Ti_{12}C_{68}: A stable $T_h$-symmetry hollow cage

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A stable $T_h$-symmetry Ti_{12}C_{68} cage was systemically investigated using density functional theory. The structure of Ti_{12}C_{68} is a hollow cage with twelve TiC_{13} subunits of three pentagons and one hexagon. The calculated frequencies are in the range 95.1 cm\(^{-1}\)–1423.9 cm\(^{-1}\). There are no imaginary frequencies, showing its kinetic stability. Ab initio molecular dynamics simulations demonstrate that the topological structure of cage-like Ti_{12}C_{68} cluster was well maintained when the effective temperature is up to 1139 K. The natural bond orbitals analysis shows that the $d$ orbit of Ti atoms form four $c$ bonds with the neighboring four carbon atoms in each TiC_{13} subunit playing an important role in the cluster stability. The molecular frontier orbitals analysis indicates that Ti_{12}C_{68} cage has a narrow HOMO-LUMO gap with metal-like property. It would be expected to enrich the species of hollow metal carbide clusters.

Recently, an exceptionally stable hollow molecule Sc_{20}C_{60} named volleyballene, has been proposed. Along with suggestion for Sc_{20}C_{60}, subsequent investigations resulted in the molecules of volleyball-like shape Y and La analogues. Sc_{20}C_{60} containing transition metals and carbon atoms belongs to the family of metal carbide clusters. Early famous metal carbide clusters, metallo-carbohedrnes (met-cars) $M_8C_{12}$, known as a unique class of cluster materials, which have been extensively investigated. The ground-state structure of met-cars was once the center of debate. Early studies proposed for the containing a pentagonal dodecahedron structure similar to C_{20}, the subsequent proposal that the isomers of TiC_{13} having different-symmetry structures with much lower energies, have been reported. In particular, the inchoative TiC_{15} geometric structure has unique bonding properties that the $d$ orbitals of Ti atoms play an important role in the cluster stability. Thus, theoretical investigations focus on an explanation for the electronic structure of novel isomers systems. Results exhibit diversities due to the existence of transition metal elements. It is worth noting that the present structures of metal carbide clusters have been different with the originally established molecular model as alluded to above. Metal carbide clusters exhibit various geometric structure that determine their novel and rich physical and chemical properties. Geometric configuration of each type met-cars cluster plays an important role in analyzing its characteristic and exploring the absorption mechanism of small molecules.

Meanwhile, metal atoms and metal carbide cluster encapsulated inside different size fullerene cages form different kinds of endohedral metallofullerenes (EMF) which have attracted special attention owing to their unique structural, electronic, and magnetic properties. For example, encapsulating La atom into C_{60} fullerene cage was first discovered by Smalley et al. Later, dimetallofullerenes C_{60}@C_{88}, D_{y}@C_{88}, $La_2@C_{80}$, metal carbide clusterfullerenes $La_2C_{12}@[C_{(574)}]_2$, $C_{100}$ and $Y_2C_{12}@[D_{(8)}]_2C_{100}$ have been extensively studied. It is noteworthy that endohedral metallofullerenes enrich the family of metal carbide clusters and have promising applications in different fields such as materials science and medicine. Up to now, the investigations of metal carbide clusters have become one of the highlights in nanoscience due to their exceptional stability and unique structures.

In the present work, we proposed a stable cage-like Ti_{12}C_{68} structure and structural properties, and the stability of Ti_{12}C_{68} cage has been systematically investigated within the density functional theory. Furthermore, the electronic properties and the natural bond orbitals analysis have been explored.

**Results and Discussion**

A schematic diagram of the optimized Ti_{12}C_{68} structure is shown in Fig. 1. It is found to be a cage-like configuration with $T_h$ symmetry, which contains twelve TiC_{13} subunits seamed together. Each TiC_{13} subunit, just as highlighting blue atoms constitute the unit in the left figure of Tab. 1, in which three pentagons share a single titanium atom with one hexagon. Each TiC_{13} subunit is bound to five neighboring TiC_{13} subunits through C-C bonds. As seen from the Fig. 1 that the cage-like Ti_{12}C_{68} is composed of 12 hexagon rings and 36 pentagonal rings.

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Figure 1. Front view (a) and top view (b) for cage-like Ti$_{12}$C$_{68}$ structure. Pink and gray spheres represent Ti and C atoms, respectively.

Figure 2. Three representative initial geometric structures and corresponding optimized structures of Ti$_{12}$C$_{68}$ cluster, which are composed by 12 titanium atoms and 68 carbon atoms, as plotted in (a–c). (d–g) Isomers of Ti$_{12}$C$_{68}$ cluster are composed of C$_{68}$ fullerene and Ti$_{12}$. The calculated relative averaged atomic binding energies for each isomer, with respect to cage-like Ti$_{12}$C$_{68}$ cluster, is listed underneath each isomer. The unit of averaged binding energies is eV.
and each of the rings contains one titanium atom. Titanium atoms occupy twelve unique positions and they have same coordination number.

In each TiC13 subunit, each Ti atom links four carbon atoms to form four Ti-C bonds. Ti-C bonds may be divided into two types. One type is in a hexagon denoted by $d_{Ti-C}^1$, another type is in a pentagon denoted by $d_{Ti-C}^2$. The pentagons and hexagons, and two neighbouring pentagons are connected by different C-C bonds which can be put into four categories, as shown in Table 1. As a result of bond-length equalization, such as 1,3-butadiene, it leads C-C bond lengths lying between bond lengths of 1.54 Å (C–C bond) and 1.34 Å (C= C bond) in the optimized structure. The calculated properties of cage-like Ti12C68 are listed in Tab. 1 at the GGA/PBE, GGA/PW91 and GGA/BLYP levels, which gave the uniform structures and similar calculation results. In the following, analyses were treated within the GGA using the PBE exchange-correlation functional.

In order to search for the ground-state structure of cage-like Ti12C68 cluster, we have accomplished an extensive search with different initial configurations which are constructed with C68 cage and 12 Ti atoms. After relaxing these configurations, it can be found that the Ti atoms prefer to approach the carbon atoms. Three representative initial geometric structures and corresponding optimized structures are plotted in Fig. 2a–c. Note that these structures are larger in averaged atomic binding energy than the cage-like molecule by 0.02, 0.06 and 0.19 eV, respectively. In order to further compare the stability of the structure, we also construct isomers which

| Average bond lengths | Frequencies |
|----------------------|-------------|
|                       | $d_{Ti-C}^1$ | $d_{Ti-C}^2$ | $d_{C-C}^1$ | $d_{C-C}^2$ | $d_{C-C}^3$ | $d_{C-C}^4$ | Lowest | Highest | $E_b$ | $E_g$ |
| PBE                  | 2.153       | 2.112       | 1.398       | 1.428       | 1.444       | 1.441       | 95.5   | 1423.9  | −6.86 | 0.05  |
| PW91                 | 2.157       | 2.121       | 1.395       | 1.427       | 1.444       | 1.440       | 96.8   | 1410.4  | −6.87 | 0.10  |
| BLYP                 | 2.179       | 2.147       | 1.398       | 1.436       | 1.455       | 1.448       | 100.0  | 1360.3  | −6.35 | 0.10  |

Table 1. Calculated properties for cage-like Ti12C68 structure at the GGA/PBE, GGA/PW91 and GGA/BLYP levels. The average bond lengths, the lowest and highest vibrational frequency, binding energy per atom ($E_b$), HOMO-LUMO gap ($E_g$) are listed. The units of bond lengths, frequencies, energy and charge are Å, cm$^{-1}$, eV and e, respectively. In the left figure, the subunit of the cage-like Ti12C68 structure is highlighted using blue atoms. Each TiC13 subunit is bound to five neighbouring TiC13 subunits through different C-C bonds. The pentagon and hexagon are connected by the two kinds different C-C bonds denoted by $d_{C-C}^1$ and $d_{C-C}^2$. The pentagons are joined by two kinds C-C bonds presented by $d_{C-C}^3$ and $d_{C-C}^4$.

Figure 3. Initial and optimized structures for three isomers of cage-like Ti12C68 cluster. (a), (b) and (c) are three isomers which are randomly choose from the molecular dynamic simulations at initial temperature of 2000 K and 3000 K, respectively, corresponding to the effective temperature of 952 K and 1343 K. The averaged atomic binding energies in eV, relative to cage-like Ti12C68 cluster, are listed underneath each isomer.
are composed of C₆₈ fullerene and Ti₁₂. As for C₆₈ fullerene, we choose two isomers with C₁ point group plotted in (d) and (e), and C₅ point group plotted in (f) and (g). The shapes of the fully optimized equilibrium structures of isomers are shown in Fig. 2(d–g). Results show that the Ti atoms prefer to be connected to the C atoms. Moreover, the isomer (d) has a 0.01 eV higher averaged atomic binding energy than the cage-like Ti₁₂C₆₈ (e), (f) and (g) isomers are found to be lower in averaged atomic binding energy than the cage-like molecule by 0.3, 0.01 and 0.34 eV, respectively. Thus, the cage-like Ti₁₂C₆₈ is a metastable structure.

In addition, in order to further confirm the stability of cage-like Ti₁₂C₆₈ cluster, we choose randomly three isomers with lower energy from the molecular dynamic simulations in the NVE ensemble at temperatures of 2000 and 3000 K. After energy minimization, the results revealed that the lowest-energy conformation is the cage-like Ti₁₂C₆₈ cluster in all isomers. The motifs of initial and optimized structures for three isomers are presented in Fig. 3. The calculated relative averaged atomic binding energies (\(\Delta E_b\)) for each isomer, with respect to cage-like Ti₁₂C₆₈ cluster, is written underneath each isomer.

Then, we evaluated the dynamical stability of the cage-like Ti₁₂C₆₈ by calculating the vibrational frequencies. Here, the harmonic vibrational frequencies are computed by diagonalizing the mass-weighted second-derivative matrix. There is no imaginary frequencies, which further validates the stability of cage-like Ti₁₂C₆₈ configuration. The lowest vibrational frequency and highest vibrational frequency corresponds to 95.1 cm⁻¹ and 1423.9 cm⁻¹, respectively. To provide more information for future experimental identification, we simulated Raman spectrum, which is based on the Raman effect of inelastic scattering of monochromatic light. The energy shift is defined by the vibrational frequency and the proportion of the inelastically scattered light is defined by the spatial derivatives of the macroscopic polarization, technical details are described by Porezag and Pederson. A Raman spectra with the temperature of 300 K and incident light of 488.0 nm was displayed in Fig. 4. We can see clearly that the spectrum has strong peaks at 98.7 and 273.1 cm⁻¹ which are due to the Ti-C and C-C stretching modes respectively. More detailed data are described in the Supporting Information (Section I). Therefore, the cage-like Ti₁₂C₆₈ cluster is kinetically stable.

In what follows, we try to confirm the thermal stability of cage-like Ti₁₂C₆₈ cluster from ab initio NVE MD simulations with the initial temperature at 1400 K, 1800 K, 2000 K, 2200 K and 2400 K, which correspond the
effective temperatures of 678 K, 877 K, 950 K, 1072 K and 1139 K. More detail information is presented in the Figs. S1 and S2, where the configurations snapshots of cage-like Ti$_{12}$C$_{68}$ cluster are shown at the 1.25 ps, 2.5 ps, 3.75 ps and 5 ps of each MD simulation. After 5 ps simulation, the topological structure of cage-like Ti$_{12}$C$_{68}$ cluster was well maintained when the initial temperature is up to 2400 K with the effective temperature of 1139 K. The above observation is an indication of high thermal stability for the cage-like Ti$_{12}$C$_{68}$ cluster.

To get insight into bonding properties of cage-like Ti$_{12}$C$_{68}$ cluster, Fig. 5c displays the deformation electron density, which reveals that electrons are donated from Ti to the C atoms. The removed electrons are mainly from the Ti 3$d$ state, and are mainly delocalized to surrounding the four Ti-C bonds. For the Ti atoms, each Ti can connect with four carbon atoms through Ti-C $\sigma$ bonds. For the carbons that adjacent to Ti atom, each carbon forms $\sigma$ bonds with neighboring two carbons. Meanwhile, the natural bond orbital (NBO) analysis further elucidates the detailed type of hybridization. Some typical NBO are presented in the Fig. 6. The occupation numbers of natural

Figure 6. Some typical natural bond orbitals of Ti$_{12}$C$_{68}$ cage. BD is short for 2c-2e bond, and under each structure the detailed hybridization types are provided. All the configurations are viewed by the same orientations.
orbitals are in the range from 1.59 to 1.97 electrons. Here, we label one Ti atom by roman numerals I, C atoms by arabic numerals 1, 2, 3, 4, 5, 6, 7, 8 and 9 as shown in Fig. 6(a). For the Ti I atom, four lobes of \(d\) orbit form four \(\sigma\) bonds with the neighboring four carbons (C1, C2, C5 and C9) atoms, as plotted Fig. 6(a–d). In the \(\sigma\)4(Ti I-C5) bond, it is a two-center two-electron (2c-2e) \(\sigma\) bond with the occupation numbers of 1.87 electrons in hexagon, in which the 26.85% and 73.15% of occupation numbers are situated on the TiI atom and C5 atom, respectively. The bond orbital of the Ti I atom mainly comes from the \(d\) orbital, and for the C5 atom, the hybrids of \(sp^2\) are a distorted \(sp^3\) hybridization. In addition, C5 atom form two \(\sigma\) (\(\sigma\)5 and \(\sigma\)6) bonds and a \(\pi\)1 bond with two neighbor carbons shown in the Fig. 6(e–g), demonstrating the distortion \(sp^2\) hybridization character of C5 atom. For the \(\sigma\)2 (Ti I-C2) bond comes from the hybridization of \(sp\)0.49 \(d\)2.71 on Ti I atom and \(sp\)2.67 on the C2 carbon in the hexagon as plotted in Fig. 6(b). It is noted that C2 atom link the neighbor C3 atom and C4 atom by \(\sigma\) bonds plotted in Fig. 6(h) and (i), and a \(\pi\)2 bond which is formed by the hybridization between \(p\) orbital of C2 atom and \(p\) orbital of C4 atom, as shown in Fig. 6(j). In addition, two identical pentagons are connected by the C7-C8 bond, from the Fig. 6(k) and (l), it can be seen that C7 atom form \(\sigma\) bond and \(\pi\)2 bond with the neighboring C8 atom. For the all \(\sigma\)(C-C) bonds, it can be found that major contribution comes from \(sp^2\)-like hybridization of C atom.

Finally, to investigate the electronic structures of cage-like Ti12C68 cluster. We plotted the projected density of states (PDOS) in Fig. 5a. As can be seen from Fig. 5a, the HOMO and LUMO orbitals show strong \(sp\)-hybridization. The region of 0.6 eV to 1.0 eV and below −0.6 eV, there is \(sp\)-hybridization character. Furthermore, the plots of frontier orbitals, including HOMO, HOMO−5, HOMO−9, HOMO−13, LUMO, LUMO+2, LUMO+6, and LUMO+10 are given in Fig. 7. As seen from Fig. 7, \(\pi\) bonds form between carbons (for example, HOMO and HOMO−5), which is crucial for stabilizing the structures of cage-like Ti12C68 cluster. For the HOMO, LUMO, LUMO+2, LUMO+6, and LUMO+10 orbitals, the \(d_{xy}\)-like orbitals and other \(d_{xy}\)-like \(d_{xy}, d_{xy}, d_{xy}\) orbitals characteristic appear on the Ti atoms. Especially for LUMO+6, and LUMO+10, orbitals characteristic mainly focus on the Ti atoms. However, HOMO-5, HOMO-9 and HOMO-13 orbitals display sole \(d_{xy}\)-like orbital characteristics on the Ti atoms. While all the given frontier orbitals on C atoms mainly exhibit the \(p\) orbital character.

The above observations are in concordance with the natural bond orbital analysis.

**Conclusions**

In summary, we have discovered a stable cage-like Ti12C68 cluster with \(T_h\) symmetry. The stability of cage-like Ti12C68 cluster has been confirmed using the molecular dynamics simulations and the vibrational frequency analysis. Meanwhile, this cluster is found to have a relatively small HOMO-LUMO gap, which suggests strong chemical activity. More importantly, the density of states and frontier orbitals distributions show remarkable orbital hybridization. The natural bond orbital analysis provides a detailed description including the bond-type of hybridization and occupancy numbers, results show that four lobes of \(d\) orbit for each Ti atom form four \(\sigma\) bonds with the neighboring four carbons atoms in each TiC13 subunit playing a significant role in the structural stability. Moreover, the calculated Raman spectrum of cage-like Ti12C68 should provide more information for
future experimental observations and computations. If this analogue can be prepared in a future experiment, it would enrich the species of hollow metal carbide clusters or analogues of metallo-carbohedrenes.

**Computational details**

All theoretical calculations are on the basis of the density functional theory (DFT), which begins with a theorem by Hohenberg and Kohn, later generalized by levy, and in which all ground-state properties are functionals of the charge density. For the considered system, except kinetic energy and the classical electrostatic energy, it includes all many-body contributions to the total energy, in particular, the exchange and correlation energies. The exchange-correlation energy requires some approximation for this method to be computationally tractable. A popular and good approximation is the gradient-corrected approximation (GGA), which can provide a considerable increase in the accuracy of predicted energies and structures as to the local density approximation (LDA). In our calculations, three different exchange-correlation functionals, the Perdew-Burke-Ernzerhof correlation (PBE), Perdew-Wang (PW91), and Becke exchange plus Lee-Yang-Parr correlation (BLYP), were employed. For the basis functions, the double numerical including polarization (DNP) were utilized with the best accuracy and highest cost. For C atom, it is 1s2s2p2p3 3p 3d, and it is 1s2s2p3s3p3d4s4d4f 4s4p for Ti atom. All geometry optimizations of cage-like Ti12C68 clusters were performed using spin-unrestricted and symmetry-unconstrained.

Ab initio molecular dynamics (MD) simulations, the most natural method of performing equilibrium statistical-mechanical calculations, was selected to evaluate the thermal stability of Ti12C68 cage. The constant energy, constant volume ensemble (NVE), also known as the microcanonical ensemble, was used. In the NVE ensemble, the total time was set to be 5 ps, with each step taking 1.0 fs at initial temperature of 1400 K, 1800 K, 2000 K, 2200 K and 2400 K. The natural bond orbital (NBO), that describe the Lewis-like molecular bonding pattern of electron pairs in optimally compact form, is analyzed at the LANL2DZ basis set in Gaussian 09 package.

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Author Contributions

Y. Liu conceived the calculation methods and the research contents, L.Y. Ai conducted the calculations, L.Y. Ai, H.Y. Zhao and Y. Liu analysed the results. All authors reviewed the manuscript.

Additional Information

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