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Methanol Adsorption and Oxidation on Gold, Platinum and Gold-Platinum Bimetallic Clusters: A Case Study on Au₆, Pt₆ and Au₃Pt₃ Clusters Using Density Functional Theory

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Abstract

Geometric orientation of the metal atoms in a bimetallic nanoparticle can play a pivotal role in its sensing and activation of different types of molecules. In the present paper, we demonstrate this complex structure-property correlation on model Au-Pt clusters by studying methanol adsorption and oxidation on various conformations of the Au₃Pt₃ cluster with different relative orientations of the Au and Pt atoms. We have further compared the results with the monometallic Au and Pt clusters. Our results reveal that the adsorption of methanol is least favourable on the monometallic Au₆ cluster as reflected from a very low free energy of complexation (-0.92 Kcal/mol), whereas, the free energy of methanol complexation for the Pt₆ is -6.69 Kcal/mol. The bimetallic Au₃Pt₃ conformers show higher free energies of methanol complexation with notable dependence on the relative orientation of the Au and Pt atoms in the conformer. Likewise, the activation barriers for methanol oxidation are found to be large for the monometallic Au₆ cluster as compared to the monometallic Pt₆ and bimetallic Au₃Pt₃ clusters. Further, the activation barriers with respect to O-H and C-H bond activation of methanol are found to be very low and highly sensitive to the relative orientation of the Au and Pt atoms in the bimetallic Au-Pt cluster. Thus, the current study demonstrates that it is possible to tune reactivity and catalytic activity of the cluster by varying its structural features.

Keywords: bimetallic clusters, geometric orientation, methanol oxidation, density functional theory, O-H and C-H dissociation.

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1. Introduction

Bimetallic clusters have an extra degree of freedom, enabling their physical and chemical properties to be tuned by varying composition and degree of atomic segregation resulting in improved performance [1-7]. Experiments resorting to doping so as to have binary or mixed clusters have resulted in a number of surprises such as aromaticity [8-10], enhanced thermal stability as compared to the pure clusters [11-12], better optical [13], magnetic [14] and catalytic properties etc. [12-17]. The properties of these bimetallic systems arise due to the synergistic electronic interactions between the different metal atoms. Further, the bimetallic clusters provide more than one reactive sites and thus act as superior catalysts compared to the monometallic clusters. Until

now, a number of bimetallic clusters of d-block elements such as Au-Pt, Rh-Pt, Pd-Pt, Au-Ag, Au-Pd, etc with varying compositions have been reported and currently the catalytic properties of these bimetallic systems is a subject of great interest [18-22].

Among the bimetallic clusters, Au-Pt binary clusters are found to have excellent catalytic properties for a wide range of applications such as alkane conversion [23], NO reduction [24], CO oxidation [25-26], CH₃OH oxidation [27-28], isotope exchange [29], C-N coupling [30], O₂ reduction etc [31]. However, the strength of these properties is seen to be dependent upon the preparation route of the bimetallic catalysts, size, and the ratio of the two metals [32-35]. It is also reported that the preparation of these bimetallic nanoparticles is complicated due to different reduction

kinetics of Au and Pt ions. For example, the alloying of Au-Pt clusters has been a subject of many controversies especially in the size of nanoscale and appears to be complicated. Due to this, Au-Pt nanostructures inevitably, form core-shell or shell-core like structures due to their thermodynamic immiscibility [36]. Most of the studies report a Pt_{core}Au_{shell} type of conformations within Au-Pt bimetallic clusters. In a remarkable experiment [37], the Au core Pt shell configuration was maintained when the bimetallic cluster was thermally annealed at 300 C for 24h but changed to layered segregation after annealing at 600 C.

Thus, challenges in preparing these binary nanomaterials and their wide range of potential applications in diverse areas has motivated many researchers to investigate the structural properties of Au-Pt clusters using theoretical methods. Although there have been many experimental studies of Au-Pt clusters, there have been few theoretical studies of these clusters. The available theoretical studies have resulted in some understanding of electronic structure and properties of Au-Pt clusters with 1-20 atoms [38-45]. Au has an electronic configuration of $5d^{10}, 6s^1$ and that of Pt is $5d^9, 6s^1$. The small s-d energy gap in Au, caused by strong relativistic effects leads to directional bonding in homogeneous Au clusters. As a result neutral Au clusters adopt planar geometries up to 14 atoms [28], whereas, homogeneous Pt clusters, prefer 3-d structures [43]. Interestingly, it is noted that in Au-Pt binary clusters with higher Au content, retain the planar geometries [46]. Similarly, binary clusters with higher Pt content prefer to orient themselves as 3-D structures [47]. Thus, the ratio of the components is seen to influence the geometry of the cluster.

Recently, binary metal clusters have found considerable interest in organic hydrogen based fuel cells such as direct methanol fuel cells (DMFCs) [48-51]. Traditionally, Pt clusters have been used as catalysts in the DMFCs. However the performance of Pt based DMFCs is limited by several factors which include: a) slow anodic oxidation of methanol b) high methanol permeation from anode to cathode and c) fuel flow obstruction at anode due to CO₂ formation. Thus efforts have been made for tackling these problems by using better mediums as well as using binary clusters (such as Pt-Ni, Pt-Co, Pt-Pd, Pt-Au etc.) which are more active for methanol oxidation at anode and simultaneously tolerant to methanol at cathode. For example, Au-Pt bimetallic clusters have shown enhanced methanol oxidation activity compared to the monometallic Pt based catalysts and it is believed that the presence of Au reduces the CO poisoning in the case of Au-Pt clusters. Further, Au-Pt nanocatalysts are reported to have greater methanol tolerance at the cathode in the case of DMFCs compared to the pure Pt nanocatalysts.

Although, a number of experimental and theoretical works have reported the electrocatalytic activity of Au-Pt clusters vis a vis methanol, to the best of our knowledge not a single theoretical study has been carried out to investigate the

precise role played by the relative orientation of the Au and Pt atoms for methanol activation and oxidation in the bimetallic Au-Pt clusters. Thus, in the current work we have studied the methanol oxidation on the Au-Pt clusters in order to gain an in depth understanding into the dissociation of methanol on the different conformers of Au₃Pt₃ cluster and compared it with its monoatomic counterparts. We have chosen various conformers of a six atom bimetallic Au-Pt cluster for this purpose with different orientations of Au and Pt atoms.

2. Computational details

Density functional theory (DFT) with PBE exchange and correlation potential as implemented in the Gaussian 09 was used to perform all the calculations [52]. For each cluster, a number of conformers with different spin multiplicities were used as a starting guess to find the ground state geometry. Geometry optimizations were carried out by using the Berny algorithm with the default convergence criterion. The LANL2DZ basis set and the corresponding Los Alamos relativistic effective core potential (RECP) was used to take into account scalar relativistic effects for the gold and platinum atoms. For the hydrogen, oxygen and carbon atoms, the TZVP basis set was used. In order to locate the energetically most favorable configurations of methanol adsorption on the Au₆, Pt₆, and various conformers of Au₃Pt₃, we considered the various possible adsorption modes (via O and C atoms), at the various possible sites on all the clusters. Vibrational frequency calculations were carried out to guarantee the optimized structures

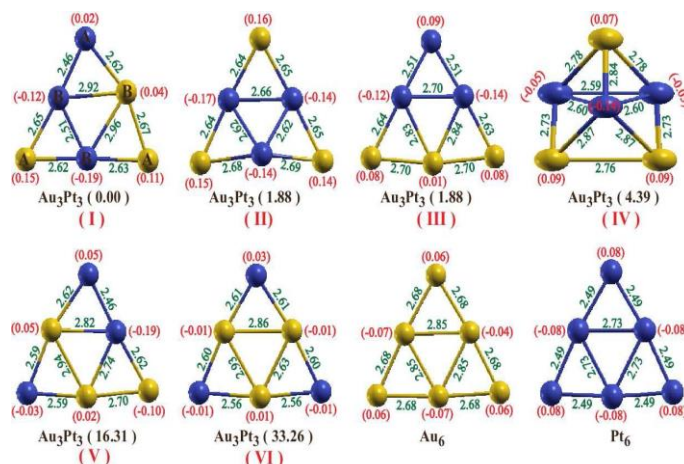


Fig. 1: Optimized geometries of the various conformers of Au₃Pt₃ cluster, and ground state geometries of Au₆ and Pt₆ clusters. The numbers in the green colour represent the calculated A-B and B-B bond distances where as the numbers in red colour are the computed NBO charges on each atom

are local minima. The free energy of complexation of the methanol-cluster complexes was calculated as the difference between the free energy of complex and its constituents (i.e. methanol molecule and atomic cluster). The absolute value of total free energy (G_{tot}) considered for each structure is calculated using the Gibbs free energy function at 298K using the following equation.

$$G_{\text{tot}} = E_{\text{elec}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{ZPE}} + PV - TS \quad (1)$$

where E_{elec} , E_{trans} , E_{rot} and E_{vib} represent the electronic, translational, rotational and vibrational contributions respectively to the total energy. E_{ZPE} is the zero point correction to the total energy and the other terms have their usual meaning. The transition states were found by using the linear synchronous transit method and were characterized by the presence of one imaginary frequency.

3. Results and Discussions

3.1 Methanol adsorption on the Au_6 , Pt_6 , and Au_3Pt_3 clusters

Several conformations of Au_3Pt_3 cluster are generated and optimized with different possible spin multiplicities. The ground state structures in all the cases were found to prefer singlet multiplicity over triplet multiplicity. The lowest conformation is a D_{3h} conformation as in case of Au_6 and Pt_6 clusters, whereas, the various bimetallic conformers are found to have slightly distorted D_{3h} conformations except for the conformer IV, which has a 3-d structure. The conformations considered in this study along with their relative energies are shown in Fig. 1. Also shown are the conformations of Au_6 and Pt_6 ground state geometries. Noticeably, the ground state isomer reported in one of the earlier studies [53] is found to be second lowest energy isomer in the current study. It can be seen from the figure that the Au_6 and Pt_6 clusters have all the A-B and B-B lengths similar and as a result the Au_6 and Pt_6 clusters are highly symmetrical. However, the bimetallic Au_3Pt_3 conformers (except II and VI) are slightly deformed with different A-B and B-B bond lengths. Fig. 1 also enlists the calculated natural bond orbital (NBO) charges on the Au and Pt atoms in Au_6 , Pt_6 and different conformations of the Au_3Pt_3 clusters. We note that there is a little charge separation between the cap (A) and the bridged atoms (B) in the pristine Au_6 and Pt_6 clusters. In contrast, the bridged Pt atoms in the various conformations of Au_3Pt_3 are seen to accumulate a higher degree of negative charge. This enhanced charge separation is expected to induce different reactivity and catalytic activity in the Au-Pt bimetallic clusters as compared to the pristine Au and Pt clusters.

We next look at the adsorption of methanol on the ground state Au_6 , Pt_6 structures and various conformers of bimetallic Au_3Pt_3 cluster. The optimized geometries of the lowest energy structures of the methanol complexes of Au_6 , Pt_6 and Au_3Pt_3

conformers are demonstrated in Fig. 2. It is important to mention here that methanol adsorption was studied through various modes (via O or C atoms) at different possible sites in all the clusters reported in the current study. We note that the methanol adsorbs on each cluster via its oxygen atom preferably, which is in accordance with the earlier reported studies of methanol adsorption on various types of metal clusters and surfaces [49,50,54,55]. Also the methanol adsorption takes place at the cap atoms of the various clusters except for II and III isomers of Au_3Pt_3 cluster. From Figure 2, it can be seen that methanol adsorption has a little effect on the structural parameters of the Au_6 , Pt_6 and the various Au_3Pt_3 conformers with the exception of II isomer, where the methanol adsorption results in a 2D to 3D transition. We have also computed the free energy of

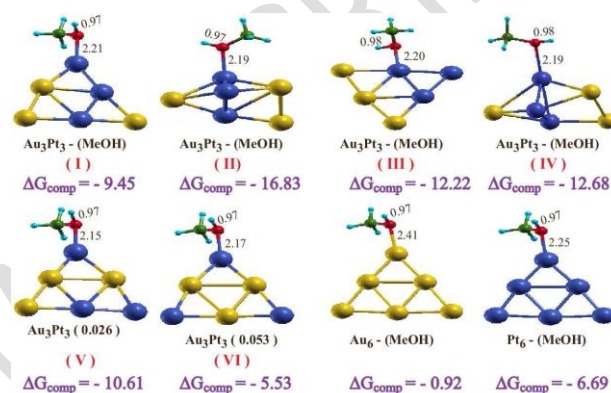


Fig. 2: Optimized geometries of the methanol adsorbed conformers of Au_3Pt_3 , and Au_6 and Pt_6 .

complexation (ΔG_{comp}) of methanol with the Au_6 , Pt_6 and the various Au_3Pt_3 clusters, and the results are also highlighted in Fig. 2. The ΔG_{comp} values for the Au_6 and Pt_6 clusters are -0.92 and -6.69 kcal/mol respectively. Among the bimetallic Au_3Pt_3 conformers, the II conformer shows highest value of ΔG_{comp} (-16.83 kcal/mol). It is important to mention here that the conformer which shows the highest value of ΔG_{comp} is the one which undergoes 2D-3D structural transition upon methanol adsorption. The ΔG_{comp} values for I, III, IV and V conformers are -9.45, -12.22, -12.68 and -10.61 kcal/mol respectively and are higher than the ΔG_{comp} values of both the Au_6 and Pt_6 clusters. However, interestingly the VI conformer shows a slightly lower ΔG_{comp} value of -5.53 kcal/mol as compared to the Pt_6 cluster. Thus, from the ΔG_{comp} values, we conclude that the methanol adsorbs much more strongly on the Au_3Pt_3 clusters as compared to the Au_6 and Pt_6 clusters. Further, it is found that the methanol adsorption depends strongly on the relative position of Au and Pt atoms in the bimetallic Au_3Pt_3 cluster.

3.2 Methanol oxidation on Au_3Pt_3 , Au_6 and Pt_6 clusters

In this section, we will focus our attention on the oxidation of methanol on the Au_6 , Pt_6 , and different conformers of

Au_3Pt_3 clusters. As shown in earlier studies [49, 50, 54, 55], the oxidation of methanol on metal clusters and surfaces occurs through the breaking of O-H and C-H bonds. Fig. 3 summarizes the activation barriers for the first step of methanol oxidation in Au_6 , Pt_6 and Au_3Pt_3 clusters. The reactants are given in the center and the pathway for C-H and O-H activation is highlighted in red and blue respectively for each conformation. First we discuss the barriers for cleavage of C-H and O-H bonds in monoatomic metal clusters, viz., Au_6 and Pt_6 . It is clearly seen from the figure that activation barrier for cleaving C-H bond is quite low as compared to the activation barrier for cleaving O-H bond on Pt_6 cluster. The activation barriers on Au_6 are substantially high (33 and 48 kcal/mol respectively, for C-H and O-H activation) as compared to those on Pt_6 . Coming to the bimetallic clusters, the O-H activation barrier ranges from 12.99 to 19.71 Kcal/mol on the different conformers of the bimetallic Au_3Pt_3 cluster.

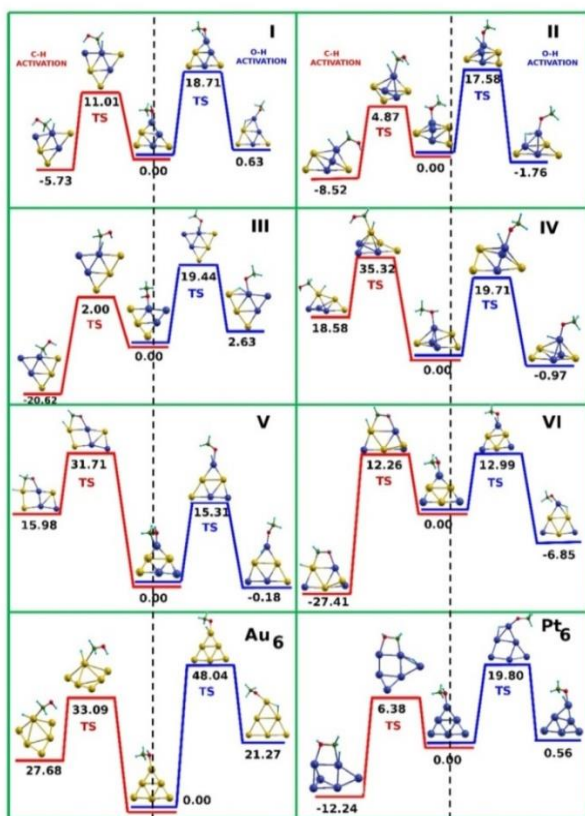


Fig. 3: Reaction pathway for methanol activation on the various conformers of Au_3Pt_3 cluster, and Au_6 and Pt_6 clusters through the cleavage of C-H and O-H bond.

The barrier is lowest for the V conformer (12.99 Kcal/mol) and highest for IV conformer (19.71 Kcal/mol). The free energy change for O-H bond dissociation becomes negative particularly in the case of V conformer (conformer which shows the lowest activation barrier), thereby, enhancing the

thermodynamic feasibility of the O-H bond dissociation. Among the bimetallic Au-Pt conformers, the II and the III conformers show very low activation barriers of 2.00 and 4.87 Kcal/mol for methanol dissociation via C-H. The I and VI conformers show activation barriers of 11.01 and 12.26 Kcal/mol respectively. However, the IV and V conformers of Au_3Pt_3 show very high activation barriers of 35.32 and 31.71 Kcal/mol respectively for the C-H dissociation. In short, the more feasible C-H activation barrier for methanol molecule on Au-Pt bimetallic cluster can be increased to the values found in pure gold nanoclusters (nearly 30 kcal/mol). This is particularly attractive when we need to have methanol tolerant nanoclusters. At the same time, few conformations such as II and III exhibit lower barriers than those noted on Pt cluster indicating them to be better catalysts for methanol electro-oxidation.

4. Conclusions

Adsorption and activation of methanol molecule on monometallic (Pt and Au) clusters as well as bimetallic clusters as a function of the relative orientation of gold and platinum clusters is studied in the present work. It is clearly seen that activation barriers are lower for C-H bond dissociation as compared to that for O-H bond in most of the cases. Barriers are highest for monoatomic gold cluster among the various clusters studied. In case of bimetallic clusters, our results highlight the critical dependence of relative orientation of the gold and platinum atoms in the cluster with respect to methanol adsorption and oxidation. Thus, by fine tuning the atomic orientations within the bimetallic cluster, it is possible to increase or decrease the activation barriers for methanol oxidation substantially and obtain the desired chemical activity.

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