Ab Initio Molecular Dynamics Simulations of Ti$_2$ on C$_{20}$ Collisions and C$_{20}$Ti$_2$ Configurations

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ABSTRACT: The dynamics of the collision process of a titanium dimer against a C$_{20}$ nanocluster in the bowl configuration is simulated by means ab initio molecular dynamics, focusing our interest on the first steps to synthesize Ti$_x$C$_{20}$ clusters, characterizing the relevant structures generated during the collision process. The electronic localization function is also calculated. The early stages of the dynamics are critical to determine the outcome because of the large kinetic energy of the Ti dimer, which allows it to wander around the C$_{20}$ cluster.

INTRODUCTION

Metallocarbohedrenes have attracted much interest since the discovery by Guo et al. of nanoscaled titanium carbides (they obey the general formula M$_n$C$_m$, and are known as metcars). They are clusters of transition metal (M) and carbon (C) atoms, and the Ti$_8$C$_{12}$ cluster has received special attention due to its stability and unique structural and electronic properties.

These properties make metal carbides (not only those known as metcars) the subject of interest because of their potential applications. For instance, in the bulk phase they have a superior ability to catalyze hydrogen related reactions.

Moreover, recently an additional application of nanosized TiC clusters has been found, namely their use for reversible hydrogen storage, in which the Ti atoms play a double role: (i) as catalysts, to mediate the dissociation of H$_2$ molecules forming carbon hydrides; and, (ii) the Ti atoms on the cluster surface are capable of coordinating a large number of H$_2$ ligands. Moreover, the clustering of Ti on a fullerene surface, and how it affects hydrogen storage, was investigated by Sun et al. for concentrations of Ti ranging from one to twelve atoms.

The experimental setup to form metcars involves laser vaporization, either of a TiC rod, or of a Ti rod in a gas carrier with some methane concentration. This approach yields magic clusters with a metal to carbon ratio close to 2:3. However, it must be noticed that the abundance of the Ti$_8$C$_{12}$ cage structure strongly depends on the experimental conditions since, for instance, varying the laser power it is possible to obtain a prominent abundance of TiC fcc nanocrystals, instead of metcar clusters. Also, the replacement of the target of a photodissociation experiment even with a similar one can drastically affect the results. For instance, using an fcc Ti$_{14}$C$_{13}$ nanocrystal as the target, the prominent adsorption line corresponds to Ti$_8$C$_{13}$ and not to the expected metcar cage Ti$_8$C$_{12}$.

An alternative strategy to tailor and functionalize nanostructures is by energetic irradiation or collisions with smaller clusters, ions or electrons. This constitutes an interesting approach because, rather than creating a new structure from scratch, the target structure and even its composition, are modified and the extent of those changes can be – at least partially – controlled by tuning the incident momentum. Also, a collision process may be useful to obtain Ti$_x$C$_M$ clusters with an N: M ratio different from the usual 2:3. However, the DFT molecular dynamics simulation of collision processes to obtain the putative global minimum, in addition to many low energy configurations, has been shown to be quite effective and efficient, and has recently been successfully applied, with promising results, to fullerene-like carbon nanostructures.

Therefore, we simulate by means of ab initio molecular dynamics, the collision of a Ti dimer against a C$_{20}$ cluster in the bowl conformation. Two different incident energies were explored and several values of the geometric parameters (i.e., impact parameter, relative orientations) were studied to obtain a representative set of results.

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**COMPUTATIONAL METHODS**

The calculations were divided into two parts: the collision dynamics of a Ti dimer against a C$_{20}$ cluster in the bowl conformation, and the characterization of the relevant structures that result from this collision process. For the former calculations, the accuracy is not crucial but it is important to avoid a large departure from the Born–Oppenheimer surface and to avoid a cumulative drift of the trajectory, which causes numerical errors. On the contrary, when studying other properties, like the electron localization function (ELF) of titanium carbides, accurate computations cannot be avoided.

We carried out the computations using the VASP code,\textsuperscript{22--24} which implements DFT using a plane waves basis. Also, we tested the GAUSSIAN code,\textsuperscript{25} obtaining agreement with VASP for several single point calculations, but due the small band gap of the initial configuration a plane waves basis achieves a better performance. Pseudopotentials of the projected augmented wave (PAW) type\textsuperscript{26} and the exchange-correlation parametrization given by Perdew et al. (PBE)\textsuperscript{27} were employed. For the dynamics the plane wave cutoff was set to 275 eV. To avoid spurious self-interactions a large simulation cell, of edges close to 20 Å was used. Due to the Ti open d-shell an unrestricted spin-polarized scheme was adopted. The energy self-consistent convergence criterion was set to 10$^{-6}$ eV. A variable time-step was used, ranging from 0.1 fs at the moment of impact to 0.7 fs when the energy spreads out over the whole system and, therefore, the velocities become smaller. In order to obtain results as close as possible to experiments, the dynamics was carried out in the microcanonical ensemble, since a thermostat would tend to establish equilibrium in a system which is inherently out of equilibrium during the initial stages of the collision process.

After the collision, and the subsequent cooling-down process,\textsuperscript{18--20} the resulting structures were optimized and analyzed, including the calculation of the ELF. To achieve an accurate description of this property the energy cutoff was raised to 400 eV, the geometries were optimized requiring forces smaller than 0.005 eV/Å, and a stringent self-consistent energy convergence criterion of 10$^{-6}$ eV was imposed.

Moreover, along the dynamics several interesting conformations were found (∼100 for each of the dynamics), which were optimized to increase our chances of finding the putative global minimum (i.e., the most stable configuration). In order to avoid a huge waste of computing time optimizing equivalent geometries we use a ‘conformational distance’ criterion\textsuperscript{28} to discard structures which converge to an already obtained local minimum.

**RESULTS**

The experimental setup we simulate is illustrated in Figure 1, and consists in a Ti dimer (the projectile) impacting a C$_{20}$ cluster (the target). Initially the dimer center of mass (CM) is 6 Å apart from the C$_{20}$ CM and carries a kinetic energy $E_k$ in the laboratory frame of reference. Two $E_k$ values were investigated: 5 and 10 eV. Initially, both target and projectile have no vibrational energy. In addition, the impact parameter $b$ for the collision ranges from 0 to 4 Å, measured relative to the target CM. Neither the projectile, nor the target are rotation invariant, but to avoid a huge number of configurations we restrict the relative orientations only to the ones shown in Figure 1, that is, with the initial velocity longitudinal or transverse to the dimer.

The target is a C$_{20}$ cluster in the bowl conformation. This isomer is especially interesting since: (i) it has a large collision cross section, and (ii) it can serve as a first try (less expensive) approach to the functionalization of fullerenes by collisions with metallic clusters. Of course, a direct extrapolation to the fullerene is inadequate, but it can be useful to provide a first insight about the mechanisms that induce the breaking of the strong C–C bonds, and of the relevant parameters ($E_k$ and $b$) that determine the fusion or scattering of the incident metal atoms by the target. For the Ti dimer, we find an equilibrium distance of 1.96 Å, a binding energy of 1.44 eV/atom, and a triplet state for the spin configuration. These values are in good agreement with the 1.95 Å and 1.54 eV obtained experimentally by Russon et al.\textsuperscript{29}

In a real experiment, charged metal clusters are accelerated in order to give them speed and use mass spectroscopy to classify the clusters. Here we restrict ourselves to neutral clusters and, to rather low energies $E_k$.

During the initial stage of the simulation, the projectile flies toward the target and impacts on it generating atomic rearrangements driven – at least initially – by the projectile. This early stage is the most important one since the Ti atoms carry a large amount of kinetic energy and can jump quickly from one energy attraction basin to another, wandering around the C$_{20}$ cluster, or even breaking the strong C–C bonds. During this early stage, the C$_{20}$ atomic displacements are mainly coordinated, for instance, changing the overall C$_{20}$ curvature. This initial regime gradually disappears, and 0.5 to 1.0 ps after the impact, the atomic motion takes the form of large and uncoordinated oscillations. After ∼2 ps (within the microcanonical ensemble) the system is cooled down by rescaling the velocities until room temperature is reached. This stage takes an additional 2 ps.

The outcome of the collision process covers several scenarios: fusion of projectile and target, target fragmentation, and projectile scattering. Here, we are interested exclusively in fusion, since our goal is the functionalization of a C$_{20}$ cluster. The structures generated by the above procedure, obtained after a cooling down process (i.e., to simulate heat radiation) were optimized locally. The results are shown in Figure 2 and their properties are listed in Table 1. This way of generating putative energy minimum structures seems to be best suited to
compare with those produced by experiments, even when they do not correspond to the most stable conformation. For instance, the structure of the Ti8C12 metcar depends on the experimental conditions, rather than the thermodynamic ones, and we expect a similar behavior in experiments that perform energetic collisions.

Whereas the C20Ti2 conformations found by means of collisions are quite diverse, some systematic trends are apparent. The lowest energy configurations (namely IV, V, XI, and XIII in Figure 2) are also the most abundant ones and correspond to nearly half of the total collision outcomes regardless the initial parameter set. Therefore, in an experiment we expect a large abundance of these structures, especially conformation IV, which accounts for around one-third of the total final geometries. It is interesting that for these geometries the C20 bowl displays just moderate damage: just two C−C broken bonds at one end of the peripheral carbon hexagons. For those structures the Ti coordination lies between 4.5 and 5.5, and it is favorable for the Ti atoms to be close to each other forming a Ti dimer. This bonding between two Ti atoms is confirmed by the existence of a Ti−Ti vibrational mode in the vicinity of 300 cm$^{-1}$. The energy gain by the formation of these C20Ti2 structures amounts to $\sim 7$ eV, which is quite large. However, when a larger fraction of C−C bond breaking occurs — even destroying the inner pentagonal carbon ring — the conformation becomes less favorable (excluding XIII). In addition, examination of Figure 2 also indicates that a minor distortion of the bowl configuration is unfavorable. Only slight changes in the curvature lead to energy reduction, like the ones illustrated in V and VI of Figure 2. Of special interest is case VII, since the Ti dimer is dissociated and both Ti atoms are just “attached” to the pristine bowl. We will return to the discussion of this conformation below.

Most of the geometries we found have zero magnetic moment. However, when the Ti coordination is small (like for VI, VII, IX), a magnetic moment of 2 $\mu_B$ per Ti atom does appear. Figure 3 illustrates several minimum energy structures found during the dynamics, which are different to the ones obtained by means of the radiative cooling-down process. The ‘a’ cluster corresponds to an intermediate stage between I and IV, however it is energetically more stable, but its attraction basin seems to be narrow since its occurrence is rare, thus confirming that not only the relative binding energy is important, but also the procedure implemented to generate the structures.

**Table 1. Properties of the Structures Resulting from the Collision Process: Energy Gained after Fusion $E_{\text{fusion}} = E_{\text{C20}} + E_{\text{Ti2}} - E_{\text{System}}$, Magnetic Moment $\mu$ and, Average Ti Coordination $n_{\text{Ti}}$ Per Atom**

<table>
<thead>
<tr>
<th>Label</th>
<th>$E_{\text{fusion}}$ (eV)</th>
<th>$\mu$ ($\mu_B$)</th>
<th>$n_{\text{Ti}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6.36</td>
<td>0</td>
<td>4.5</td>
</tr>
<tr>
<td>II</td>
<td>4.49</td>
<td>0</td>
<td>6.5</td>
</tr>
<tr>
<td>III</td>
<td>6.28</td>
<td>0</td>
<td>7.5</td>
</tr>
<tr>
<td>IV</td>
<td>6.79</td>
<td>0</td>
<td>5.5</td>
</tr>
<tr>
<td>V</td>
<td>7.12</td>
<td>0</td>
<td>5.5</td>
</tr>
<tr>
<td>VI</td>
<td>4.79</td>
<td>2</td>
<td>3.5</td>
</tr>
<tr>
<td>VII</td>
<td>6.03</td>
<td>4</td>
<td>2.0</td>
</tr>
<tr>
<td>VIII</td>
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<td>6.0</td>
</tr>
<tr>
<td>IX</td>
<td>5.52</td>
<td>4</td>
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</tr>
<tr>
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<td>5.30</td>
<td>0</td>
<td>4.5</td>
</tr>
<tr>
<td>XI</td>
<td>6.79</td>
<td>0</td>
<td>4.5</td>
</tr>
<tr>
<td>XII</td>
<td>-</td>
<td>2</td>
<td>3.0</td>
</tr>
<tr>
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<tr>
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<tr>
<td>b</td>
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</tr>
<tr>
<td>c</td>
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<tr>
<td>d</td>
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<td>8.0</td>
</tr>
</tbody>
</table>

*aThe roman numbered labels (I to XIII) correspond to the structures in Figure 2, whereas the lowercase labels (a to d) denote those shown in Figure 3.*

**Figure 2.** (color online) Results of the collision of a Ti2 dimer against C20 in the bowl configuration. The color coding is the same as in Figure 1. The impact parameter $b$ (measured in Å) is given at the left and the initial kinetic energy, in eV units, is given at the top. The labels A and B refer to the initial Ti dimer orientation, parallel, or perpendicular to the dimer initial velocity, as in Figure 1. All of the structures were cooled until reaching 300 K and then locally optimized. The frames labeled with a ‘*’ or ‘**’ have the same conformation. For ($b = 0, E_K = 10$) no Ti atoms appear because they are scattered.

**Figure 3.** (color online) Relevant C20Ti2 structures found during the collision dynamics, after cooling and local optimization. They are labeled from a to d in order of decreasing stability.
conformation marked as ‘b’ is very close to XIII, but has a key
difference (which accounts for its ~0.7 lower binding energy): in
the latter one Ti atom (upper left in Figure 2) tends to form
Ti–C bonds closer to 90° with each other, whereas in the ‘a’
conformation the same angles are notoriously acute. A similar
feature can be seen in the ‘c’ conformation, which is somewhat
similar to the putative groundstate (V), having one Ti atom
inside a C hexagon, but the under-coordination of the second
Ti and its bonding, quenching the d-orbital tendency to form
right angles, makes this geometry ~0.9 eV higher in energy
than structure ‘a’. Finally, the ‘d’ conformation shows a large
rearrangement of the whole carbon bowl resulting in one of the
energetically unfavorable structures.

Next, we analyze the results obtained by the use of the
electron localization function (ELF) to understand the type
of bonds formed in the different systems. The numerical
values of the ELF are between zero and one, and a region of the
space where the value of the ELF is large, say higher than 0.7, is
interpreted as a region where it is possible to find a localized
spin paired electrons. In Figure 4, various snapshots of the ELF
values for two representative outcomes of the collisions are displayed;
one where the Ti dimer bond is not broken, and the other one
where this bond is broken. To simplify the comparison the ELF
function for values 0.5 < ELF < 0.8 for some representative
(sub)structures. The contour color is darker (redish) for larger ELF
values. To help with the visualization the charge density is drawn as a
light gray shadow.

![Figure 4](image_url)

Figure 4. (color online) Contour plots of the electron localization function for values 0.5 < ELF < 0.8 for some representative (sub)structures. The contour color is darker (redish) for larger ELF values. To help with the visualization the charge density is drawn as a light gray shadow.

for two representative outcomes of the collisions are displayed;
one where the Ti dimer bond is not broken, and the other one
where this bond is broken. To simplify the comparison the ELF
of the Ti dimer, and the C20 bowl cluster are also presented.
Figure 4 clearly depicts the existence of a δ bond. Recall that
Ti₂ is a triplet, with an electronic configuration of \( \sigma^2 \delta^2 \) in a \( ^3\Delta \) state, since the δ orbitals are degenerate. The ELF plots of the
C20 bowl cluster also illustrate this well-known qualitative
interpretation. The basins split for large ELF values meaning
that the electrons are delocalized all over the carbon atoms.34,35
Even more interesting is the interpretation of the ELF pictures
for the carbon cluster doped with Ti. The first system, where
the Ti dimer bonding is not broken, shows that Ti forms some
kind of complex bond, with five or six carbon atoms and two
open carbon rings. However, the rest of the electrons of the
carbon structure remains delocalized. One suspects that Ti,
being an atom which is less electronegative than the C atom it is
able to donate charge to the C skeleton. On the other hand,
for the doped system where the Ti dimer bond is broken, one
can see from the ELF pictures that the interaction of the Ti
atoms with the C skeleton is very weak, and consequently the
delocalization is lost. The ELF basins split at ELF \( \approx 0.5 \), which
implies that the possible reactivity of the two doped clusters
should be different.

**SUMMARY AND CONCLUSIONS**

We present a DFT molecular dynamics treatment of the
collision of a Ti₂ dimer and a C20 nanocluster in the bowl
configuration to shed light on the dynamics of the synthesis of
the titanium carbides. Transverse and longitudinal initial
velocities of the Ti dimer and several impact parameter and
energy values were explored. The characterization of the
properties of the relevant structures that develop, during and
after the collision process are provided as well, by evaluation of
their energies, electronic distribution, and electronic local-
ization function (ELF). The lowest energy configurations
correspond to structures where the two Ti atoms are nearest
neighbors. It is also observed that a large fraction of the low
energy configurations correspond to basically a C20 bowl, with
just two C–C broken bonds at one end of peripheral C
hexagons, plus two Ti first neighbor atoms bonded to the
structure. As far as the ELF is concerned, localization around
the Ti atoms, and delocalization in the vicinity of the C atoms
is observed. The dynamics is mainly determined during the early
stages of the simulation because throughout that time the large
kinetic energy of the Ti dimer allows it to easily overcome the
energy barriers of the C20 cluster.

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**Notes**

The authors declare no competing financial interest.

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