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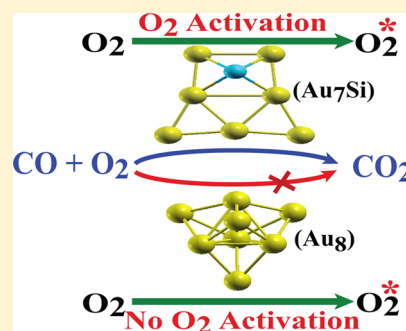
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S Supporting Information

ABSTRACT: Doping is known to be an excellent and simple way of catalyst design. Although notable progress has been made in understanding the reactivity and catalytic activity of gas-phase and supported gold clusters, very few studies have been carried out on the doped gold clusters. In the present work, we have carried out density functional theory calculations to investigate the effect of silicon doping on the reactivity and catalytic activity of gold nanoclusters. The present work particularly focuses on the adsorption and activation of molecular oxygen on the pristine and silicon-doped gold clusters. The results confirm that the silicon-doped Au₇Si cluster shows considerable binding and activation of the O₂ molecule in comparison to the pristine Au₈ cluster as reflected in the relevant geometrical parameters (O–O and Au–O bond lengths) and O–O stretching frequency. However, silicon doping has no contrasting effect on the reactivity and catalytic activity of the Au₇ cluster. In addition to the stronger binding and activation of the O₂ molecule, the doped Au₇Si cluster leads to a significant reduction in the activation barrier (0.57 eV) for the environmentally important CO oxidation reaction in contrast to the catalytically inactive pristine Au₈ cluster (1.22 eV). Thus, our results highlight the critical role of doping foreign impurities for future endeavors in the field of gold nanocatalysis.



INTRODUCTION

During the past decade, gold clusters at the subnano level have been debated for their excellent catalytic properties as compared to their bulk form. It was the pioneering work of Haruta et al. that opened the doors for the catalytic activity of gold at the nanoscale.¹ Since then, a number of experimental and theoretical studies have focused their attention on the catalytic activity of gold clusters.^{2–5} The most notable reaction that the gold clusters catalyze is the oxidation of the environmentally harmful CO molecule to CO₂ at temperatures far below the room temperature.^{6–10} The extraordinary catalytic activity has prompted many researchers to understand the structure and reactivity of the gold clusters (and the factors affecting them), thereby making its significance to heterogeneous catalysis as one of the important topics in current research. The structure and reactivity of these clusters are highly influenced by the strong relativistic and quantum mechanical effects, particularly in the 1–5 nm range.^{11,12} It is well-known that gold clusters with 4–12 atoms exhibit 2D planar structures.^{13–15} This planarity is due to the strong relativistic effects seen in gold. Further, in some of the recent and very interesting works,^{16,17} it was shown that anionic gold clusters with 16–18 atoms possess cage-like structures and can act as efficient catalysts because of their large surface-to-volume ratio. Similarly, it was shown that both neutral and anionic Au₂₀ clusters have tetrahedral structures.^{18,19}

A number of theoretical investigations have illustrated that the reactivity of gold clusters with molecular oxygen depends on factors such as size and shape of the cluster,^{20,21} charge state

of the cluster,^{22–25} ligand adsorption,^{26,27} and nature of the supporting material.^{28–31} These studies further show that even atomic anionic clusters bind with molecular oxygen strongly, leading to its activation. It was further revealed that there is an electron transfer from the gold cluster to the oxygen molecule, and thus, oxygen behaves as an electron acceptor. However, most of the above-mentioned studies concentrate on the pristine gold clusters. Doping is known to be an excellent and general way of catalyst design. Gold clusters have significant charge localization, and doping with a foreign atom is an important way of tuning the electronic environment in these clusters. This makes the doped gold clusters as attractive candidates for catalysis. In this respect, recently, in an interesting study, the effect of hydrogen doping on the reactivity and catalytic activity of a neutral gold cluster was studied by Jena et al.³² Their results showed that not only does hydrogen doping result in preferential activation of an oxygen molecule but also leads to reduction in the activation barrier for the CO oxidation reaction. Balbás and co-workers,^{33–35} using first-principles calculations, investigated the effect of transition-metal (Ti, Fe) doping on the adsorption of O₂ and CO molecules on gold clusters. The authors further studied the CO adsorption and CO₂ desorption mechanisms on the doped clusters. Similarly, Häkkinen and co-workers³⁶ found that strontium doping in an Au₄ activates the cluster for strong O₂

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binding and activation. Apart from the above-mentioned studies, the effect of doping on the reactivity and catalytic activity of gold clusters remains largely unexplored.

There have been a relatively fewer number of studies on the silicon-doped gold clusters. One of the fascinating findings reported on the silicon-doped gold clusters is the gold–hydrogen analogy.^{37,38} Recently, on the other hand, Pal et al.³⁹ have carried a systematic study on the structural evolution of silicon-doped gold clusters and have shown that silicon-doped gold clusters have a significantly different structure. Although the reactivity of gold clusters strongly depends on their shape and electronic distribution,^{40,41} little is known about the catalytic activity of silicon-doped gold clusters that show contrastingly different structures and electronic structures as compared to the pristine gold clusters.

Thus, in this work, we have explored the effect of silicon doping on reactivity of gold clusters towards molecular oxygen. Further, to have insight into the catalytic activity of silicon-doped clusters, we have considered the well-studied reaction of oxidation of CO to CO₂. We have calculated the activation barrier heights for this reaction and compared our results with the pristine gold clusters. Since temperature-programmed reaction (TPR) measurements have shown that Au₈ is the smallest gold cluster to catalyze the oxidation of CO¹⁰ and it is believed that the effect of doping can be better understood in the case of small clusters, we have chosen Au₇ and Au₈ clusters as our model systems.

■ COMPUTATIONAL DETAILS

All the calculations were performed by density functional theory (DFT) as implemented in the Gaussian 09 package.⁴² For each cluster, more than 10 isomers were used as a starting guess to find the ground-state geometry. The optimized structures of the various clusters (Au₇, Au₈, Au₆Si, and Au₇Si) and their O₂ adsorbed complexes were obtained using PBE, TPSS, and BPV86 types of functionals. These types of functionals are known to adequately describe the structure of gold clusters and their interaction with small molecules like O₂.^{43–45} The relative energies of various low-energy isomers are listed in the Supporting Information. The default convergence criterion (10^{−4}) was used for geometry optimizations, and the optimizations were carried out using the Berny algorithm. For gold, the LANL2DZ+ECPs basis set and, for the rest of the atoms, the TZVP basis set were used. Harmonic frequency calculations were performed to confirm that each optimized structure corresponds to a minima. The O₂ binding energies have been calculated as the difference between the energy of the O₂ adsorbed complex and its constituents (i.e., O₂ and cluster). The basis set superposition error (BSSE) has not been considered for calculation of O₂ binding energies as it has been demonstrated recently that the BSSE has a negligible effect on the O₂ adsorption energies on gold clusters.^{46,47} Since the results obtained using various types of functionals for the binding energies are quite consistent, the barrier height for CO oxidation has been computed by using the PBE functional only. The transition states were characterized by the presence of one imaginary frequency.

■ RESULTS AND DISCUSSION

We begin with a discussion of the structure and adsorption of molecular oxygen on the pristine and silicon-doped gold clusters as adsorption and activation of molecular oxygen are

the important and primary steps in the oxidation of CO to CO₂. The optimized geometries of the pristine Au₇ and Au₈ and their Si-doped counterparts (Au₆Si and Au₇Si) are shown in Figure 1. Since there are a number of contradictory reports

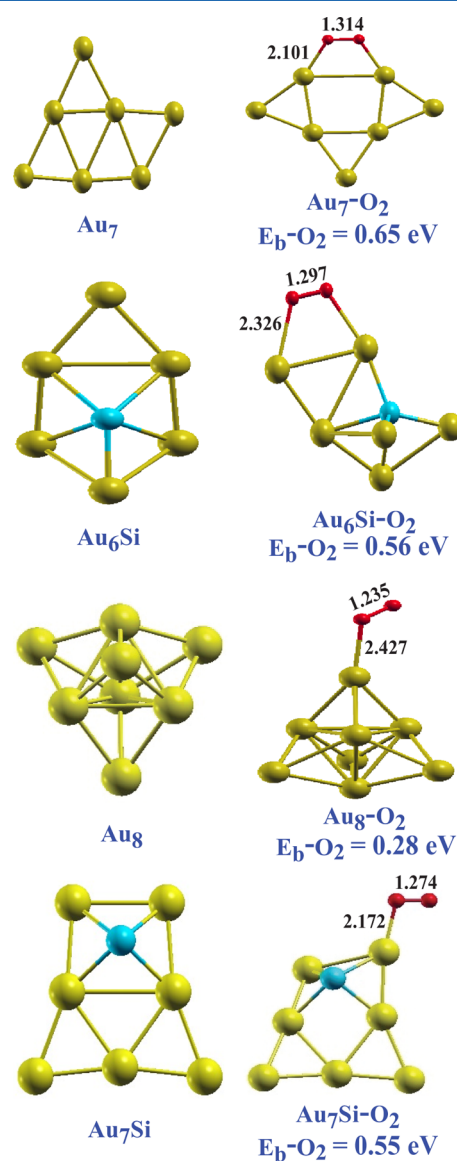
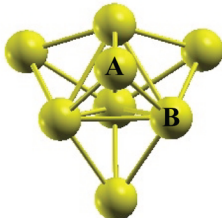
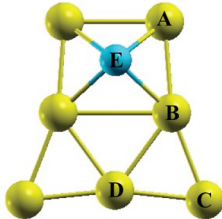


Figure 1. Optimized geometries of Au₇, Au₈, Au₆Si, and Au₇Si clusters and their O₂ adsorbed complexes as obtained with the PBE method. $E_{\text{b-O}_2}$ represents the O₂ binding energy on the pristine and Si-doped gold clusters.

about the ground-state geometry of Au₈^{48,49} being planar or nonplanar, the reactivity and catalytic property of both the planar and the *T_d* isomers have been studied in the current work. The results of the planar Au₈ are presented in the Supporting Information. The Au₆Si and Au₇Si clusters have quasi-planar structures where the silicon atom is in a square-pyramidal environment. The optimized geometries of Au₆Si and Au₇Si are in close agreement with the earlier reported results.^{50–52} Similar structures were found for Au₆Si[−] and Au₇Si[−] by Pal et al.³⁹ using photoelectron spectroscopy and density functional theory. The authors attributed the quasi-planar structure to the dominance of the tendency of gold clusters to form planar structures over that of silicon to form

tetrahedral structures. Figure 1 also shows the optimized geometries of the complexes of the oxygen molecule with the Au₇, Au₈, Au₆Si, and Au₇Si clusters (oxygen was adsorbed both in peroxo and atop modes at different possible positions; only the lowest-energy structures are shown here). We have further identified the most reactive atom in the Au₈ and Au₇Si clusters with the help of the Fukui function, a local descriptor known to predict the most reactive site in a cluster.^{53,54} The values of the Fukui function for the various atoms in the pristine Au₈ as well as the silicon-doped Au₇Si clusters are listed in Table 1. It can

Table 1. Fukui Function Values for the Electrophilic Attack on the Various Sites in the Pristine Au₈ and Doped Au₇Si Clusters

Cluster	Structure	Sites	f_k^-
Au ₈		A	0.161
		B	0.088
Au ₇ Si		A	0.149
		B	0.082
		C	0.114
		D	0.086
		E	0.103

be seen from the table that the most reactive atoms (atoms with the largest value of f_k^-) in the clusters Au₈ and Au₇Si are those that form the most stable complex with the O₂ molecule. The structures shown in Figure 1 were optimized using the PBE functional, and without stated, the results correspond to the above functional. The optimized geometries obtained using BPV86 and TPSS functionals are similar to those obtained using the PBE functional and are shown in the Supporting Information. From Figure 1, it can be seen that the O₂ molecule binds strongly with the Au₇ and Au₆Si clusters, leading to the distortion in the shape of the clusters. The O₂ molecule shows the peroxo mode of bonding with two Au–O bonds. The O₂ adsorption energies on Au₇ and Au₆Si clusters are 0.65 and 0.56 eV with O–O bond lengths of 1.31 and 1.29 Å, respectively. It can also be seen from Figure 1 that the geometry of the silicon-doped Au₇Si cluster undergoes slight distortion upon O₂ adsorption, whereas the pristine Au₈ cluster geometry remains unaffected. We also note that the mode of binding of O₂ with the gold clusters is different than that of CO. The Au–O–O bond angle is almost equal to 120°, whereas earlier studies have shown the Au–C–O bond angle close to 180°. The binding energy of the O₂ molecule with the pristine gold Au₈ cluster is 0.28 eV (for planar isomer, the binding energy is 0.31 eV). This weak interaction of O₂ with the Au₈ cluster supports the fact that the neutral and cationic gold clusters with an even number of electrons bind oxygen poorly and do not induce activation of O₂ as reported by Yoon et al. earlier.²⁰ On the other hand, O₂

binds strongly with the Au₇Si cluster with a binding energy of 0.55 eV. The enhancement in the binding energy of the O₂ molecule and distortion in shape in the case of the silicon-doped Au₇Si cluster clearly indicate significant activation of the O₂ molecule.

The interaction of molecular oxygen with Au₇Si and Au₈ clusters can be qualitatively understood in terms of the frontier molecular orbital concept. The O₂ molecule acts as an electron acceptor and interacts strongly with clusters having an odd number of electrons. The molecular orbitals of the complexes of O₂ with both the Au₈ and the Au₇Si clusters are shown in Figure 2. The SOMO and SOMO-1 of the Au₇Si–O₂ complex

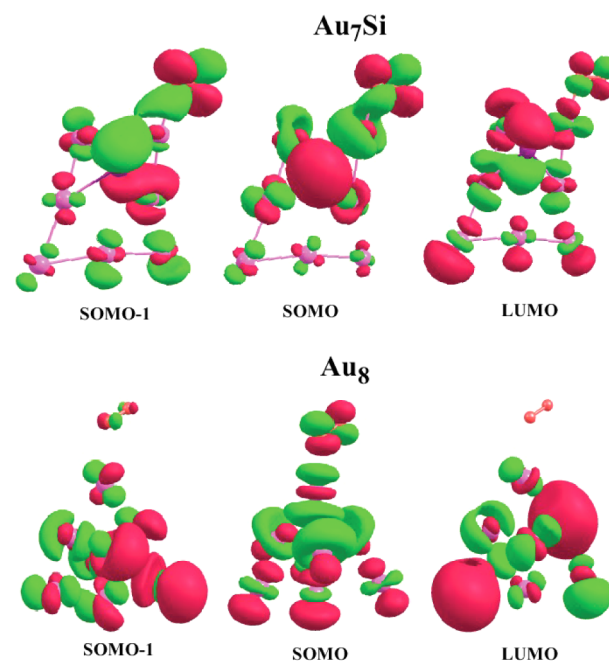


Figure 2. Frontier molecular orbitals of O₂ adsorbed complexes of Au₇Si and Au₈ clusters.

shows considerable overlap between the d-orbital of Au and p-orbital of the O₂ molecule, leading to a strong Au–O bond. This type of overlap is lacking in the case of the pristine Au₈–O₂ complex as can be seen clearly. This is further reflected in the relevant geometrical parameters (Table 2), such as the r_{O-O}

Table 2. Optimized Geometrical Parameters Such as O–O Bond Length (r_{O-O}), Au–O Bond Length (r_{Au-O}), and O–O Stretching Frequency (ν_{O-O}) Obtained Using Various Types of Functionals

functional	system	r_{O-O} (Å)	r_{Au-O} (Å)	ν_{O-O} (cm ⁻¹)
PBE	Au ₇ –O ₂	1.314	2.101	1069
	Au ₆ Si–O ₂	1.297	2.326	1103
BPV86	Au ₇ –O ₂	1.302	2.115	1058
	Au ₆ Si–O ₂	1.291	2.213	1202
TPSS	Au ₇ –O ₂	1.326	2.094	1051
	Au ₆ Si–O ₂	1.296	2.132	1099
PBE	Au ₈ –O ₂	1.235	2.427	1404
	Au ₇ Si–O ₂	1.274	2.172	1242
BPV86	Au ₈ –O ₂	1.237	2.426	1395
	Au ₇ Si–O ₂	1.276	2.174	1232
TPSS	Au ₈ –O ₂	1.239	2.398	1387
	Au ₇ Si–O ₂	1.278	2.142	1210

(oxygen–oxygen bond length) and $r_{\text{Au-O}}$ (gold–oxygen bond length). We note that there is a decrease in the Au–O bond length and an increase in the O–O bond length in the case of the Si-doped cluster irrespective of the functional used. Finally, to validate our results further, the O–O stretching frequencies were calculated on both the pristine and the doped clusters. The calculated O–O stretching frequencies on $\text{Au}_7\text{-O}_2$ and $\text{Au}_8\text{-O}_2$ complexes are in close agreement with the earlier reported experimental and theoretical results.^{55,56} The O–O stretching frequency shows little change on silicon doping in the case of the Au_7 cluster, whereas the O–O stretching frequency decreases notably on doping silicon in the Au_8 cluster. Thus, by doping a single silicon atom, the bonding and activation of the O_2 molecule changes significantly as compared to that of the pristine gold octamer, Au_8 . The O_2 molecule bonds strongly with the Au_7Si cluster, and this bonding is characterized by a substantial increase in the binding energy (0.55 eV) and activation of the O_2 molecule (bond length 1.27 Å).

We now focus our attention on the oxidation of the CO molecule on the pristine and Si-doped clusters. Landman and co-workers have revealed a Langmuir–Hinshelwood (L-H) type of reaction mechanism for CO oxidation on Au_8 supported on the defect-free and defect-rich magnesia thin films using TPR experiments and ab initio calculations.⁵⁷ We have also considered the L-H type of reaction where both the O_2 and CO molecules are initially coadsorbed on the metal cluster. It is important to mention here that, recently, Zeng et al.⁵⁸ have shown that transition-metal-doped gold clusters can act as very efficient catalysts for CO oxidation with low activation barriers (0.2–0.3 eV) following a more direct reaction mechanism. However, the activation barriers were found to be very high (>1 eV) for the above clusters using an L-H type of reaction mechanism by the same authors. The reaction pathways for CO oxidation on the Au_7 , Au_6Si , Au_8 (for planar Au_8 , see the Supporting Information), and Au_7Si clusters are presented in Figures 3, 4, 5, and 6, respectively. We note that the geometries of the transition state and the product differ considerably from that of the reactant in the case of the pristine Au_8 cluster. The

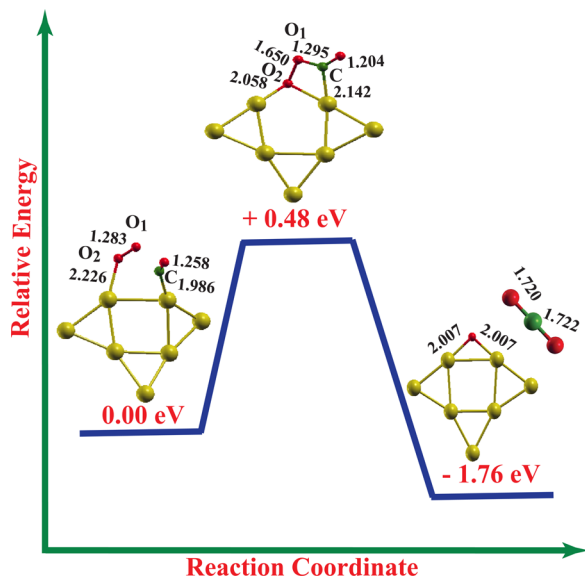


Figure 3. Reaction pathway for the oxidation of CO on the pristine Au_7 cluster.

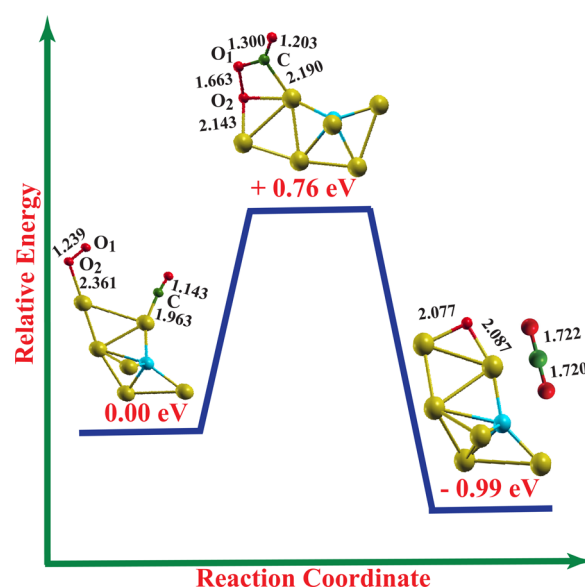


Figure 4. Reaction pathway for the oxidation of CO on the doped Au_6Si cluster.

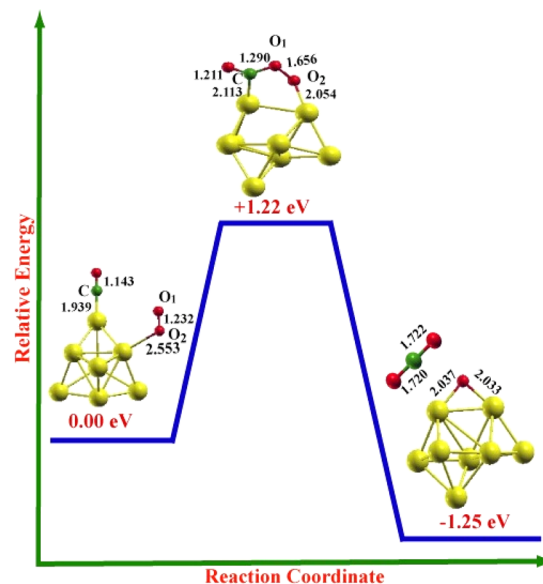


Figure 5. Reaction pathway for the oxidation of CO on the pristine Au_8 cluster.

possible reason for this difference in the geometries may be that the gold octamer sits at the borderline between the 2D and 3D gold clusters. However, the reactant, the transition state, and product geometries are almost similar for the Au_7 and doped Au_6Si and Au_7Si clusters. Although both Au_7 and Au_6Si show almost similar O_2 activation and adsorption energies, surprisingly, the activation barrier for CO oxidation is higher on the silicon-doped Au_6Si (0.76 eV) with respect to the Au_7 cluster (0.48 eV). Interestingly, the calculated barrier height for CO oxidation is very low (0.57 eV) on the Au_7Si cluster as compared to the activation barrier of 1.22 eV on pristine Au_8 cluster (for the planar isomer, the activation barrier is 1.19 eV). Thus, the present study demonstrates the effect of doping in modifying the reactivity and catalytic ability of gold clusters.

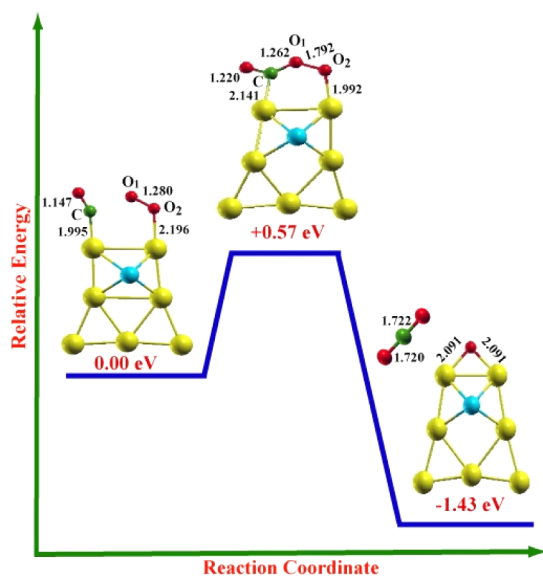


Figure 6. Reaction pathway for the oxidation of CO on the doped Au₇Si cluster.

CONCLUSION

In conclusion, the present computational study illustrates the effect of silicon doping on the reactivity and catalytic activity of gold clusters. Our results show that the silicon-doped Au₇Si cluster preferentially binds and activates the O₂ molecule in comparison to the pristine Au₈ cluster, whereas silicon doping has a little effect on the reactivity and catalytic activity of the Au₇ cluster. The frontier molecular orbital analysis together with the increment of the O–O bond length and red shift in the stretching frequency of the O–O bond confirms the strong binding and O₂ activation in the case of the Au₇Si cluster. Further, the silicon-doped Au₇Si cluster shows enhanced catalytic activity for the CO oxidation reaction with a very low activation barrier of 0.57 eV as compared to the pristine Au₈ cluster. Thus, in summary, our results stress upon the importance of doping foreign impurities in the design of catalytically active nanoscale gold clusters.

ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates of the transition states for CO oxidation on the pristine and silicon-doped gold clusters, and figures showing the relative energies of various low-energy isomers of the clusters, binding energy and catalytic activity of planar Au₈, and optimized geometries of O₂ adsorbed Au₈ and Au₇Si complexes obtained using BPV86 and TPSS functionals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Haruta, M.; Kobayashi, T.; Samo, H.; Yamada, N. Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature Far Below 0°C. *Chem. Lett.* **1987**, *2*, 405–408.
- (2) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. Gold Catalysts Prepared by Coprecipitation for Low-Temperature Oxidation of Hydrogen and of Carbon Monoxide. *J. Catal.* **1989**, *115*, 301–309.
- (3) Landon, P.; Collier, P. J.; Papworth, A. J.; Kiely, C. J.; Hutchings, G. J. Direct Formation of Hydrogen Peroxide from H₂/O₂ Using a Gold Catalyst. *Chem. Commun.* **2002**, 2058–2059.
- (4) Hughes, M. D.; Xu, Y.; Jenkins, P.; McMorn, P.; Landon, P.; Enache, D. I.; Carley, A. F.; Attard, G. A.; Hutchings, G. J.; King, F.; Stitt, E. H.; Johnston, P.; Griffin, K.; Kiely, C. J. Tunable Gold Catalysts for Selective Hydrocarbon Oxidation under Mild Conditions. *Nature* **2005**, *437*, 1132–1135.
- (5) Haruta, M. Size- and Support-Dependency in the Catalysis of Gold. *Catal. Today* **1997**, *36*, 153–166.
- (6) Hashmi, A. S. K.; Hutchings, G. J. Gold Catalysis. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896–7936.
- (7) Jena, N. K.; Chandrakumar, K. R. S.; Ghosh, S. K. DNA Base–Gold Nanocluster Complex as a Potential Catalyzing Agent: An Attractive Route for CO Oxidation Process. *J. Phys. Chem. C* **2012**, *116*, 17063–17069.
- (8) Pyykkö, P. Theoretical Chemistry of Gold. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412–4456.
- (9) Pina, C. D.; Falletta, E.; Prati, L.; Rossi, M. Selective Oxidation Using Gold. *Chem. Soc. Rev.* **2008**, *37*, 2077–2095.
- (10) Sanchez, A.; Abbet, S.; Heiz, U.; Schneider, W.-D.; Häkkinen, H.; Barnett, R. W.; Landman, U. When Gold Is Not Noble: Nanoscale Gold Catalysts. *J. Phys. Chem. A* **1999**, *103*, 9573–9578.
- (11) Lopez-Acevedo, O.; Kacprzak, K. A.; Akola, J.; Häkkinen, H. Quantum Size Effects in Ambient CO Oxidation Catalyzed by Ligand-Protected Gold Clusters. *Nat. Chem.* **2010**, *2*, 329–334.
- (12) Häkkinen, H.; Moseler, M.; Landman, U. Bonding in Cu, Ag, and Au Clusters: Relativistic Effects, Trends, and Surprises. *Phys. Rev. Lett.* **2002**, *89*, 033401–033404.
- (13) Assadollahzadeh, B.; Schwerdtfeger, P. A Systematic Search for Minimum Structures of Small Gold Clusters Au_n (*n* = 2–20) and Their Electronic Properties. *J. Chem. Phys.* **2009**, *131*, 064306–064317.
- (14) Häkkinen, H.; Yoon, B.; Landman, U.; Li, X.; Zhai, H. J.; Wang, L. S. On the Electronic and Atomic Structure of Small Au_N[−] (*N* = 4–14) Clusters: A Photoelectron Spectroscopy and Density Functional Study. *J. Phys. Chem. A* **2003**, *107*, 6168–6175.
- (15) Furche, F.; Ahlrichs, R.; Weis, P.; Jacob, C.; Gilb, S.; Bierweiler, T.; Kappes, M. M. The structures of Small Gold Cluster Anions As Determined by a Combination of Ion Mobility Measurements and Density Functional Calculations. *J. Chem. Phys.* **2002**, *117*, 6982.
- (16) Bulusu, S.; Li, X.; Wang, L.-S.; Zeng, X. C. Evidence of Hollow Golden Cages. *PNAS* **2006**, *103*, 8327–8330.
- (17) Xing, X.; Yoon, B.; Landman, U.; Parks, J. H. Structural Evolution of Au Nanoclusters: From Planar to Cage to Tubular Motifs. *Phys. Rev. B* **2006**, *74*, 165423–165428.
- (18) Gruene, P.; Rayner, D. M.; Redlich, B.; van der Meer, A. F. G.; Lyon, J. T.; Meijer, G.; Fielicke, A. Structures of Neutral Au₇, Au₁₉, and Au₂₀ Clusters in the Gas Phase. *Science* **2008**, *321*, 674–676.
- (19) Li, J.; Li, X.; Zhai, H.-J.; Wang, L.-S. Au₂₀: A Tetrahedral Cluster. *Science* **2003**, *299*, 864–867.
- (20) Yoon, B.; Häkkinen, H.; Landman, U. Interaction of O₂ with Gold Clusters: Molecular and Dissociative Adsorption. *J. Phys. Chem. A* **2003**, *107*, 4066–4071.

- (21) Pal, R.; Wang, L.-M.; Pei, Y.; Wang, L.-S.; Zeng, X. C. Unraveling the Mechanisms of O₂ Activation by Size-Selected Gold Clusters: Transition from Superoxo to Peroxo Chemisorption. *J. Am. Chem. Soc.* **2012**, *134*, 9438–9445.
- (22) Bürgel, C.; Reilly, N. M.; Johnson, G. E.; Mitric, R.; Kimble, M. L.; Castleman, A. W., Jr.; Bonačić-Koutecký, V. Influence of Charge State on the Mechanism of CO Oxidation on Gold Clusters. *J. Am. Chem. Soc.* **2008**, *130*, 1694–1698.
- (23) Socaciu, L.; Hagen, J.; Bernhardt, T.; Wöste, L.; Heiz, U.; Häkkinen, H.; Landman, U. Catalytic CO Oxidation by Free Au⁺: Experiment and Theory. *J. Am. Chem. Soc.* **2003**, *125*, 10437–10445.
- (24) Tang, D.; Hu, C. DFT Insight into CO Oxidation Catalyzed by Gold Nanoclusters: Charge Effect and Multi-State Reactivity. *J. Phys. Chem. Lett.* **2011**, *2*, 2972–2977.
- (25) Yoon, B.; Häkkinen, H.; Landman, U.; Wörz, A.; Antonietti, J.; Abbet, S.; Judai, K.; Heiz, U. Charging Effects on Bonding and Catalyzed Oxidation of CO on Au₈ Clusters on MgO. *Science* **2005**, *307*, 403–407.
- (26) Liu, C.; Tan, Y.; Lin, S.; Li, H.; Wu, X.; Li, L.; Pei, Y.; Zeng, X. C. CO Self-Promoting Oxidation on Nanosized Gold Clusters: Triangular Au₃ Active Site and CO Induced O–O Scission. *J. Am. Chem. Soc.* **2013**, *135*, 2583–2595.
- (27) Gao, Y.; Zeng, X. C. Water-Promoted O₂ Dissociation on Small-Sized Anionic Gold Clusters. *ACS Catal.* **2012**, *2*, 2614–2621.
- (28) Zhang, C.; Yoon, B.; Landman, U. Predicted Oxidation of CO Catalysed by Au Nanoclusters on a Thin Defect-Free MgO Film Supported on a Mo(100) Surface. *J. Am. Chem. Soc.* **2007**, *129*, 2228–2229.
- (29) Molina, L. M.; Hammer, B. Active Role of Oxide Support during CO Oxidation at Au/MgO. *Phys. Rev. Lett.* **2003**, *90*, 206102–206106.
- (30) Wang, C.-M.; Fan, K.-N.; Liu, Z.-P. Origin of Oxide Sensitivity in Gold-Based Catalysts: A First Principle Study of CO Oxidation over Au Supported on Monoclinic and Tetragonal ZrO₂. *J. Am. Chem. Soc.* **2007**, *129*, 2642–2647.
- (31) Harding, C.; Habibpour, V.; Kunz, S.; Farnbacher, A. N.-S.; Heiz, U.; Yoon, B.; Landman, U. Control and Manipulation of Gold Nanocatalysis: Effects of Metal Oxide Support Thickness and Composition. *J. Am. Chem. Soc.* **2009**, *131*, 538–548.
- (32) Jena, N. K.; Chandrakumar, K. R. S.; Ghosh, S. K. Beyond the Gold–Hydrogen Analogy: Doping Gold Cluster with H-atom–O₂ Activation and Reduction of the Reaction Barrier for CO Oxidation. *J. Phys. Chem. Lett.* **2011**, *2*, 1476–1480.
- (33) Fernández, E. M.; Torres, M. B.; Balbás, L. C. Theoretical Study of Oxygen Adsorption on Pure Au_{n+1} and Doped MAu_n⁺ Cationic Gold Clusters for M = Ti, Fe and n = 3–7. *J. Phys. Chem. A* **2008**, *112*, 6678–6689.
- (34) Fernández, E. M.; Torres, M. B.; Balbás, L. C. Theoretical Study of the Coadsorption of CO and O₂ on Doped Cationic Gold Clusters MAu_n⁺ (M = Ti, Fe, Au; n = 1, 6, 7). *Eur. Phys. J. D* **2009**, *52*, 135–138.
- (35) Fernández, E. M.; Torres, M. B.; Balbás, L. C. First Principles Study of CO Adsorption–CO₂ Desorption Mechanisms on Oxidized Doped-Gold Cationic Clusters MAu_nO_m⁺ (M = Ti, Fe; n = 1, 4–7; m = 1–2). *Int. J. Quantum Chem.* **2011**, *111*, 510–519.
- (36) Häkkinen, H.; Abbet, S.; Sanchez, A.; Heiz, U.; Landman, U. Structural, Electronic, and Impurity-Doping Effects in Nanoscale Chemistry: Supported Gold Nanoclusters. *Angew. Chem., Int. Ed.* **2003**, *42*, 1297–1300.
- (37) Li, X.; Kiran, B.; Wang, L.-S. Gold as Hydrogen. An Experimental and Theoretical Study of the Structures and Bonding in Disilicon Gold Clusters Si₂Au_n⁺ and Si₂Au_n (n = 2 and 4) and Comparisons to Si₂H₂ and Si₂H₄. *J. Phys. Chem. A* **2005**, *109*, 4366–4374.
- (38) Kiran, B.; Li, X.; Zhai, H.-J.; Wang, L.-S. Gold as Hydrogen: Structural and Electronic Properties and Chemical Bonding in Si₃Au₃⁽⁺⁰⁻⁾ and Comparisons to Si₃H₃⁽⁺⁰⁻⁾. *J. Chem. Phys.* **2006**, *125*, 133204–133211.
- (39) Pal, R.; Wang, L.-M.; Huang, W.; Wang, L.-S.; Zeng, X. C. Structural Evolution of Doped Gold Clusters: MAu_X⁻ (M = Si, Ge, Sn; X = 5–8). *J. Am. Chem. Soc.* **2009**, *131*, 3396–3404.
- (40) Mostafa, S.; Behafarid, F.; Croy, J. C.; Ono, L. K.; Li, L.; Yang, J. C.; Frenkel, A. I.; Cuenya, B. R. Shape-Dependent Catalytic Properties of Pt Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132*, 15714–15719.
- (41) Narayanan, R.; El-Sayed, A. M. Catalysis with Transition Metal Nanoparticles in Colloidal Solution: Nanoparticle Shape Dependence and Stability. *J. Phys. Chem. B* **2005**, *109*, 12663–12676.
- (42) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, P. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.
- (43) Molina, L. M.; Hammer, B. Oxygen Adsorption at Anionic Free and Supported Au Clusters. *J. Chem. Phys.* **2005**, *123*, 161104–161109.
- (44) Johansson, M. P.; Lechtken, A.; Schooss, D.; Kappes, M. M.; Furche, F. 2D–3D transition of gold cluster anions resolved. *Phys. Rev. A* **2008**, *77*, 053202–053208.
- (45) Yu, S.; Zeng, Q.; Lou, Z.; Yang, M.; Wu, D. First-Principles Study of O₂ Activation on Ligand-Protected Au₃₂ Clusters. *Phys. Chem. Chem. Phys.* **2013**, *15*, 9742–9751.
- (46) Joshi, A. M.; Delgass, W. N.; Thomson, T. K. Analysis of O₂ Adsorption on Binary–Alloy Clusters of Gold: Energetics and Correlations. *J. Phys. Chem. B* **2006**, *110*, 23373–23387.
- (47) Lyalin, A.; Taketsugu, T. Reactant-Promoted Oxygen Dissociation on Gold Clusters. *J. Phys. Chem. Lett.* **2010**, *1*, 1752–1757.
- (48) Han, Y.-K. Structure of Au₈: Planar or Nonplanar? *J. Chem. Phys.* **2006**, *124*, 024316.
- (49) Hansen, J. A.; Piecuch, P.; Levine, B. G. Communication: Determining the Lowest-Energy Isomer of Au₈: 2D, or not 2D. *J. Chem. Phys.* **2013**, *139*, 091101.
- (50) Zhang, M.; Chen, S.; Deng, Q. M.; He, L. M.; Zhao, L. N.; Luo, Y. H. Structures and Electronic Properties of M@Au₆ (M = Al, Si, P, S, Cl, Ar) Clusters: A Density Functional Theory Investigation. *Eur. Phys. J. D* **2010**, *58*, 117–123.
- (51) Li, Y.-F.; Mao, A.-J.; Li, Y.; Kuang, X.-Y. Density Functional Study on Size-Dependent Structures, Stabilities, Electronic and Magnetic Properties of Au_nM (M = Al and Si, n = 1–9) Clusters: Comparison with Pure Gold Clusters. *J. Mol. Model.* **2012**, *18*, 3061–3072.
- (52) Majumder, C. Effect of Si Adsorption on the Atomic and Electronic Structure of Au_n Clusters (n = 1–8) and the Au (111) Surface: First-Principles Calculations. *Phys. Rev. B* **2007**, *75*, 235409.
- (53) De, H. S.; Krishnamurthy, S.; Pal, S. Understanding the Reactivity Properties of Au_n (6 ≤ n ≤ 13) Clusters Using Density Functional Theory Based Reactivity Descriptors. *J. Phys. Chem. C* **2010**, *114*, 6690–6703.
- (54) Das, S.; Pal, S.; Krishnamurthy, S. Understanding the Site Selectivity in Small-Sized Neutral and Charged Al_n (4 ≤ n ≤ 7) Clusters Using Density Functional Theory Based Reactivity Descriptors: A Validation Study on Water Molecule Adsorption. *J. Phys. Chem. A* **2013**, *117*, 8691–8702.
- (55) Woodham, A. P.; Meijer, G.; Fielicke, A. Charge Separation Promoted Activation of Molecular Oxygen by Neutral Gold Clusters. *J. Am. Chem. Soc.* **2013**, *135*, 1727–1730.
- (56) Fernández, E. M.; Ordejón, P.; Balbás, L. C. Theoretical Study of O₂ and CO Adsorption on Au_n Clusters (n = 5–10). *Chem. Phys. Lett.* **2005**, *408*, 252–257.

(57) Arenz, M.; Landman, U.; Heiz, U. CO Combustion on Supported Gold Clusters. *ChemPhysChem* **2006**, *7*, 1871–1879.

(58) Gao, Y.; Shao, N.; Bulusu, S.; Zeng, X. C.; Effective, C. O. Oxidation on Endohedral Gold-Cage Nanoclusters. *J. Phys. Chem. C* **2008**, *112*, 8234–8238.