



Density functional study of NO binding on small Ag_nPd_m ($n + m \leq 5$) clusters

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ABSTRACT

Density functional theory calculations were performed to investigate the binding of NO on small Ag_nPd_m clusters ($n + m \leq 5$). NO prefers binding to Pd site when both Ag and Pd atoms co-exist in the cluster. Generally the binding energies increase as the Pd composition increases for the given cluster size. The most probable dissociation channels and the corresponding dissociation energies for the most stable Ag_nPd_m and $\text{Ag}_n\text{Pd}_m\text{NO}$ clusters are determined. Our calculation suggests that Ag_nPd_m may react with NO dissociatively by ejecting metal monomer or dimer. The binding site is the most sensitive factor to the N–O stretching frequency shifts.

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1. Introduction

There is no doubt that nitric oxide is a main part of the air pollution, and experimental investigations show that nanosized palladium clusters have significant capacity to catalyze the CO + NO reaction at low temperatures [1–4]. As one of the key factors to understand the catalytic mechanism, the adsorption behaviors of NO on Pd clusters have been extensively studied [5–10]. Viñes et al. performed a combined experimental and theoretical study on the adsorption of NO on Pd nanoparticles, using infrared reflection adsorption spectroscopy (IRAS) and calculations based on density functional theory (DFT) [5]. NO molecules are shown to most favorably adsorb on 3-fold hollow sites on (1 1 1) facets of Pd_n clusters. Grybos et al. investigated the adsorption of NO on small Pd_n clusters with $n = 1–6$ [6]. In all cases NO adsorbs in a bent configuration. Silver can also facilitate the selective catalytic reduction of nitric oxide by light hydrocarbons over alumina [11–14]. Citra et al. carried out the matrix isolated infrared spectroscopy experiments and DFT study on the Ag_xNO_y ($x, y = 1, 2$) clusters [15]. Grönbeck et al. studied the adsorption of NO molecule on Ag_n ($n = 1–8$) clusters using DFT method with the generalized gradient approximation (GGA) [16]. They found that generally NO adsorbs on top site and the binding energies have a clear odd–even alternation pattern.

In recent years, bimetallic clusters have attracted considerable attention both in experiment and theory primarily because the

doped pure metals often exhibit distinct properties from the non-doped pure metals [17,18]. The geometric, electronic and bonding properties of the metal clusters can be strongly modified by the impurity atoms [19,20]. Theoretical studies of the bimetallic Ag/Pd clusters have also appeared. The geometries of small Ag_nPd_m clusters up to five atoms were found to shift from two-dimensional to three-dimensional as the Pd content increases [21]. H_2 can be easily dissociated at Pd site rather than at Ag site on AgPd dimer [22]. Very recently we have presented DFT calculations of the geometrical and energetic properties of small $\text{Ag}_n\text{Pd}_m\text{H}$ clusters ($n \leq 5$) [23] and $\text{Ag}_n\text{Pd}_m\text{CO}$ clusters ($n + m \leq 4$) [24]. Since the binding of NO on pure Pd_n and Ag_n clusters have been extensively studied, it is of interest to see how the mixing of Ag and Pd will influence the chemical reactivity of the metal clusters. In this contribution, we systematically investigate the interaction between NO and small Ag_nPd_m ($n + m \leq 5$) clusters using the first principles methods on the basis of DFT. The results of geometry, binding energy, dissociation channel and frequency for bimetallic and monometallic clusters were analyzed and discussed in Section 3. Before presenting the results, we summarize the computational details in Section 2. Finally, the conclusion is drawn in Section 4.

2. Computational details

The calculations are carried out using Gaussian 03 package [25]. The PW91PW91 [26] exchange and correlation functional was employed for all the calculations in this study. The Los Alamos relativistic effective core potential (RECP) plus DZ basis set [27] augmented with the f polarization functions [28] were used for Ag (f exponent, 1.611) and Pd (f exponent, 1.472) atoms. The 6-311++G(3df) basis set was used on N and O atoms.

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To have the results of bare clusters and complex clusters for comparison, we first studied the geometries and properties of Ag/Pd clusters up to five atoms. Results for the most stable bare clusters are displayed in Fig. 1. The geometries of Ag_nPd_m ($n + m \leq 4$) clusters are taken from our previous work [24]. For tetramers and pentamers the clusters shift from two-dimensional to three-dimensional structures with the addition of Pd atoms. Those results are in good agreement with previous theoretical study [21].

Based on those Ag_nPd_m clusters, wherever the geometry allows it, 1-fold top, 2-fold bridge, and 3-fold face site were tested upon the binding of NO on them. Because of the unique electronic configuration of NO molecule, two different multiplicities are examined for each structure. With the exception of Ag_3NO and Ag_5NO (triplets), all the complex clusters prefer the lowest multiplicities (singlets or doublets). The most two stable structures of NO binding on bimetallic Ag_nPd_m clusters are displayed in Tables 1–4, together with the negative charges on NO, binding energy, N–O and metal–N frequencies, as well as the corresponding N–O and metal–N bond lengths. The NO binding energy (BE) is defined by the follow equation:

$$BE = E(Ag_nPd_m) + E(NO) - E(Ag_nPd_mNO)$$

where $E(Ag_nPd_m)$ and $E(Ag_nPd_mNO)$ are the total energies of the bare cluster and the complex cluster, respectively. The more positive the BE is, the stronger the bond is. All calculations were performed with (99,590) pruned grid (ultrafine grid as defined in Gaussian 03). Natural bond orbital (NBO) [29] analysis was used to provide the natural charge distribution. Vibrational frequency calculations including thermochemical analysis are carried out at 298.15 K and 1 atmosphere of pressure. These frequency calculations also guarantee the optimized structures locating the minima, not as transition structures.

3. Results and discussions

3.1. Structures and stability

In most cases the NO molecule is bound to the cluster in a bent configuration with metal–N–O bond angles ranging between 115° and 145° . This phenomenon is related with electron donation from the $2p\pi^*$ highest occupied orbital (HOMO) in NO to the cluster lowest unoccupied molecular orbital (LUMO) in addition to the back donation from the cluster HOMO to the unoccupied $2p\pi^*$ orbital of NO [6,16]. The PW91PW91 results indicate that the most preferred binding site for Ag_n is top site with $n = 2-4$ while bridge site with $n = 5$, for Pd_n clusters is bridge site with $n = 2, 3$ and 5 while top site

with $n = 4$. These observations agree well with previous theoretical studies [6,16,30,31]. For alloying dimer, it is found that NO prefers binding on top-Pd site with the N–Pd–Ag angle of 125.6° . This structure is about 1.76 eV higher in energy than the top-Ag binding isomer. It is remarkable that the NO is out of the metal plane for all the trimers. Similar to bimetallic dimer, the most stable Ag_2PdNO contains top-Pd bound NO. For $AgPd_2NO$ with two Pd atoms, Pd–Pd bridge site is the most favorable, followed by the top-Pd site. For Ag_3PdNO only one stable structure (top-Pd binding) was found, although many different initial configurations were tried. Like the case of $AgPd_2NO$, the most stable Ag_2Pd_2NO and $AgPd_3NO$ are Pd–Pd bridge binding structures while the second stable isomers of them are top-Pd binding structures. For bimetallic pentamer the most stable complex clusters all prefer top-Pd binding structures except for Ag_3Pd_2NO , in which the Pd–Pd bridge site is the most preferred. Although the Pd–Pd bridge binding isomers are less stable than the top-Pd binding isomers, the energy difference between them is only 0.07 eV and 0.02 eV, for Ag_2Pd_3NO and $AgPd_4NO$, respectively. In summary, it seems that NO prefers to bound with Pd atoms when both Ag and Pd site co-exist in the cluster. Significant effects of association of NO to bimetallic Ag/Pd clusters on stability of metal framework have been noted. For example, the metal part in the most stable Ag_2Pd_2NO and Ag_3Pd_2NO are of near-planar structures, while bare Ag_2Pd_2 and Ag_3Pd_2 have the most stable three-dimensional structures. Notable changes in geometry also take place in Ag_4PdNO , Ag_2Pd_3NO and $AgPd_4NO$ in comparison with the frameworks of their corresponding bare clusters. In other complex clusters, the metal frameworks are less changed upon NO binding.

3.2. Binding energies

The PW91PW91 calculations indicate that NO interacts quite strongly with Pd_n clusters than Ag_n clusters. Similar results have been previously reported by Miyamoto and co-workers [32]. They investigated the adsorption properties of M_4 clusters ($M = Ph, Pd, Ag, Ir, Pt$ and Au) toward NO using the density functional calculations and found that Ag and Au show relatively lower activity towards NO than other metals. From the data in Tables 1–4, it seems that NO prefers binding to Pd when both Ag and Pd sites co-exist in the cluster. Combining Pd atoms with Ag_n clusters can greatly increase the binding energy with respect to pure Ag_n when NO adsorbed to the Pd atom. Ag_2 is the least reactive clusters with the BE of only 0.46 eV while Pd_2 is the most reactive clusters with the BE of 2.88 eV in this study. It is not surprising that the NO BE on $AgPd$ (2.37 eV with Pd atom bound) is between that on Ag_2 and Pd_2 . The NO BE on Ag_2Pd (1.72 eV for 3Ag_2PdNO in Table 2) is great-

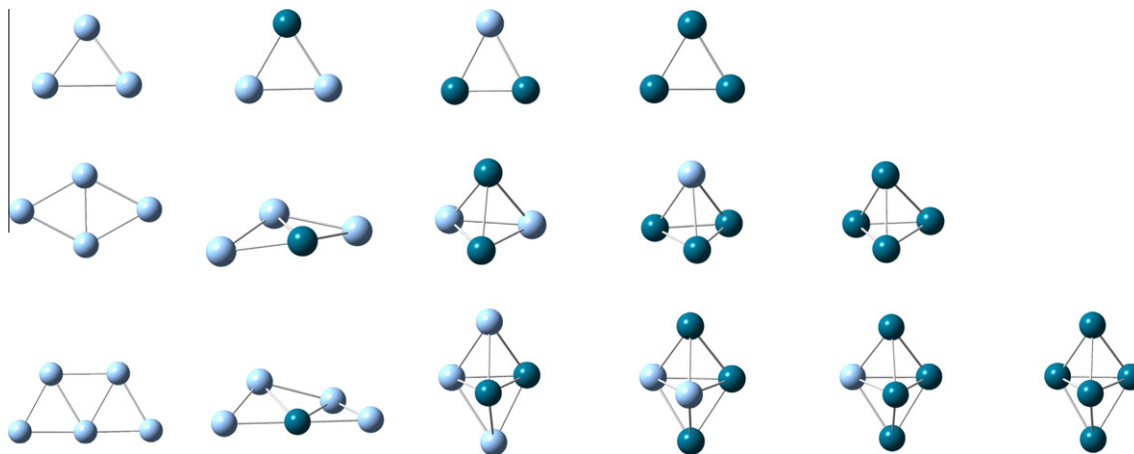


Fig. 1. The most stable structures for bare Ag/Pd clusters up to five atoms. The isomers are arranged in the order of increasing Pd composition.

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