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Reactivity and Lability Modulated by a Valence Electron Weaving in and out of the 25-Atom Gold Nanoclusters

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Abstract: The ability to pursue heterogeneous catalysis or nanocatalysis at a single-electron level has been largely unsuccessful. The emergence of atomically precise metal nanoclusters with unique electronic structures provides access to currently inaccessible issues. Here we investigate the catalytic behaviours by performing the incoming and outgoing of a free valence electron of Au 6s¹ on the Au₂₅(SR)₁₈ nanoclusters. Our studies reveal the distinct performances: Au₂₅(SR)₁₈⁻ from donating an electron to neutral Au₂₅(SR)₁₈⁰ loses the reactivity and Au₂₅(SR)₁₈⁺ from dislodging an electron from neutral $\text{Au}_{25}(\text{SR})_{18}{}^0$ loses the stability. The reactivity diversity of the three Au₂₅(SR)₁₈ clusters stems from the different affinities with reactants and different extents of intramolecular charge migration during the reactions, which are closely associated with the valence occupancies of the clusters varied by one electron. The stability difference in the three clusters is attributed to their different equilibria established between the AuSR dissociation and polymerization influenced by one electron.

Introduction

Significant research efforts have been witnessed on the singleelectron oxidation or reduction catalysis by organometallic complexes.^[1-3] However, it is extremely challenging to exploit oneelectron-transfer catalysts in heterogeneous catalysis or nanocatalysis, as the catalysts with identical structure but only one-electron difference have never been available. The emergence of atomically precise metal nanoclusters (e.g., $Au_n(SR)_m$, where SR is the thiol ligand; n = number of gold atoms; m = number of ligands) brings opportunities to address the above issues, since crystal structures of such nanoclusters have been solved and electronic structures can be determined.[4-9] Coupled with operando spectroscopy and theoritical studies, very fundamental understanding of catalysis is expected at the singleatom or single-electron level.^[10-12] Atomically precise Au_n(SR)_m (abbreviated as Au_n hereafter) nanoclusters possess free valence electrons, which typically differ from the organometallic complexes, and have been used as model catalysts for establishing the relationship between catalytic properties and atomic-level structures, as well as identifing the active sites of catalysts based on nanoclusters.[13-21]

Within this field, Au_{25} is a pioneer in opening up new horizons in catalysis science.^[15-18,22] Especially, the Au_{25} nanoclusters have three charge states (-1, 0, +1), which can be recognized as the

1S²1P⁶, 1S²1P⁵ and 1S²1P⁴ superatom-like electron configuration, respectively.^[23-27] Therefore, the three Au₂₅ clusters, that is, Au₂₅⁻, Au₂₅⁰ and Au₂₅⁺, offer us a platform to assess the nature of the valence electrons, i.e., play what role in heterogeneous catalysis or nanocatalysis. Previously, the comparisons of Au₂₅⁻, Au₂₅⁰, and Au₂₅⁺ have been made to understand the three structurally similar clusters with distinguishable properties.^[17,18,28-30] Their different properties have been mostly attributed to their different valence occupancies, which is most likely true, but the real connections between the minorly different electronic structures and exhibited distinguishable properties have not been clarified explicitly in most cases.

This work is focused on understanding the nature of how one electron affects catalytic properties of the Au_{25} nanoclusters, with combined experimental and computational efforts. We demonstrate that the valence electron originating from the Au 6s orbital can regulate the reactivity and stability of the Au_{25} nanoclusters by weaving in and out of the nanoclusters, and the previously inaccessible mechanistic pathways can be reached at one-electron precision.

Results and Discussion

The three Au₂₅(SR)₁₈ (SR: 2-phenylethanethiol, denoted PET for short) clusters adopt a similar structural framework with a quasi- D_{2h} symmetry, which is made up of an icosahedral Au₁₃ kernel wrapped by six dimeric staples of Au₂(SR)₃ (Figure 1).^[23] The average Au_{core}-Au_{innershell} bond lengths are respectively 2.775, 2.783, and 2.807 Å for Au_{25}^{-} , Au_{25}^{0} , and Au_{25}^{+} , implying the distinct distortion of Au₁₃ kernels of the three clusters. The continuous symmetry measure (CSM) is quantified to describe the structural distortion from the ideal symmetry.^[31] The CSM values of Au₁₃ kernels are 0.07, 0.20 and 0.52 for Au_{25}^{-} , Au_{25}^{0} and Au_{25}^{+} , respectively, indicating the structural distortion increase with the Au₂₅ charge increase (Figure 1). The electronic structures of the three clusters are notably different, as are shown in their UV-vis spectra (Figure S1a). For Au₂₅-, two prominent bands at 678 and 445 nm, respectively, with a shoulder at 400 nm are observed. For Au₂₅⁰, a prominent band is at 400 nm with a broad band at 687 nm. For Au₂₅⁺, the broad band is centered at 660 nm and the prominent band is at 390 nm. The corresponding HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gaps are 1.33, 1.47 and 1.54 eV for Au_{25}^{-} , Au_{25}^{0} and Au_{25}^{+}

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(Figure S1b), respectively.



Figure 1. Structure comparison of the anionic, neutral and cationic Au_{25} nanoclusters. Color code: orange = Au; yellow = S. C and H atoms are omitted for clarity. The middle panel shows the deviation of Au_{13} kernels quantified by CSM. The lowest panel shows an energy level diagram of the P orbitals.

Intramolecular hydroamination of alkyne toward indole was selected as a probe reaction to evaluate the catalytic behaviours of the anionic, neutral and cationic Au_{25} clusters. As shown in Figure 2a, regardless of the solvent being N, Ndimethylformamide (DMF), toluene (TOL) or paraxylene (PX), the same activity evolution trend was observed: Au₂₅⁰ showed the highest activity, followed by Au25+, and Au25- had little activity, which can be presented in a descending sequence: $Au_{25}^{0} > Au_{25}^{+}$ > Au₂₅⁻. The recyclability of the three catalysts indicated that Au₂₅⁰ afforded catalytic stability, while both ${\rm Au_{25}^-}$ and ${\rm Au_{25}^+}$ lost activities after the first run reactions (Figure 2b). From UV-vis spectra of the spent Au₂₅ catalysts, the Au₂₅⁻ and Au₂₅⁰ clusters appeared to undergo no significant decomposition during the reactions, but Au₂₅⁺ completely degraded (Figure S2). The results justifiably revealed that neutral Au250 had the best catalytic performance, whereas anionic Au₂₅⁻ had the lowest activity and cationic Au₂₅⁺ had the worst stability.



Figure 2. (a) Catalytic performances of the Au₂₅⁻, Au₂₅⁰, and Au₂₅⁺ catalysts for intramolecular hydroamination of 2-ethynylaniline in different solvents. Reaction conditions: 1 mg Au, 1 mmol substrate, 5 mL solvent, 60 °C. (b) Recyclability of the spent catalysts in DMF. TOF = turnover frequence. The catalytic data are averaged over three independent measurements.

Furthermore, time-resolved in situ UV-vis spectroscopy was employed to illustrate the distinct stability of the three clusters under reaction conditions. Au_{25}^- was essentially stable with the smallest absorbance derivative shown in Figure 3a. Au_{25}^0 slightly changed within 1 h and no further changes occurred with time expand (Figure 3b). Of note, the characteristic peaks of Au_{25}^+ obviously weakened within 5 h and then fully disappeared with the largest absorbance derivative observed (Figure 3c), indicating that Au_{25}^+ facilely decomposed. Figure S3 further showed that UV-vis spectra of the three Au_{25} clusters all comparatively changed with increased temperature, supporting that Au_{25}^+ was impressively labile.



Figure 3. Time-resolved in situ UV-vis spectra of (a) Au_{25}^- , (b) Au_{25}^0 and (c) Au_{25}^+ in DMF at 60 °C and the corresponding absorbance derivatives. The derivatives at 0 h are set to zero (dotted line), and the derivatives with time refer to the corresponding differences relative to 0 h.

The missing electron of Au25⁺ compared to Au25⁰ is considered as a minor perturbation to the total electronic structure; it, however, completely changes solution stability of Au₂₅. This implies that the solution stability is likely governed by certain variable with a critical value. Deciphering such phenomena may help understand fundamental thermodynamics of gold nanocluster solutions, and potentially benefit the design and synthesis of gold nanoclusters. Previously, the lability of Au₂₅⁺ was mainly ascribed to the Jahn-Teller distortion effect due to its $\mathsf{S}^2\mathsf{P}^4$ valence state, $^{[31]}$ or ascribed to $\mathsf{Au}_{25}{}^+$ being susceptible to redox reactions which form more stable states such as Au₂₅^{-.[30]} However, the geometry difference of the three Au₂₅ clusters caused by Jahn-Teller distortion is only significant for the singlecrystal structure, much less for the gas-phase clusters, according to the density function theory (DFT) calculations, and likely not considerable for the solvated clusters (the detailed discussion about geometry distortion of the Au₂₅⁻, Au₂₅⁰ and Au₂₅⁺ clusters in single-crystal, gas and solution phases is shown in Supporting Information). Apparently, the degradation of Au₂₅⁺ occurs readily under mild conditions, which means no external electric field or redox agents are necessary. Furthermore, the self-redox reactions of Au25⁺, such as disproportionation, are improbable under mild conditions, as removing valence electrons from the S²P⁴ Au₂₅⁺ is thermodynamically difficult. UV-vis spectroscopy showed no sign of conversion of Au_{25}^+ into Au_{25}^0 or Au_{25}^- (Figure 3 and S3). Thus, the previous hypotheses are not in accord with the fact that Au25⁺ facilely degrades in solution without forming reduced Au₂₅ species. To further understand the lability of Au₂₅⁺, we performed DFT calculations.

First, the dissociation reactions of the three Au₂₅ clusters are investigated at the DFT level. Au₂₅⁺, Au₂₅⁰, and Au₂₅⁻ are modelled with [Au₂₅(SR)₁₈][PF₆], [Au₂₅(SR)₁₈]⁰, and [Au₂₅(SR)₁₈][NR'₄], respectively, where the computationally affordable CH₃ group is used for R and R' to simplify the actual thiol and octyl groups. In the solution, the dissociation will most likely yield neutral leaving fragments, as removal of otherwise ionic fragments has to overcome strong electrostatic attraction and is hence unfavorable, so the neutral dissociation reactions with AuSR as the minimal-

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sized removal unit are considered. As shown in Figure 4a, for all three Au₂₅ clusters, the dissociation of first AuSR from the staple is most endergonic ($\Delta G^{298} = ~45$ kcal mol⁻¹), indicating that the initial dissociation of the intact staple may be rate-limiting. The removal of the second AuSR from the staple is endergonic by ~35 kcal mol⁻¹, resulting in Au₂₃(SR)₁₆ with a terminal AuSR containing an innershell Au and a staple SR. The dissociation of Au₂₃(SR)₁₆ with the removal of the terminal AuSR is predicted to be endergonic by ~35 kcal mol⁻¹ for Au₂₅⁰ and Au₂₅⁻, and by ~30 kcal mol⁻¹ for Au₂₅⁺. Overall, the dissociation of Au₂₅⁰ and Au₂₅⁻ counterparts.



Figure 4. (a) Predicted AuSR dissociation reactions for Au₂₅⁺, Au₂₅⁰, and Au₂₅⁻ at the PBE/LANL2DZ level. Gibbs free energies at 298 K are given in kcal mol⁻¹. (b) Relative electronic energy of Au₂₅⁺, Au₂₅⁰, and Au₂₅⁻ with respect to the fully-relaxed intact clusters during the rigid reaction coordinate scan for the vertical dissociation of the first staple AuSR. The reaction coordinate is chosen as the inter-fragment distance between leaving AuSR and the remaining cluster (Δ). (c) The molecular orbital level diagram for fully-relaxed gas-phase Au₂₅(SR)₁₈ (Δ = 0) and Au₂₄(SR)₁₇ (Δ = ∞). (d) The molecular orbital level diagram for fully-relaxed solution-phase Au₂₅(SR)₁₈ and Au₂₄(SR)₁₇ with the DMF solvent using the SMD-IEFPCM computational solvation model.

Figure 4 shows that, in gas phase, the rate-limiting dissociation of the first AuSR from Au₂₅⁺ is ~3 kcal mol⁻¹ more favorable than the counterpart reactions for Au₂₅⁰ and Au₂₅⁻. Further, the solution-phase dissociation of the first staple AuSR from the Au₂₅ clusters in DMF is predicted using the SMD-IEFPCM (the SMD variation of integral-equation-formalism polarizable continuum) solvation model at the DFT level.^[32] In DMF, the ΔG^{298} for the removal of AuSR from Au₂₅⁺, Au₂₅⁰, and Au₂₅⁻ is reduced to 34.2, 37.4, and 40.3 kcal mol⁻¹, respectively. The AuSR dissociation for Au₂₅⁺ is 6 kcal mol⁻¹ less endergonic than that for Au₂₅⁻, suggesting that the difference in lability of the two clusters becomes more significant with the DMF solvent.

Next, the vertical dissociation of AuSR from the three Au_{25} clusters is investigated computationally; here, "vertical" indicates that the geometries of the AuSR and $Au_{24}(SR)_{17}$ fragments remain frozen as in the fresh catalyst during the dissociation. This is done by using a rigid reaction coordinate scan calculation where the leaving AuSR is pulled away from the equilibrium position until a distance of 5 Å is reached between AuSR and the remaining cluster. The inter-fragment distance is defined as the reaction

coordinate Δ . During vertical dissociation the major parts of the electronic structures of the fragments are close to the electronic structure of the intact Au₂₅ cluster. The energetics for the vertical dissociation of AuSR from the three Au₂₅ clusters are shown in Figure 4b. No dissociation barrier is found for the vertical dissociation for all three clusters, implying that the activation energy for the AuSR dissociation can be well approximated by the reaction endergonicity. The vertical dissociation energies of the three clusters only differ slightly. At an inter-fragment distance of 5 Å, the vertical dissociation energy for Au₂₅⁺ is 68.7 kcal mol⁻¹, ~1.5 kcal mol⁻¹ lower than those of Au₂₅⁰ and Au₂₅⁻. This means that the vertical dissociation only accounts in part for the different dissociation thermodynamics of the three Au₂₅ clusters and the relaxation of electronic structures due to the formation of the Au₂₄ clusters might also play sufficient roles. The electronic structures of the fully relaxed Au₂₅, vertically dissociated Au₂₅ with Δ = 5 Å, and fully relaxed Au₂₄ as the dissociation product are compared, with the transition of molecular orbital levels analyzed (Figure S4-S6). The analysis shows that upon the dissociation, the S^2P^4 , S^2P^5 and S²P⁶ valence states of Au₂₅⁺, Au₂₅⁰ and Au₂₅⁻ are significantly altered.^[28] For all three clusters, the S orbital of Au₂₅ shifts toward negative energy and becomes a core orbital of Au₂₄, the three P orbitals of Au₂₅ remain in the valence, and a core Au-thiolate bonding orbital (denoted as 't') in Au₂₅ becomes localized around the terminal thiolate of Au24 which rises in energy to be the new HOMO (Figure 4c and 4d). For Au₂₅⁺, one of the P orbitals turns into a localized orbital, essentially an Au s polaron associated to the exposed innershell Au of Au₂₄⁺, due to symmetry breaking; the localization of P is less apparent for the dissociation of Au₂₅⁰ and Au₂₅⁻. As a result, Au₂₄⁺, Au₂₄⁰ and Au₂₄⁻ exhibit the t²P²s², t¹P⁶ and t²P⁶ valence states respectively. The stabilization of the Au₂₄⁺ dissociation product, which contributes to the lability of Au24+, could be due to the fact that the energy increase of its HOMO t orbital is the least and the energy decrease of its S orbital is the most for the AuSR dissociation of the three clusters (Figure 4c). We hypothesize that the higher formation energies of Au₂₄⁰ and Au24⁻ are likely due to the conflicting electronic structure preferences by the molecular structure and by the valence electron counts: the molecular structure favors forming polaron over the exposed innershell Au site whereas the valence electron counts of Au_{24}^0 and Au_{24}^- favor the full-shell P⁶ state over the polaron state. The transition of molecular orbital levels with the SMD-IEFPCM solvation model suggests that DMF stabilizes the HOMO t orbital of Au24⁺ substantially while it does not give notable changes to the electronic structures of Au₂₄⁰ and Au₂₄⁻ (Figure 4d), which explains the further divergence of AuSR dissociation thermodynamics for the three Au₂₅ clusters in DMF.



Figure 5. (a) Optimized geometries for selected (AuSR)_n. (b) Predicted normalized binding energy of AuSR to form $(AuSR)_n$, $n \le 13$. Electronic reaction energy at 0 K and Gibbs reaction free energy at 298 K are predicted at PBE/LANL2DZ level in kcal mol⁻¹. (c) Predicted HOMO-LUMO gap for $(AuSR)_n$.

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The next question is whether there exists a driven force for the endergonic AuSR dissociation reaction for Au_{25}^+ . The key is to find the bound states for the leaving AuSR fragments. One straightforward possibility is that AuSR polymerizes into $(AuSR)_n$ clusters. Previously, global minima for the $(AuSR)_n$ (R = CH₃ and n ≤ 13) clusters were predicted using a genetic algorithm.^[33] Based on the reported structures, we predicted the polymerization thermodynamics for the AuSR fragments (Figure 5a and S7). The normalized binding energy for AuSR to form $(AuSR)_n$, <BE>(n), is calculated using equation (1):

$$\langle BE \rangle (n) = E((AuSR)_n)/n - E(AuSR)$$
 (1)

The AuSR polymerizations are mildly exergonic, from which the consumption of AuSR may be conducive to the dissociation of Au₂₅⁺. It is found that <BE>(n) Gibbs free energy at 298 K increases drastically for $n \le 4$ and decreases slightly for $n \ge 4$ as n increases. The early convergence of <BE>(n) is due to (AuSR)_n exclusively being pseudo-one-dimensional torus or linked tori, for which increasing n does not increase the number of bonds per n (which cluster stability scales with). This implies (AuSR)₄ might be the dominant (AuSR)_n species formed from the AuSR monomers. <BE>(4) is predicted to be 30.7 kcal mol⁻¹ at 298 K without any solvent. The existence of (AuSR)₅ might also be possible with <BE>(5) predicted to be 30.4 kcal mol⁻¹. The early convergence of <BE>(n) and small dominant size for (AuSR)_n are key for the stable existence of many non-stoichiometric $Au_n(SR)_m$ (n \neq m) clusters, because otherwise the spontaneous growth of (AuSR)_n into large clusters will drive the dissociation of most Aun(SR)m clusters. To confirm our hypothesis, matrix-assisted laser desorption ionization mass (MALDI-MS) spectrometry for the degraded Au₂₅(PET)₁₈⁺ clusters was measured. Notable peaks were found for Au₃(PET)₂, Au₄(PET)₃, and Au₄(PET)₄ based fragments in the low m/z range, which might result from the fragmenting of Au₄(PET)₄ (Figure S8). A number of major peaks for Au_{25-x}(PET)_{18-x} were found in the high m/z range, and frequent Au(PET) intervals were observed between the major peaks (Figure S9). It is noted that the Au(PET) intervals were not found in the high m/z range of MALDI-MS spectra of the fresh Au₂₅(PET)₁₈⁺ clusters (Figure S10). Hence, the hypothesis of Au25⁺ undergoing neutral dissociation reaction with AuSR as minimal removal unit is supported by the mass experiments. Since the dissociation rate-limiting step of Au25⁺, Au25⁰ and Au25⁻ is 44.4, 47.9 and 47.4 kcal mol⁻¹ without solvent, the reaction energy for the net degradation reaction, given by equation (2),

$$Au_{25} \rightarrow Au_{24} + \frac{1}{4} (AuSR)_4 \tag{2}$$

is 13.7, 17.2 and 16.7 kcal mol⁻¹ for Au_{25}^+ , Au_{25}^0 and Au_{25}^- in the gas phase, respectively. Using the SMD-IEFPCM solvation model, <BE>(4) is found to be 22.6 kcal mol⁻¹, and the reaction energy for the net degradation reaction is evaluated to be 11.6, 14.8 and 17.7 kcal mol⁻¹. Our prediction is in excellent agreement with the experimental observation from UV-vis spectroscopy that Au25+ readily degrades, Au₂₅⁰ slightly degenerates and Au₂₅⁻ persists under mild conditions (Figure 3). The low endergonicity for the net degradation reaction of Au25+ implies that this reaction is temperature-sensitive, which is confirmed from the evolution of UV-vis spectra with increased temperature (Figure S3). The UVvis spectra also show that as Au₂₅⁺ degrades, major absorption peaks in the visible range essentially disappear. The predicted evolution of UV-vis spectra for the step-by-step AuSR dissociation from Au₂₅⁺ to Au₂₂⁺ exhibits a qualitatively similar pattern (Figure S11a). The predicted HOMO-LUMO gaps for (AuSR)₄ and

 $(AuSR)_5$ are 3.95 and 3.66 eV (Figure 5c), which forbid absorption with wavelength longer than 314 and 339 nm respectively (Figure S11b). Therefore, all of the resultant fragments and consequent clusters, based on our hypothesis, exhibit absorption properties that are compatible with the experimental UV-vis spectra, and our hypothesis holds well against the experimental examination. Overall, our computation and experiment reveal that the lability of Au_{25}^+ is due to the combination of its facile AuSR removal and the consequent AuSR aggregation. The relatively high stabilities of Au_{25}^0 and Au_{25}^- are owing to the comparatively high AuSR dissociation energies and pseudo-one-dimensional (AuSR)_n ceasing to grow at small n.



Figure 6. (a) FT-IR spectra of the adsorbed species onto the Au_{25}^{-} , Au_{25}^{0} , and Au_{25}^{-} clusters in the presence of 2-ethynylaniline. (b) FT-IR spectra of pyridine adsorbed onto the Au_{25} clusters. (c) Au 4f XPS profiles of the Au_{25} clusters. (d) XANES profiles of the Au_{25} clusters. Inset: energy in 11916-11922 eV window.

Moreover, to unveil the mystery of the superior reactivity of Au_{25}^{0} to both Au_{25}^{+} and Au_{25}^{-} , the chemisorbed modes of 2ethynylaniline over the three cluster catalysts were studied by Fourier-transformed infrared (FT-IR) spectroscopy. As presented in Figure 6a, two stretching bands at 3280 and 2095 cm⁻¹, respectively assigned to $v_{s}(\equiv C-H)$ and $v_{s}(C\equiv C)$,^[34] were observed on the three catalysts, suggesting the internal binding mode of ethynylaniline on the three catalysts. Notably, two N–H stretching bands at 3470 and 3370 cm⁻¹, assigned to free NH₂ species, were found on Au_{25}^{-} . For Au_{25}^{0} and Au_{25}^{+} , one of the N–H stretching bands at 3470 cm⁻¹ underwent a red shift and the other at 3370 cm⁻¹ substantially weakened, especially nearly vanished for Au_{25}^{0} . It is proposed that Au-amine species formed onto Au_{25}^{0} and Au_{25}^{+} might effectively boost the hydroamination reaction.

The Lewis acidity property of the catalysts was probed by the IR spectra of adsorbed pyridine. The bands at ~1444 cm⁻¹ assigned to pyridine adsorbed on the Lewis acid sites were observed on the three Au₂₅ clusters (Figure 6b), suggesting the electron-deficient sites available on the three catalysts.^[35,36] Additionally, two IR bands in the ranges of 1590~1596 and 1479~1497 cm⁻¹ on Au₂₅⁰ shifted higher wavenumbers than those on Au₂₅⁺, the corresponding bands of which in turn shifted higher wavenumbers than those on Au₂₅⁻, meaning that the interaction

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of the reactant and $Au_{25}{}^{0}$ may differ from the cases of $Au_{25}{}^{-}$ and $Au_{25}{}^{+}.$

The gold valence states in the three Au₂₅ clusters were monitored by X-ray photoelectron spectroscopy (XPS). The Au 4f_{7/2} binding energies on the three clusters were higher than that of metallic Au (Figure 6c), which was correlated with the electron deficiency on the gold by the electron withdrawing nature of the thiol ligands.^[37] Notably, the Au 4f_{7/2} binding energies sequenced slightly positive shifts from Au_{25}^{-}, Au_{25}^{0}, to Au_{25}^{+}, which was consistent with X-ray absorption near edge structure (XANES) studies (Figure 6d). Extended X-ray absorption fine structure (EXAFS) experiments indicated that local coordination environments in the Au₂₅ clusters were not obviously different (Figure S12 and Table S1). Taken together, it is suggested that distinct catalysis of the three Au₂₅ clusters was mainly determined by the electronic structures, rather than the geometrical structures, which can influence on their affinities with the reactants.

For the molecular-level understanding of the superior activity of Au_{25}^{0} , the hydroamination reaction pathways on the Au_{25}^{0} catalysts are proposed based on the DFT results. First, 2ethynylaniline dissociatively adsorbs at an outer-Au of the catalyst to form CAT[C₈H₆N(EA)]H (Figure 7a and S13; EA indicates the adsorbate being structurally related to ethynylaniline and CAT stands for Au₂₅⁺, Au₂₅⁰, or Au₂₅⁻), during which the Au-S bond of the staple is cleaved to adsorb the amino-H on S and the C8H6N on Au. The adsorption Gibbs free energy at 298 K is in the order of Au_{25}^{0} (25.1 kcal mol⁻¹) < Au_{25}^{-} (29.6 kcal mol⁻¹) < Au_{25}^{+} (31.6 kcal mol⁻¹). The superior activity of Au₂₅⁰ is probably in part related to its facile adsorption of ethynylaniline. Then, the intramolecular H^+ transfer reaction (followed by cyclization), C_8H_6N (EA) \rightarrow C₈H₆N (*ID*), proceeds by transferring a H from N to ethynyl C (where ID indicates that the structure is related to indole). For this reaction, the in-situ barrier height is impractical to determine due to the complex role solvent might play in mediating the proton transfer and the ex-situ barrier without solvent is also difficult to predict, as the proton transfer seamlessly leads to cyclization with high exergonicity which prevents computationally locating the transition state. The in-situ barrier, though, should scale with the binding strength of the N-H (or the deprotonation energy) while also being affected by the choices of the solvent. Therefore, we provide predictions for the fictitious fully-deprotonated CAT[C₈H₅N(EA)]⁻H and CAT[C₈H₅N(ID)]⁻H products, in order to provide the upper bounds for the intramolecular proton transfer barriers. Note that for the actual solution-phase reaction, partial deprotonation likely occurs because of the short proton migration path and the proton mediation effect of the solvent molecules. More supplemental discussion about intramolecular proton transfer of ethynylaniline catalyzed by Au250 with and without DMF can be found in Supporting Information.

The predicted Gibbs free energy at 298 K for the full deprotonation of an amino-H of CAT[C₈H₆N(*EA*)]H is in the following ordering: Au₂₅⁺ (312.9 kcal mol⁻¹) \approx Au₂₅⁰ (318.4 kcal mol⁻¹) < Au₂₅⁻ (352.1 kcal mol⁻¹), which explains the lack of reactivity for Au₂₅⁻. Based on our proposed proton transfer mechanism, solvents with high proton affinity and high dielectric constant can facilitate the intramolecular proton transfer step. The proton affinity for DMF, TOL, and PX are calculated to be: DMF (202.5 kcal mol⁻¹) > TOL (185.7 kcal mol⁻¹) > PX (182.4 kcal mol⁻¹), which is consistent with the order of the hydroamination reactivity in these solvents (Figure 2a). It is found that the CHO moiety of DMF mainly accounts for its high proton affinity. The dielectric

constants for the three solvents also follow the same order with DMF (38.25) > TOL (2.38) > PX (2.27).^[38] This validates our proposed mechanism, to some extent. The intramolecular proton transfer and cyclization lead to CAT[C₈H₆N(*ID*)]H. The total formation reaction of CAT[C₈H₆N(*ID*)]H (CAT + ethynylaniline \rightarrow CAT[C₈H₆N(*ID*)]H) is exergonic for all three catalysts. Formation of [C₈H₆N(*ID*)]H over Au₂₅⁰ is ~10 kcal mol⁻¹ more exergonic than the corresponding reactions over Au₂₅⁻ and Au₂₅⁺. The [C₈H₆N(*ID*)] in CAT[C₈H₆N(*ID*)]H can recombine with H (on S), which exergonically forms the indole. Consequently, the cleaved staple recombines into an intact staple and the catalyst returns to the initial state.



Figure 7. (a) Predicted reaction Gibbs free energies and enthalpies (kcal mol⁻¹) at 298 K for the proposed hydroamination reaction pathway over Au_{25}^{0} . Enthalpies are given in brackets. '*EA*' and '*ID*' in parentheses indicate ethynylaniline-like and indole-like respectively. Color code: orange = Au, yellow = S, black = C, green = H, pink = N. PET is simplified by SCH₃. (b) Adsorbate formal charges based on the predicted natural atomic charges for the adsorbate fragments during the hydroamination of ethynylaniline over Au_{25}^{0} , Au_{25}^{-} , and Au_{25}^{+} . * denotes CAT. For CAT[C₈H₆N(*EA*)]H and CAT[C₈H₆N(*ID*)]H, the adsorbate formal charge is equal to the net atomic charge of the adsorbate fragments; for CAT[C₈H₆N(*EA*)]⁻H, the adsorbate formal charge is equal to the net atomic charge is equal to the n

The electronic structures of the reaction intermediates over Au₂₅ catalysts are examined to understand their different performances in catalyzing hydroamination of ethynylaniline. The amount of charge transferred from the adsorbates to the Au₂₅ catalysts during the reactions can be indicated by the adsorbate formal charges (Figure 7b) based on the predicted natural atomic charges at the DFT level. It is shown that upon dissociative adsorption of ethynylaniline over the catalyst to form CAT[C₈H₆N(*EA*)]H, electron is transferred from the catalyst to its adsorbates. The electron transfer is notable for Au₂₅⁻ and Au₂₅⁺, but less significant for Au₂₅⁰. We hypothesize that the loss of valence electron will impair the S²P⁶ and S²P⁴ valence states of fresh Au₂₅⁻ and Au₂₅⁺ and hence destabilize the corresponding CAT[C₈H₆N(*EA*)]H intermediates. The weaker electron depletion

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upon ethynylaniline adsorption over Au₂₅⁰ is probably because in the ground-state $Au_{25}{}^{0}[C_8H_6N(EA)]H$, the spin-polarized C_8H_6N adsorbate back-donates electron to the catalyst. Therefore, the S^2P^5 valence occupancy of the fresh Au_{25}^0 catalyst is essentially retained despite the dissociative adsorption of ethynylaniline, which might avoid severe destabilization. Note that the ground state of $Au_{25}{}^{0}[C_8H_6N(EA)]H$ is 2.5 kcal mol⁻¹ lower in energy than a low-lying excited state with non-spin-polarized adsorbates where the electron transfer results in fractional valence occupancy like those of $Au_{25}^{+}[C_8H_6N(EA)]H$ and Au₂₅-[C₈H₆N(EA)]H (Figure S14). The different tendencies for intramolecular proton transfer for CAT[C₈H₆N(EA)]H, indicated by deprotonation energies, is also evident from electron transfer behaviors (Figure 7b). For the full deprotonation of $Au_{25}^{-}[C_8H_6N(EA)]H$ to form $Au_{25}^{-}[C_8H_5N(EA)]^{-}H$, the resultant excessive electron resides on the C8H5N adsorbate due to the full $S^{2}P^{6}$ "valence-shell" of Au₂₅⁻ repelling the excessive electron, so this reaction is similar to gas-phase reaction without catalyst. For the Au₂₅⁰ and Au₂₅⁺ cases, intramolecular electron transfer is found (Figure 7b), where electron is transferred from the adsorbates to the cluster (> 0.5 e⁻) to combine with the valence hole there. This may stabilize the deprotonation product by changing the valence occupancy of the Au₂₅ core. For the Au₂₅⁺ system the recombination (S $^2\text{P}^4 \rightarrow S^2\text{P}^5)$ occurs naturally due to the cationic nature, as well as the low S²P⁴ valence occupancy, of the cluster. For the Au₂₅⁰ reaction, the injection of the excessive electron into the catalyst ($S^2P^5 \rightarrow S^2P^6$) is driven by the high thermodynamic stability of the shell-closing S²P⁶ occupancy. In the following reaction steps, as proton is transferred back to alkynyl-C of the adsorbate followed by a spontaneous cyclization to form CAT[C₈H₆N(*ID*)]H, the electronic structure of the cluster is reverted back to a state similar to that of CAT[C₈H₆N(EA)]H, via a reverse intramolecular electron transfer from Au₂₅ to the adsorbates.

Overall, doublet nature of Au_{25}^{0} allows for charge redistribution between the cluster and the adsorbate, which helps to prevent fractional occupancies deviating from S²P⁵ occupancy to promote the dissociative adsorption of reactants and better initialize the hydroamination, and also enables intramolecular electron transfer from adsorbates to facilitate the intramolecular proton transfer. The Au_{25}^+ system also benefits from the intramolecular electron transfer mechanism, and thus Au_{25}^+ exhibits better activity than Au_{25}^- , but the catalytic performance of Au_{25}^+ is likely limited by its lability under reaction conditions.

Conclusions

In summary, our results indicate that the catalytic properties of the three Au_{25} nanoclusters can be ordained by the valence electrons originating from the Au 6s orbital. The Au_{25}^{0} nanocluster shows the best performance, while the donation of an electron to Au_{25}^{0} results in the loss in activity and the dislodgment of an electron from Au_{25}^{0} causes the decay in stability. The correlation of the free valence electrons and physicochemical properties of nanoclusters may not only facilitate the rational design and synthesis of nanoclusters, but also stimulate the future research on controlling heterogeneous catalysis at a single-electron level.

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Keywords: nanocluster • catalysis • valence electron • activity • lability

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In this work, we investigate the catalytic reactivity and lability by performing the incoming and outgoing of a free valence electron of Au 6s orbital on the neutral Au₂₅ nanocluster. We demonstrate that the Au₂₅⁻ nanocluster from donating an electron to the neutral Au₂₅⁰ nanocluster loses the reactivity and the Au₂₅⁺ nanocluster from dislodging an electron from the neutral Au₂₅⁰ nanocluster loses the stability. The correlation of the free valence electrons and catalytic properties of the Au₂₅ nanoclusters can be achieved at a single-electron level.

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Reactivity and Lability Modulated by a Valence Electron Weaving in and out of the 25-Atom Gold Nanoclusters