THEORETICAL STUDY OF EFFECT OF RHODIUM DOPING ON SILVER NANOCLUSTERS TOWARDS CO OXIDATION

Devendra Kumar Mahawar*
Department of Chemistry, University of Rajasthan, Jaipur 302004, Rajasthan, India
*devendramahawar@gmail.com

Nisha Rajput
Department of Chemistry, University of Rajasthan, Jaipur 302004, Rajasthan, India

Priyanka Madhukar
Department of Chemistry, University of Rajasthan, Jaipur 302004, Rajasthan, India

Shrikant G. Kalane
Department of Chemistry, Late Pundalikrao Gawali Mahavidyalaya, Sirpurjain, Maharastra, India

Abstract
This study investigates the adsorption of CO molecules on pure Ag_8 and Rh_8 nanoclusters, as well as Ag/Rh bimetallic systems, using density functional theory (DFT) within the generalized gradient approximation (GGA). The optimization of these clusters was carried out in their singlet states and lowest energy spin states. Our results reveal that doping an Ag nanocluster with Rh atoms causes considerable change in the binding energy and hence the catalytic activity of the cluster. The results indicated that Rh doping activated the otherwise inactive Ag nanoclusters by increasing the adsorption energy almost 8 times for Ag_7Rh (-87.81213 kcal/mol) and Ag_6Rh_2 (-84.50410 kcal/mol) in comparison to pure Ag_8 (-10.61040 kcal/mol) towards CO oxidation. The improved catalytic activity of the Ag_7Rh system for CO oxidation is attributed to enhanced charge transfer between the metals, explained by the ensemble effect. As the number of dopant atoms increases, the adsorption energy values decrease, reaching a saturation level. This study suggests that further exploration is needed to understand the CO oxidation mechanism and determine the optimal doping percentage for maximum catalytic efficiency.
Keywords: nanocatalysis, CO oxidation, DFT, bimetallic

Introduction

Research involving nanoparticles is expanding rapidly due to a growing understanding of their impact across various fields of science and technology. In recent years, transition metal clusters have garnered significant attention because of their remarkable properties. These clusters exhibit unique optical, magnetic, and electronic characteristics, making them promising candidates for novel catalysts with enhanced activity and selectivity[1-3]. As metal cluster catalysis plays a pivotal role in the modern chemical industry, considerable efforts are dedicated to their development. A review by Aiken and Finke provides valuable insights into the synthesis, characterization, and catalytic applications[4] of transition metal nanoclusters.

Studies[5-7] have demonstrated that appropriate doping can induce substantial changes in the geometric structures, chemical reactivity, and magnetic properties of clusters. Transition metals are excellent dopants due to their ability to form diverse bonds. Bimetallic nanoclusters, which combine two different metals, often exhibit superior properties compared to their pure counterparts. These hybrid materials enable intermetallic interactions, enhancing catalytic performance. Additionally, optimizing their structural features,

such as the choice of doping element and its concentration, further improves their catalytic activity. Therefore, understanding how the composition influences the reactivity of nanoclusters is crucial for designing advanced catalysts.

Bimetallic clusters are highly efficient catalysts for a range of reactions, including hydrosilylation[8], hydrogenation of aromatic nitro compounds[9], oxidation of benzyl alcohol[10], Suzuki[11] and Heck-type[12] couplings, and various other organic reactions[13, 14]. Among these, the CO oxidation reaction stands out as a prototype for heterogeneous catalysis due to its significance in environmental protection. This reaction finds widespread applications in air purification systems, CO detectors, and fuel cells[15-17], while also playing an important role in organometallic chemistry, bridging the gap with surface chemistry.

The foundational study on the interaction between CO and metal surfaces was conducted by Blyholder, using a model based on Hückel molecular orbitals[18]. This model proposed that the interaction of CO with transition metal surfaces is driven by two primary factors: (1) a σ bond formed between the carbon atom of CO and the metal surface, facilitated by charge transfer from CO to

the metal, and (2) back-donation of electrons from the metal's d-orbitals to the π* orbitals of CO.

Extensive theoretical studies have since been performed on CO adsorption and oxidation using various clusters, including Au, Ag, Pt, Pd_n, Rh_n, Au-Pd, Ag-Au, Pd-Rh, Zr-Sc, Au-Cu, and Pd-Ni, along with other supported catalysts[19-27]. Investigations into CO oxidation on Au-Cu clusters, for instance, reveal that the reaction predominantly follows the Langmuir-Hinshelwood mechanism, where CO and O_2 are co-adsorbed on the cluster[28]. This mechanism appears to be a common pathway for CO oxidation on bimetallic clusters, further emphasizing their catalytic efficacy.

Numerous experimental and theoretical studies have explored the use of Rh and Ag-based clusters for CO oxidation. Fielicke et al. investigated the CO adsorption activity of rhodium clusters using infrared multiple photon dissociation spectroscopy and density functional theory (DFT) calculations[29]. Their work, along with other studies, has revealed the presence of a non-zero magnetic moment in small rhodium clusters. Additionally, Beltran et al.'s ab initio and anion photoelectron studies[19] of Rh_n clusters highlighted their unique structural, electronic, and magnetic properties. Experimental research on silver nanoclusters has demonstrated their high activity and selectivity for CO oxidation, particularly at low temperatures[21]. However, recent studies have shown that Ag/Rh bimetallic nanoclusters exhibit enhanced catalytic activity. Hirakawa et al. have experimentally demonstrated the formation of Ag/Rh bimetallic nanoclusters with an Ag-core and Rh-shell structure, derived from Ag and Rh monometallic nanoparticles in solution[30]. The Ag_xRh_{1-x} (x = 0.4 and 0.5) system, studied in detail by Yang et al., revealed that the electronic structure of the Ag-Rh 1:1 cluster is similar to that of Pd, a known efficient catalyst[31]. DFT calculations by Roy et al. also indicated significant charge transfer between Ag and Rh atoms in the bimetallic system, suggesting that doping an Ag nanocluster with Rh atoms significantly alters its binding energy and catalytic properties[32]. Recent reports on supported Au-Rh based[33-35] and Cu-based[36] bimetallic nanoclusters (such as Cu_3Au_7, Cu_3Pt_7, and Cu_3Rh_7) for CO oxidation have further inspired the present study.

When designing a bimetallic nanocatalyst, several factors must be considered, such as the structural stability, the optimal ratio of the two atoms, and the binding energies of the adsorbate at various positions on the cluster. Theoretical methods are particularly well-suited for such studies, as they provide detailed insights into optimized configurations and reaction mechanisms, which are not easily accessible through experimental approaches. In this study, we theoretically explore the activation of an Ag8 nanocluster through Rh doping and examine its impact on CO oxidation. We conducted a detailed analysis of pure Ag_8 and Rh_8 clusters, as well as Ag_xRh_{8-x} bimetallic systems with x ranging from 1 to 7. Computational simulations are employed to assess the strength of CO adsorption on these different clusters. The observed differences in cluster behavior are analyzed based on dopant concentration, electronic properties, and the binding energy of the adsorbents.

Computational Details

Symmetry-unrestricted full geometry optimizations were carried out for the Ag_xRh_{8-x} (x = 0 to 8) clusters, as well as for all possible structural isomers of CO adsorbed on these clusters. Multiple spin multiplicity states were considered for each structure, with the lowest-energy configuration identified for each cluster type. Additionally, harmonic vibrational frequency calculations were performed for all CO-cluster complexes.

All DFT calculations were performed using the ORCA[37] package. Geometry optimizations and single-point energy calculations were conducted at the BP86 level[38,39], which combines the Becke 88 exchange functional and the Perdew 86 correlation functional, as well as using the B3LYP hybrid functional, a mix of Becke's three-parameter hybrid exchange functional[40] and the Lee–Yang–Parr nonlocal correlation functional[41]. The def2-SVP basis set was used for all electrons. Initial geometries were generated with Gabedit[42] software. Isotropic polarizability values were calculated for all the clusters. Bond lengths, dipole moments, and vibrational frequencies for both CO and the corresponding complexes were computed. The adsorption energies (E_{ads}) were determined using the following equations:

$$E_{ads} = E_{cluster-CO} - (E_{cluster} + E_{CO})$$

$$E_{ads} = E_{cluster-O2} - (E_{cluster} + E_{O2})$$

where $E_{cluster-CO}$, $E_{cluster}$, E_{CO}, $E_{cluster-O2}$ and E_{O2} are the total energies of the cluster–carbonyl complex, the cluster, molecular CO, cluster—O_2 complex and molecular O_2 respectively. A more negative E_{ads} indicates stronger adsorption of CO/O_2 to the cluster, reflecting the stabilization of the cluster–CO and cluster–O_2 bonds.

Results and Discussions

Geometry optimization and single-point energy calculations were performed for the CO molecule and all nine clusters (Ag_xRh_{8-x} where x = 0 to 8) across various spin states to determine the lowest energy configurations. The CO molecule is most

stable in the singlet state, while the ground state spin multiplicities of the clusters vary depending on their electronic configurations. The optimized structures of the clusters at their lowest energy spin states, obtained using the DFT-based BP86 functional, are shown in Fig. 1. The optimized geometry of Ag_8 exhibits D_2d symmetry, while Rh_8 has Cs symmetry. Doping a Rhodium atom into the silver cluster results in symmetry lowering. For instance, Ag_7Rh follows Cs symmetry, whereas the equally distributed Ag_4Rh_4 system retains D_2d symmetry. These findings are consistent with previous reports[32]. Table 1 presents the single-point energies of the clusters at different spin states and the relative energy differences for each state compared to the ground state in each cluster type.

Table 1 clearly shows that the lowest energy spin multiplicities for the clusters are 1, 3, 3, 5, 7, 9, 11, 7, and 11 for Ag_8, Ag_7Rh, Ag_6Rh_2, Ag_5Rh_3, Ag_4Rh_4, Ag_3Rh_5, Ag_2Rh_6, $AgRh_7$, and Rh_8, respectively. The ground state spin multiplicities, along with the single-point energies of the optimized clusters and the energies for the formation of clusters from their constituent atoms, are provided in Table 2.

Table 2 clearly shows that Rh_8 has the highest energy for cluster formation, while the formation of the Ag_8 cluster is the least favored. However, the introduction of a Rh atom into the silver cluster increases the formation energy, indicating that the presence of Rhodium stabilizes the cluster.

An important observation when doping pure metal clusters is the charge transfer between atoms. The charge density for each system was assessed using Natural Bond Orbital (NBO) charge analysis. It was found that as the number of Rh atoms increases in the bimetallic system, the effective charge density on Rh gradually decreases. In the case of Ag_7Rh, the single rhodium atom carries a substantial negative charge of -0.609 a.u., with the corresponding positive charge distributed across the silver atoms. However, in the highest-doped Rh_7Ag cluster, the largest charge on Rh is only -0.177 a.u. This difference in charge distribution can significantly influence the binding properties of the cluster systems.

The enhanced catalytic activity of diluted bimetallic nanoclusters can be attributed to the "ensemble effect[43]." When a metal species is diluted with another metal, isolated catalytic sites of smaller size are created, which reduces the number of possible adsorption configurations for reactant molecules. This phenomenon, known as the ensemble effect, leads to fewer reactive pathways originating from these active centers, thereby increasing the selectivity of the catalyst compared to clusters composed of a single metal.

The catalytic activity of Ag is enhanced by the incorporation of Rh into the bimetallic system. This addition prevents the aggregation of Rh atoms, thereby generating more active catalytic sites within the bimetallic cluster.

The dipole moments of the pure Ag_8 and Rh_8 clusters, as well as the bimetallic systems, were calculated to investigate their relationship with the cluster-CO adsorption energy values.

For CO–cluster complexes, initial structures for all possible structural isomers were generated and optimized, considering various spin states. Adsorption energies were calculated for each complex at both the singlet and lowest energy spin states. The isomer with the lowest adsorption energy (E_{ads}) was identified for each cluster type. Table 4 presents the lowest energy spin multiplicities of the optimized complexes along with the calculated adsorption energies for both singlet and lowest energy spin states.

The significant difference in adsorption energy (E_{ads}) values between the two spin states highlights the importance of considering various spin multiplicities when performing DFT calculations to determine the lowest energy configurations. The E_{ads} value was lowest for the Ag_8-CO complex (-10.6104 kcal/mol), and when a Rh atom was introduced into the cluster, the adsorption energy increased more than eightfold for Ag_7Rh (-87.8121 kcal/mol). As the number of Rh dopant atoms increased, the adsorption energy gradually decreased, reaching a saturation level of -49.981 kcal/mol with further doping.

Mulliken atomic charges on the metal atoms to which CO was adsorbed were analyzed. The highest charge observed was 0.0746, which was on the Rh atom of Ag_7Rh-CO, followed by a charge of 0.0629 on one of the Rh atoms in the Ag_6Rh_2-CO complex. The charge transfer from the metal atom to the unoccupied antibonding 2π level of CO destabilizes the CO bond, resulting in an increase in the CO bond length. The CO bond lengths for the Ag_7Rh-CO and Ag_6Rh_2-CO complexes were nearly identical, both measuring 1.17 Å. However, a larger bond length of 1.201 Å was observed for the Ag_4Rh_4-CO complex.

Single-point energy calculations for the clusters and complexes at their singlet states were performed at both the BP86 and B3LYP levels to examine the variation in adsorption energy (E_{ads}) calculated by both methods. Although there was a variation in E_{ads} in the range of 5 – 10 kcal/mol, the overall trend observed was consistent in both cases. The binding energies were plotted for the clusters at their singlet states and lowest energy spin states, as shown in Graph 1 and Graph 2.

The adsorption energies did not exhibit a strong linear relationship with either the polarizability or the HOMO-LUMO gap of the metal clusters. Additionally, the dipole moment of the clusters did not appear to significantly influence the strength of the CO–cluster bond.

Based on the results above, we can conclude that Ag_7Rh and Ag_6Rh_2 are promising candidates for CO adsorption, with the highest adsorption energies (E_{ads}) of -87.81 kcal/mol and -84.50 kcal/mol, respectively, in their ground states. Further investigations can focus on calculating the adsorption energies of O_2 using similar methodologies. Additionally, CO oxidation studies could be conducted using the intrinsic reaction coordinate (IRC) approach.

Conclusion

In this study, we optimized both pure Ag_8 and Rh_8 nanoclusters, as well as Ag/Rh bimetallic systems, in their singlet states and lowest energy spin states. The adsorption of CO molecules on these clusters was investigated using density functional theory (DFT) calculations within the generalized gradient approximation (GGA). Adsorption energies were calculated and analyzed for all clusters. The results showed that Rh doping significantly enhanced the activity of otherwise inactive Ag nanoclusters, increasing the adsorption energy by nearly eight times. The improved catalytic activity of the Ag_7Rh system for CO oxidation is attributed to the enhanced charge transfer within the bimetallic system. This enhanced activity can be explained by the ensemble effect. The Ag/Rh bimetallic system shows a synergistic effect where the interaction between the two metals leads to improved catalytic activity. This suggests that bimetallic clusters may offer advantages over pure metal systems in certain catalytic processes. As the number of dopant atoms increased, the adsorption energy values gradually decreased, eventually reaching a saturation point. This implies that there is an optimal range of doping concentration beyond which additional dopant atoms may not significantly enhance or may even reduce the catalytic efficiency. Future studies could focus on understanding the CO oxidation mechanism on these clusters and determining the optimal doping percentage for achieving maximum catalytic efficiency. The enhanced catalytic activity due to Rh doping warrants a deeper investigation into the reaction mechanisms, specifically the role of charge transfer and atomic interaction in the bimetallic system. This could lead to a more detailed understanding of how to further optimize these systems for practical applications.

References

1. Yan, J. M.; Zhang, X. B.; Han, S.; Shioyama, H.; Xu, Q., *J. Power Sources* 2009, 194, 478−481.
2. Li, N.; Tittl, A.; Yue, S.; Giessen, H.; Song, C.; Ding, B.; Liu, N., *Light: Sci. Appl.* 2014, 3, 226.
3. Shi, J., *Chem. Rev.* 2013, 113, 2139−2181
4. John D. Aiken III, Richard G. Finke, *Journal of Molecular Catalysis A: Chemical*, 1999, 145, 1-44
5. Gruene, P., Fielicke, A., Meijer, G., Janssens, E., Ngan, V. T., Nguyen, M. T., and Lievens, P., *ChemPhysChem* 2008, 9, 703
6. Lu, P., Wu, C., Li, Y., Yu, Z., Cao, H., Wang, S., *Journal of Mat. Sci.*, 2013, 48, 8552-8558
7. Hirabayashi S, Ichihashi M, *J Phys Chem A*, 2015, 119(32), 8557-8564
8. G. Schmid, H. West, H. Mehles, A. Lehnert, *Inorg. Chem.* ,1997, 36, 891–895
9. I.I. Obraztsova, N.K. Eremenko, G.Yu. Simenyuk, A.N. Eremenko, B.G. Tryasunov, *Solid Fuel Chem.*, 2012, 46, 364-367
10. Nagy, G., Benkó, T., Borkó, L., Csay, T., Horvath, A., Frey, K., Beck, A., *Reac Kinet Mech Cat*, 2015, 115, 45-65
11. M.T. Reetz, R. Breinbauer, K. Wanninger, *Tetrahedon Lett.* 1996, 37, 4499–4502.
12. M.T. Reetz, G. Lohmer, *J. Chem. Soc., Chem. Commun.* 1996, 1921–1922
13. M.N. Vargaftik, V.P. Zargorodnikov, I.P. Stolarov, I.I. Moiseev, D.I. Kochubey, V.A. Likholobov, A.L. Chuvilin, K.I. Zamaraev, J. Ž. *Mol. Catal.* 1989, 53, 315–348
14. M.T. Reetz, R. Breinbauer, P. Wedemann, P. Binger, *Tetrahedron*, 1998, 54, 1233–1240
15. G. G. Jernigan and G. A. Somorjai, *J. Catal.*, 1994, 147, 567.
16. P. A. Wright, S. Natarajan, J. M. Thomas and P. L. Gai-Boyes, *Chem. Mater.*, 1992, 4, 1053
17. S. D. Gardner, G. B. Hoflund, B. T. Upchurch, D. R. Schryer, E. J. Kielin and J. Schryer, *J. Catal.*, 1991, 129, 114
18. G. Blyholder, *J. Chem. Phys.,* 1964, 68, 2772

19. Marcela R. Beltran, Fernando Buend´ıa Zamudio, Vikas Chauhan, Prasenjit Sen, Haopeng Wang, Yeon Jae Ko, and Kit Bowen, *Eur. Phys. J. D*, 2013, 67, 63

20. Dianyong Tang, Zhongzhu Chen,b Jianping Hu, Guofeng Sun, Shenzhuang Lua and Changwei Huc, *Phys. Chem. Chem. Phys*.,2012,14,12829–12837

21. B. Kalita and R.C. Deka, *Eur. Phys. J. D*, 2009, 53, 51–58

22. Jorge I. Benítez, Raúl Flores, and Miguel Castro, *Can. J. Chem*., 2013, 91, 1033-1042

23. Liang Zhang, Hyun You Kim, Graeme Henkelman, *J. Phys. Chem. Lett*. 2013, 4, 2943−2947

24. Xiao-Na Li, Hua-Min Zhang, Zhen Yuan, Sheng-Gui He, *Nat. Commun*., 2016, 7, 11404

25. Wenqiang Ma, Fuyi Chen, *Catal Lett*, 2013, 143:84–92

26. Ayman D. Allian, Kazuhiro Takanabe, Kyle L. Fujdala, Xianghong Hao, Timothy J. Truex, Juan Cai, Corneliu Buda, Matthew Neurock, Enrique Iglesia*, J. Am. Chem*. Soc. 2011, 133, 4498–4517

27. H. Guan, J.Lin, B.Qiao, X.Yang, L.Li, S.Miao, A. Wang, X. Wang, T. Zhang, *Angew.Chem.Int. Ed*. 2016, 55,2820–2824

28. L. Zhang, H. Y. Kim and G. Henkelman, *J. Phys. Chem. Lett*., 2013, 4, 2943–2947

29. Andre Fielicke, Gert von Helden, Gerard Meijer, David B. Pedersen, Benoit Simard, and David M. Rayner, *J. Phys. Chem. B* 2004, 108, 14591-14598

30. K Hirakawa, N Toshima, Chem. Lett., 2003, 32(1), 78-79

31. Anli Yang, Osami Sakata, Kohei Kusada, Tomoe Yayama, Hideki Yoshikawa, Takayoshi Ishimoto, Michihisa Koyama, Hirokazu Kobayashi, Hiroshi Kitagawa, *Appl. Phy. Lett*., 2014, 105, 153109

32. Anindita Roy, Biplab Debnath, Ramkrishna Sahoo, K. R. S. Chandrakumar, Chaiti Ray, Jayasmita Jana, Tarasankar Pal, *J. Phys. Chem. C* 2016, 120, 5457−5467

33. Lee, H.; Liao, Z.-H.; Hsu, P.-W.; Hung, T.-C.; Wu, Y.-C.; Lin, Y.; Wang, J.-H.; Luo, M.-F. . *J. Chem. Phys*. 2017, *147* (4), 044704.

34. Hsu, P.-W.; Liao, Z.-H.; Hung, T.-C.; Lee, H.; Wu, Y.-C.; Lai, Y.-L.; Hsu, Y.-J.; Lin, Y.; Wang, J.-H.; Luo, M.-F. *Phys. Chem. Chem. Phys*. 2017, *19* (22), 14566–14579.

35. Li, H.; Luo, L.; Kunal, P.; Bonifacio, C. S.; Duan, Z.; Yang, J. C.; Humphrey, S. M.; Crooks, R. M.; Henkelman, G. *J. Phys. Chem. C* 2018, *122* (5), 2712–2716.

36. Liu, Y.; Li, H.; Cen, W.; Li, J.; Wang, Z.; Henkelman, G. *Phys. Chem. Chem. Phys*. 2018, *20* (11), 7508–7513.

37. F Neese, *WIREs Comput Mol Sci*., 2012, 2, 73-78

38. Becke, A.D. *Phys. Rev. A*, 1988, 38, 3098

39. Perdew, J.P, *Phys. Rev. B*, 1986, 33, 8822

40. Becke, A. D. *J. Chem. Phys*. 1993, 98 (7), 5648

41. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* 1988, 37 (2), 785

42. Allouche A.R., J. Comput. Chem., 2011, 32, 174-182

43. Zaera, F.; Gellman, J.A.; Somorjai G.A. Surface Science studies of catalysis: Classifications of reactions. *Acc. Chem. Res*. 1986, 19, 24-31