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# DFT study on ammonium perchlorate bond activation by Pt clusters supported by carbon nanotubes and graphene

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Activation of the N–H bond of ammonium perchlorate is a vital channel for thermal decomposition mechanism. The N–H bond breaking on $Pt_4$ clusters supported by carbon nanotubes and graphene has been investigated by the density functional theory method. In this study, comparison of (10-10), (8-8), (10-0) and (5-5) carbon nanotube models in zigzag and armchair forms is presented. The results show that opportune selection of size and chirality of carbon nanotubes supports can provide stable support for Pt clusters and improve their catalytic activity.

**Keywords:** Theoretical chemistry, Density functional calculations, Ammonium perchlorate, Platinum clusters, Carbon nanotubes, Graphene, Transition metals

Composite solid propellants are self-sustaining combustible materials that can be used as fuel and oxidizer for application as gas generators for airbags, control systems, propulsion for space vehicles and tactical missiles, and as pressure generators in deep sea oil operations[1]. In spite of this, the generation of efficient solid propellant is related to understanding the combustion characteristics and mechanism of these materials[2]. In these materials, the solid crystal particle of oxidizer is mixed into long hydrocarbon chains that are polymerized into rubber.

Ammonium perchlorate (AP, $NH_4ClO_4$) is an oxidizer largely used in formulation of solid propellants[3] because it is cheap and contains oxygen that generate stable reaction products in combustion reactions[4,5]. AP based propellant is used in rocket propulsion like missiles and rocket launchers. The main advantagesof AP are good specific impulses, and a simple manufacturing process[6]. The structure of AP crystals shows the ammonium cations ($NH_4^+$) and perchlorate anions ($ClO_4^-$)[7].

Platinum clusters have been reported as highly active and selective catalysts for oxidative dehydrogenation reactions. A comparison of platinum clusters and monoliths show much greater catalytic activities for Pt clusters[8] due to under-coordination of Pt atoms and high surface area-to-volume ratio in the clusters.

N-H bond activation in ammonium perchlorate provides a suitable model for studying a highly selective and efficient catalytic system. Carbon nanotubes (CNTs) and graphene have been proposed as supports for transition metal catalysts[9-12], because of their surface area and capability to stabilize these clusters. Recent experimental advances in the separation of single chirality CNTs[13,14] have increased the possibility of usingsubnanometer clusters as CNT supports to improve the catalytic potential of the combined system.

In this study we have investigated effect of CNT support on the catalytic activity of subnanometer clusters due to the formation of cluster-support bonds. The effect of curvature of CNT support on the catalytic activity has also studied.

## Methodology

AP bond activation by supported $Pt_4$ was studied with density functional theory (DFT) and def 2-svp/j basis set was applied by the ORCA 301 software package. As support structures graphene, (10-10), (8-8), (10-0) and (5-5) CNT models (in order to increasing curvature) were investigated with 66 carbon atoms and 22 hydrogen atoms. The (8-8) system is shown in Fig. 1.

The support structure for a given curvature was formed by transformation of planar graphene to a cylinder of radius *r* given by Eq. (1),

$$r_0 = \sigma \frac{\sqrt{3(n^2+nm+m^2)}}{2\pi} \quad \ldots(1)$$

where n and m are the lattice vectors and σ is the carbon–carbon covalent bond length (σ = 1.41 Å)[15]. CNTs of both zigzag (n, 0) and armchair (n, n) chiralities were considered in this work. The geometry of these structures was optimized with the hydrogen atoms fixed to hold the curvature. The unrestricted spin was applied in optimization of structures and closed shell singlet were the lowest energy spin configurations for all cases. Then Pt cluster was placed near the optimized support structure and binding energies of the Pt-CNT were calculated. Stability of $Pt_4$ on the CNT was considered by the binding energy, $E_b$, (Eq. 2),

$$E_{\mathrm{b}} = E_{(\mathrm{Pt_4-CNT})} - E_{\mathrm{Pt_4}} - E_{\mathrm{CNT}} \quad \ldots(2)$$

where $E_{(\mathrm{Pt4\text{-}CNT})}$, $E_{\mathrm{Pt4}}$ and $E_{\mathrm{CNT}}$ are the total energy of the combined $Pt_4$ and CNT system, energy of the cluster and energy of the support, respectively.

Then, AP was added to the minimized cluster-support systems and then optimized to obtain the molecular adsorption (MA), dissociative adsorption (DA) and transition state (TS) of the AP on the supported cluster. The energy of adsorption, $E_{\mathrm{MA(DA)}}$, was calculated by Eq. (3),

$$E^{\mathrm{Pt}}_{\mathrm{MA\,(DA)}} = E^{\mathrm{MA}}_{(\mathrm{AP-Pt_4-CNT})} - E_{(\mathrm{Pt_4-CNT})} - E_{\mathrm{AP}} \quad \ldots(3)$$

where $E^{\mathrm{MA}}_{(\mathrm{AP-Pt_4-CNT})}$ , $E_{(\mathrm{Pt4\text{-}CNT})}$ and $E_{\mathrm{AP}}$ are the total energy of the combined AP-$Pt_4$-CNT system in the configuration corresponding to MA, total energy of the combined $Pt_4$ and CNT system and the total energy of the AP, respectively.

The apparent barrier ($E^{\mathrm{M}}_{\mathrm{a}}$) of the transition state was calculated by Eq. (4),

$$\mathrm{E}^{\mathrm{Pt}}_{\mathrm{a}} = \mathrm{E}^{\mathrm{Pt}}_{\mathrm{TS}} - \mathrm{E}_{(\mathrm{Pt_4-CNT})} - \mathrm{E}_{\mathrm{AP}} \quad \ldots(4)$$

$E^{\mathrm{Pt}}_{\mathrm{TS}}$ is the total energy in the transition states.

## Results and discussion

In Fig. 2, the comparison of binding energies show that $E_b$ increases with CNT curvature and optimized structures show direct relation between the number of Pt-CNT bonds and curvature because of the reactivity of small CNTs[16]. A comparison of singlet and triplet systems show that in singlet $Pt_4$–CNT systems, clusters bind in zigzag CNT much stronger than in armchair CNT. However, in triplet $Pt_4$-CNT systems, the clusters bind in armchair CNT much stronger than in zigzag supports except at curvature of higher than 0.2 Å. It is

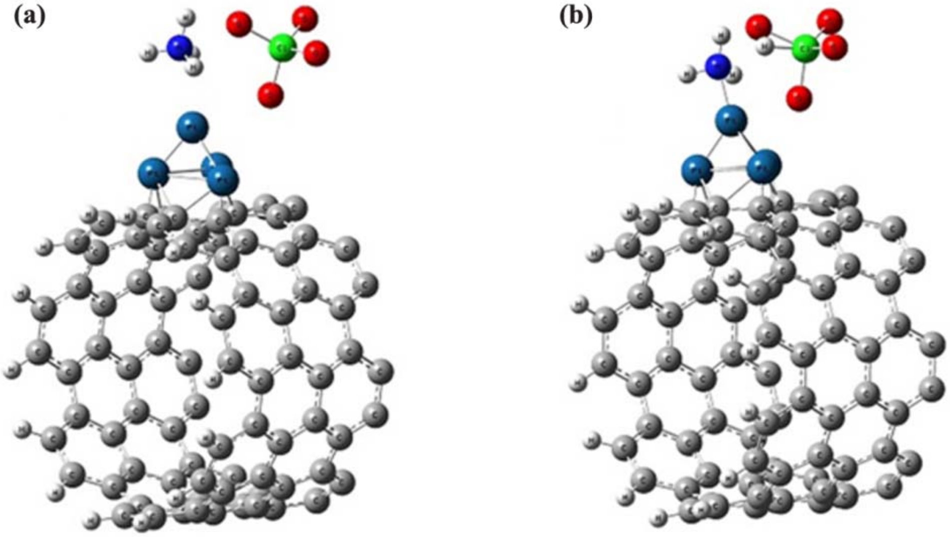

Fig. 1 — Calculated structures of an AP molecule reacting with a Pt clusters supported on a (8, 8) CNT. [(a) molecular adsorption; (b) transition state].

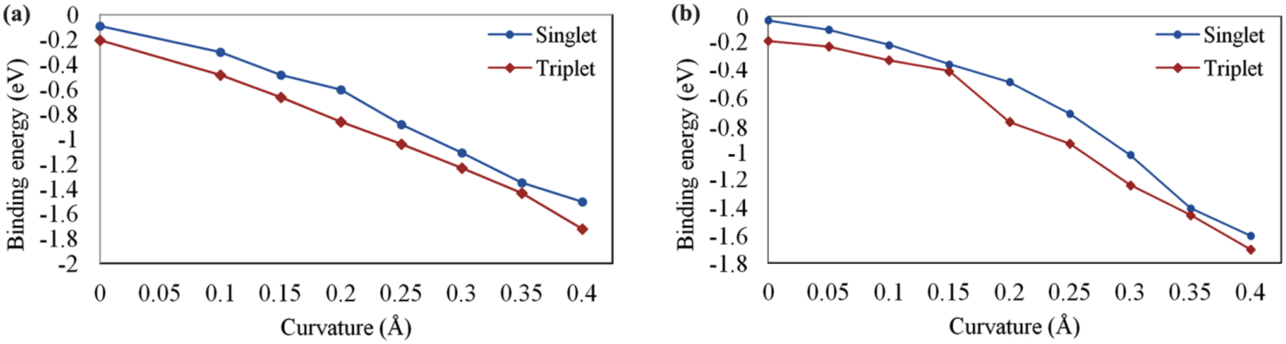

Fig. 2 — Calculated $Pt_4$ cluster binding energy to the CNT support as a function of CNT curvature and chirality. [(a) armchair; (b) zigzag].

clear that the binding properties of the cluster is related to electronic effects of the support as armchair CNTs are metallic and zigzag CNTs are mostly semiconducting[17].

Further, the results show that in singlet $\mathrm{Pt}_4$-CNT systems, the binding of clusters in armchair CNT is stronger than in zigzag CNT except at curvature higher than 0.3 Å, while in triplet $\mathrm{Pt}_4$–CNT systems, the cluster binding in armchair CNT is stronger than in zigzag supports.

The effect of the support on catalytic activity was investigated since the additional bonds from the cluster to the support may reduce the under-coordination that is characteristic of cluster activity. In the lowest energy configurations of unsupported $\mathrm{Pt}_4$, the clusters are trigonal pyramids in triplet states. The reaction starts with ammonium perchlorate and the cluster separates, preceded by molecular adsorption to the N–H bond insertion transition state. The unpaired spin density resides on the cluster throughout the reaction with very little contribution from the carbon atom. The N–H bond breaking reaction is exothermic on a $\mathrm{Pt}_4$ cluster as shown in Fig. 3. The apparent barrier to N–H bond insertion on $\mathrm{Pt}_4$ is much lower at 1.01 eV in comparison to other barriers for N–H bond breaking. Overall, this shows that $\mathrm{Pt}_4$ has a high activity for N–H bond breaking of ammonium perchlorate.

The adsorption of AP on clusters can be affected by size and chirality of the CNT. In Fig. 4 the energies of adsorption, $E_{\mathrm{MA}}^{\mathrm{Pt}}$, for AP adsorbed on $\mathrm{Pt}_4$ clusters supported by CNTs are shown as a function of curvature. The reaction on Pt is exothermic because $E_{\mathrm{DA}}<E_{\mathrm{MA}}$ for large diameter CNTs while the reaction energy is less endothermic for small diameter CNTs. The most exothermic$\mathrm{Pt}_4$ reaction occurs when the Pt cluster is weakly bound to a large diameter CNT support.

Further, the reaction is more exothermic on CNTs of particular sizes and chiralities, which may be understood as islands of stability. For Pt, the most favorable sizes are (10, 10) and (8, 8) armchair CNTs. The least favorable size and chirality, i. e., an island of instability for AP N-H bond insertion reactions on Pt are (10, 0) CNTs. We propose that the reason some supports have lower or higher adsorption energies are due to geometric and electronic effects of the support. The bond energy of the metal bond increases with curvature. However, the increased metal-CNT bond energy is offset by distortion of the CNT and the cluster away from an optimal geometry in order to fit multiple binding sites on the support. We define the distortion energy as the difference in energy between the supports optimized in the reaction steps and the initial relaxed configuration. For $\mathrm{Pt}_4$ clusters, the distortion energy for the support is inversely proportional to the support curvature.

To study the ammonium perchlorate activation by clusters,Pt cluster binding to the concave side of a (10, 10) model support was compared with results for the convex surface. Calculations showed that $\mathrm{Pt}_4$ binds to concave support with –1.8 eV compared to –2.5 eV to the convex side. Reaction energies on the concave support are similar to those found on the convex side. Dissociative adsorption energies and the adsorption energies for $\mathrm{Pt}_4$ are –0.23 and –0.60 eV, respectively. Therefore, the reaction energies for N-H bond breaking on a concave CNT is –0.31 eV, more exothermic than the reaction on the outer side of the CNT wall.

Overall, this shows that the Pt clusters are more stable on the outer CNT surface and less stable on the inside of a CNT support. The reasoning for the weaker cluster interaction to the concave CNT wall is because of steric strain of the CNT due to greater

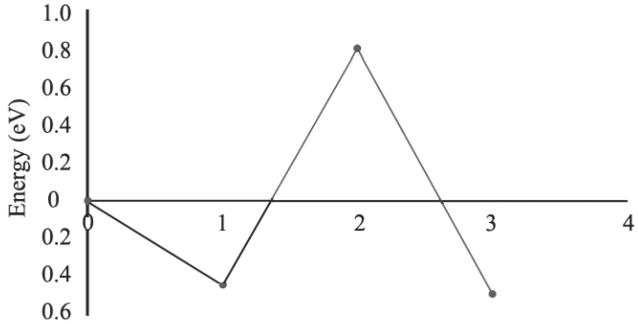

Fig. 3 — Adsorption energies and reaction barriers of N–H bond. [(1) to molecular adsorption; (2) to transition station; (3) to dissociative adsorption].

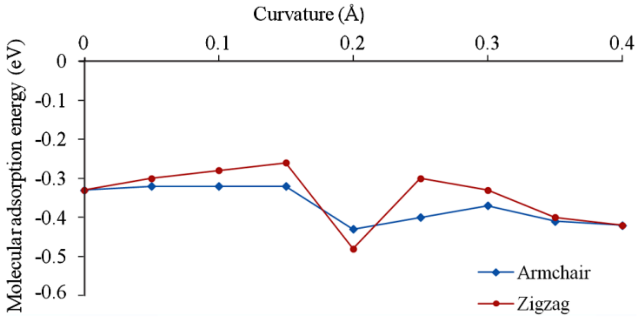

Fig. 4 — Energies of molecular adsorption, $E_{\mathrm{MA}}^{\mathrm{Pt}}$ as a function of support curvature and chirality, including graphene (curvature = 0:0 Å).

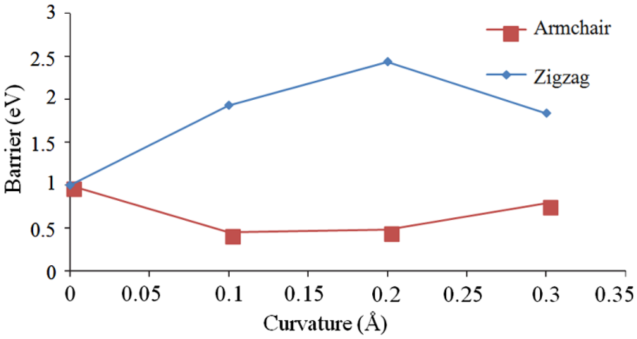

Fig. 5 — Calculated apparent barriers for N-H bonds with $Pt_4$ catalysts on supports by curvature and chirality, for armchair, and zigzag CNTs.

electron density on the CNT exterior surface as compared to the interior surface since the carbon atoms gain more $sp^3$ character with increasing CNT curvature.

The relation between apparent barriers and curvature and chirality of CNT was studied. The $E_a^M$ for N-H bond of ammonium perchlorate (insertion on supported $Pt_4$ clusters) for support curvature and chirality is shown in Fig. 5. The trends in the apparent barriers can be compared to those of the cluster-support binding energies. The trend in the Pt apparent barriers with curvature is opposite to barrier energies decreasing with binding energies. Two regions in are observed in the plot of apparent barrier as function of curvature. Zigzag CNTs have lower $E_a^{pt}$ at curvature below 0.2 Å and maximum apparent barrier appears at 0.2 Å with 2.44 eV. However, in armchair forms, apparent barriers increase from 0.45 eV to 0.79 eV at curvature from 0.1 to 0.3Å. However, apparent barriers for Pt N-H bond activation are lower for armchair CNTs than for zigzag CNTs.

In conclusions, the negative binding energies show stability of platinum clusters on carbon nanotube supports. In the triplet state, platinum has opposite ordering of binding energies relative to the chirality of the support, with armchair supports having lowest energy for $Pt_4$. This is observed in the higher energy singlet state. Reaction energies on supported platinum clusters are exothermic. When an initial state of a bound cluster-support system is compared with a separated ammonium perchlorate, all reactions on $Pt_4$ are exothermic, except for armchair supports with high curvature. For platinum clusters, barriers for bond activation increase with increasing carbon nanotube curvature. Our results show that carbon nanotube supports can be selected by size and chirality to provide stable support for subnanometer platinum clusters and fit their catalytic activity.

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