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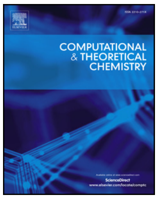

Structure stability and electronic properties of Pt_mIr_n ($m + n = 2–7$) clusters: A DFT study

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ABSTRACT

Structure, stability and electronic properties of Pt_mIr_n ($m + n = 2–7$) clusters have been systematically investigated by using density functional theory (DFT) with considering the generalized gradient approximation (GGA). The results reveal that the ground state structures change from planar to three-dimensional structures with the increase of the number of atoms, and Ir atoms play a decisive role in the formation of Pt_mIr_n clusters. The addition of a small amount amount of Ir improves the stability of pure Pt clusters. The stability analysis indicates that most of the Pt-rich clusters are more stable than those of the Ir-rich with same cluster size. The PtIr cluster charge transfer analysis illustrates that it not only occurs in different orbits, but also occurs between different atoms. $PtIr_3$, Pt_4Ir, Pt_4Ir_2, Pt_3Ir_3, Pt_2Ir_4, $PtIr_5$ and Ir_7 clusters exhibit comparatively large magnetism.

1. Introduction

The transition-metals play important roles in the field of metallurgy and catalysis due to containing d electrons, which make formed clusters exhibit special electronic structures and physical-chemical properties. High-temperature alloy materials, magneto-optical recording materials, shape memory materials and the most important catalyst of chemical industry are all transition metal alloy materials. The chemical and physical properties of transition metal clusters can be changed by doping with other metal, and bimetallic clusters have a wide application prospect in catalysis science, surface science, nanoscience and nanotechnology.

Therefore, transition metal doped clusters have been extensively investigated [1–10]. For example, the magnetic properties of $Co_{12}X$ (X = Ni, Ag, Pt, Au) clusters were analyzed by LU [9], which show that the impurities of the X atom break the symmetry of molecular orbitals of Co_{13}. They induce the redistribution of the electrons, which dramatically alters the magnetism of $Co_{12}X$ clusters, and the total magnetic moments of $Co_{12}Pt$ cluster is 22 μB. And the geometrical structure, stability, electronic and magnetic properties of Pd_nIr ($n = 1–8$) clusters have been systematically studied by Bouderbala et al. [10]. They found that the total magnetic moment of Pd_nIr clusters is mainly localised on the Ir atom for $Pd_{1\text{-}6}Ir$ clusters. Meanwhile, the 5d orbital plays the key role in the magnetic moment of the Ir atom. Our research group has done some other atomic clusters studies [11–14]. For example, all the possible geometrical structures of Pt_nNi_m ($n + m = 7$, $n,m \neq 0$) clusters are optimized with density functional theory [14]. The results show that all the ground state structures of Pt_nNi_m clusters are cube structures. Pt_5Ni_2 is the most stable one of Pt_nNi_m clusters. Ni atom plays a leading role in magnetism of the binary Pt_nNi_m clusters.

Noble platinum metallic clusters are often used as a catalyst in the chemical industry because of their exhibiting remarkably higher chemical stability and catalytic activity. Iridium is platinum-group metal which not only is one of the most corrosion-resistant metal, but also plays an important role in the catalytic process. At present, platinum or iridium metals have been extensively studied both theoretically [15–29,35–44] and experimentally [30]. Guo et al. [28] reported the possible geometrical configurations and stability of $PtIr_n^{0,\pm}$ ($n = 1–5$) clusters by using density functional theory. Based on the stability analysis, they found that thermodynamics stability of clusters improves with the increase of atoms. Iridium atoms play a dominant action in stability of $PtIr_n^{0,\pm}$ clusters. Moreover, the energetic stability, electronic structure and magnetic properties of $Pt_{8\text{-}n}Ir_n$ clusters have been investigated by N Long et al. [29]. They found that the average binding energy of all the clusters presents the linear increment trend versus iridium atoms, bader charge analysis shows how tiny charge transfers from iridium to platinum. Experimentally, Pt–Ir catalysts with different atomic ratios were synthesized by Hu et al. [30], which illustrate that the addition of an appropriate amount of Ir improves the catalytic activity of pure Pt.

In this paper, we have comprehensively studied the optimized structure, stability and electronic properties of Pt_mIr_n bimetallic clusters

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with $m + n = 2$–7 to explore the effect of different ratio of Pt and Ir elements on the properties aforementioned. Which may provide a theoretical reference for the preparation of platinum iridium nanomaterials.

2. Computational method

All calculations of the optimized configuration, stability and electronic properties of Pt_mIr_n ($m + n = 2$–7) clusters were performed using DFT semi-core pseudopots in the $Dmol^3$ package in Material Studio. The exchange-correlation interaction of between electrons was treated within the generalized gradient approximation (GGA) [31] using PW91 [32] functional. The double numerical basis set augmented with polarization functions (DNP) [33] was utilized. The convergence criterion of self-consistent field (SCF) was set to be 10^{-5}Hartree. And the direct inversion in an iterative subspace (DIIS) [34] approach was used to accelerate the speed of SCF convergence. We considered the smearing in calculation, and the smearing of molecular orbital occupation was set to be 0.005 Hartree. In the process of geometric optimization of the system, converge thresholds of the forces, displacement and energy were set to be 0.004 Hartree/Å, 0.005 Å and 2.0×10^{-5} Hartree, respectively, and the other parameters all adopted the default values. Then ground state structures was selected to analyze structure stability and electronic properties.

To check the validity of the computational method in our work, we firstly performed the calculation on the Pt_2 and Ir_2 clusters and the correlation data are as listed in Table 1. For Pt_2, the bond length we obtained is 2.395 Å, which is in good agreement with previous theoretical data of 2.38 Å [17,22], 2.40 Å [35] and 2.34 Å [18,37,38,39], and the experimental values of 2.34 Å [36] and 2.45 Å [40]. Meanwhile, the binding energy (1.733 eV) is very close to previous theoretical data of 1.76 eV [38]. Similarly, for Ir_2, our calculated bond length (2.284 Å) and E_b (2.233 eV) are in excellent agreement with the previous theoretical values (2.22 Å [22], 2.209 Å [27], 2.228 Å [41] and 2.28 eV [3]). All these results validate that our approach provides an efficient way to investigate Pt_mIr_n clusters.

3. Results and discussion

3.1. Geometrical structures

In general, finding the ground state structure of binary alloy cluster is much more difficult than that of corresponding single pure cluster due to there exists non-equivalence of spatial geometric structure of atoms exchange position, and the quantity of possible configurations clusters increases exponentially with the increasing number of atoms. In order to find the ground state structures of Pt_mIr_n ($m + n = 2$–7) clusters, we considered about 500 possible initial configurations, and constructed the initial configurations in two ways: (i) is guess the initial configuration directly; (ii) use the ground state structures of pure Pt_n and Ir_n clusters as the basic framework, and then construct the initial configuration by capping, replacing and filling at different locations of the framework. The structure optimization and frequency calculation were carried out for each size of specific cluster on the premise of fully considering the spin multiplicity. The structure with lowest energy and real frequency was defined as the ground state stable structure. The lowest-energy optimized configurations of Pt_mIr_n ($m + n = 2$–7) clusters are shown in Fig. 1. The symmetry, spin multiplicity and average bond lengths are listed in Table 2.

Table 1
Calculated bond length, binding energy; the experimental results and previous theoretical studies.

Dimer		Bond length (Å)	E_b (eV/atom)
Pt_2	Our work	2.395	1.733
	Theoretical	2.38 [17,22] 2.40 [35] 2.34 [18,37,38,39]	1.76 [38]
	Experimental	2.34 [36] 2.45 [40]	
Ir_2	Our work	2.284	2.233
	Theoretical	2.22 [22] 2.209 [27] 2.228 [41]	2.28 [3]

3.1.1. Pure Pt_n and Ir_n clusters ($n = 2$–7)

In order to investigate the ground state structures of bimetallic Pt_mIr_n clusters, we first discuss the structures of pure Pt_n and Ir_n clusters ($n = 2$–7) by using the method in Section 2. This range has also been studied by other workers [16–20,26,27,35,39,41–44], but in some cases, our ground state structures are different. For pure Pt_n clusters, the ground state structures of our calculated results are consistent with the previous theoretical results [44] except that Pt_4 and Pt_7. But the lowest-energy geometry of Pt_4 cluster is in agreement with the theoretical result [42]. The isomer of Pt_7 with C_{3v} symmetry is evaluated to be the ground state structure which can be regarded as capping one Pt atom on the vertex of the triangular prism structure. For pure Ir_n clusters, the ground state structures of our calculated results are in accordance with the theoretical results [20] except for Ir_7. We obtain the ground state structure of Ir_7 cluster with C_{2v} symmetry by optimizing the side-face-capped triangular prism.

3.1.2. Pt_mIr_n clusters ($m + n = 2$–7)

Here we explore about bimetallic Pt_mIr_n clusters. The Pt-Ir bond length in PtIr cluster with $C_{\infty v}$ symmetry is 2.356 Å. The lowest-energy geometries of Pt_2Ir and $PtIr_2$ clusters are all planar isosceles triangle structures with C_{2v} symmetry. The Pt-Ir bond length of Pt_2Ir cluster (2.497 Å) is less than of $PtIr_2$ cluster (2.509 Å). In the case of Pt_3Ir, the ground state structure is a tetrahedral structure with C_{3v} symmetry which can be regarded as a Pt atom at the top of the Pt_4 cluster replaced by a Ir atom. The Pt-Pt bond length in Pt_3Ir (2.660 Å) is longer than the Pt-Pt bond length (2.637 Å) in Pt_4 cluster. For Pt_2Ir_2 cluster, the planar quadrilateral structure with C_{2v} symmetry is found to be ground state structure. The ground state structure of $PtIr_3$ cluster can be viewed as a Ir atom of the Ir_4 cluster substituted and connected all Pt-Ir bond, the configuration is C_{2v} symmetry and the Ir-Ir bond length (2.360 Å) is less than the bond length (2.396 Å) in Ir_4 cluster. The isomer of Pt_4Ir with C_{4v} symmetry whose structure is the rectangular pyramid with Ir atom on the vertex is evaluated to be the ground state structure The Pt-Pt bond length (2.625 Å) is smaller than the Pt-Pt bond length (2.660 Å) in Pt_3Ir clusters. For Pt_3Ir_2 cluster, the ground state structure is the Ir edge capped the triangular structure of tetrahedral structure with C_s symmetry. In the isomer of Pt_2Ir_3 cluster, the ground state structure is trigonal pyramid structure with Pt on the vertex and D_{3h} symmetry. The structure of $PtIr_4$ cluster with C_{2v} symmetry is selected as the ground state structure.

For Pt_mIr_n ($m + n = 6$), the ground state structure of Pt_5Ir cluster is an oblique triangular prism structure with C_s symmetry which can be seen as filling a Pt atom on Pt_4Ir cluster ground state structure. The Pt-Pt bond length (2.657 Å) is greater than the Pt-Pt bond length (2.625 Å) in Pt_4Ir cluster. Pt_4Ir_2, Pt_3Ir_3, Pt_2Ir_4 and $PtIr_5$ clusters are all triangular prism structures which can be regarded as substituting atoms in the ground state structure of Ir_6 cluster. Their symmetries are C_{2v}, C_{3v}, C_{2v} and C_s, respectively. Finally, we investigate the Pt_mIr_n ($m + n = 7$). The lowest-energy geometry of Pt_6Ir cluster is similar to the lowest-energy structure of the Ir_7 cluster with C_{2v} symmetry and the Pt-Pt bond length is 2.634 Å. For Pt_5Ir_2 cluster, it can be obtained by capping a Pt atom to the Pt_4Ir_2 cluster. The isomer of Pt_4Ir_3 with C_{2v} symmetry is evaluated to be the ground state structure which is resemble to the ground state structure of the Ir_7 cluster. In the Pt_3Ir_4 cluster, the Ir edge capped the triangular structure with C_s symmetry is the most stable one. The calculations show that the isomer Pt_2Ir_5 with C_s symmetry is the ground state structure, which can be obtained by by capping a Pt atom to the ground state structure of $PtIr_5$ cluster. The isomer $PtIr_6$ with C_{3v} symmetry is found to be the most stable structure among all optimized