solvation and adsorption dynamics at interface region. Followings are our brief summary.

1. Au–Pd NC has many stable geometric structures and electronic states that are close in energy, which were located using GA algorithm and DFT calculations. These structures and spin states would contribute to the reaction via internal conversion or spin crossing.

2. Although the Pd atoms prefer to be located in core, both Au and Pd sites appear on the NC surface. Pd sites are considered to be reactive sites on NC surface in the present homocoupling reaction. The energy barrier is around 10–15 kcal mol\(^{-1}\) at Pd sites, while it is as high as about 30 kcal mol\(^{-1}\) at Au sites even by considering the indirect alloy effect of Pd atoms.

3. In colloidal phase NC catalysts, the surrounding polymer matrix like PVP or PVA has a role of stabilizing the NC at suitable size. Beside this, the surrounding PVP works to donate electrons to NC which results in activating the NC for reaction, for example, the energy barrier of oxidative addition is reduced by the electron donation of matrix. The electron donation of PVP can also be observed by XPS measurement.

4. The present homocoupling reaction is a complex multi-step reaction. The reaction cycle and its energetics have been clarified by the DFT calculations. Two possible reaction mechanisms have been proposed. The difficult point is that the oxidative addition of Ar–Cl should occur twice on NC surface at least without hydrogenation. The rate-determining step is the hydrogen transfer from DMF to NC which is assisted by the water molecule via proton shuttle.

5. The observed inverse halogen dependence has been examined. The energy barrier of the oxidative addition of Ar–Br is lower than that of Ar–Cl. The leaching of Pd complex occurs from the NC surface in the case of Ar–Br, which reduces the catalytic activity of Au–Pd NC.

6. MD simulations on NCs in aqueous EP shows that EP is preferentially adsorbed on to the NCs compared to
water; yet very few water molecules that is devoid of a typical tetrahedral structure are trapped close to the NCs that exist in high energy. These water molecules may be displaced for reactant adsorption or may be utilized in certain reactions. These simulations along with DFT calculations signify the importance of NC-protective agents on the structure, dynamics and catalytic activities of NCs.

The series of the present theoretical studies clarified the various aspects regarding the catalytic activity of the colloidal Au–Pd NC for homocoupling reaction and also suggested theoretical approach for the NC catalysts. The obtained chemical insights give the useful view for the design of NC catalysts.

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References

Gold-palladium bimetallic nanocluster catalyst in colloidal phase performs homocoupling reaction of various aryl chlorides under ambient conditions. The geometric and electronic structures of nanocluster, reactive Pd sites, electron-donating effects of surrounding polymer matrix, full reaction mechanism, inverse halogen dependence and solvation dynamics at interface have been clarified by using the DFT calculations and MD simulations as well as genetic algorithm approach.

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Gold-Palladium Nanocluster Catalysts for Homocoupling: Electronic Structure and Interface Dynamics