



## Physical Chemistry Properties of $\text{Fe}_3\text{O}_4$ @ Cyclodextrin@ (12, 12) SWCNTs as a Catalyst

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### ABSTRACT

$\text{Fe}_3\text{O}_4$  is used in the water gas shift reaction as a catalyst in the “Haber process”. In this work, the physical and chemical properties of  $\text{Fe}_3\text{O}_4$  @  $\alpha$ -Cyclodextrin @ (12, 12) SWCNTs has been investigated. Our calculations have been done in point of chemical phenomenon and electronic properties. The Magnetic behavior, Electron densities and electrical properties such as NMR Shielding, potential energies densities, energy density, ellipticity for electron densities, ELF, LOL, index of eta and finally ECP for  $\text{Fe}_3\text{O}_4$  @ -Cyclodextrin@ (12, 12) SWCNTs have been calculated and simulated in our system. Our Calculation indicate that the  $\text{Fe}_3\text{O}_4$  @ -Cyclodextrin@ (12, 12) SWCNTs are suitable surfaces for  $\text{Fe}_3\text{O}_4$  such silica surfaces.

**Keywords:**  $\text{Fe}_3\text{O}_4$ , Nano-Particles, electron density, (12, 12) SWCNTs, Cyclodextrin.

### INTRODUCTION

The great temperature shifts catalyst (HTS) of iron oxide<sup>1-3</sup> stabilized by chromium oxide<sup>1-5</sup>. This chrome-iron alloys as a catalyst is diminished at chemical-reactor-start up for generating  $\text{Fe}_3\text{O}_4$  from  $\alpha\text{-Fe}_2\text{O}_3$ <sup>4</sup> and  $\text{Cr}_2\text{O}_3$ <sup>5</sup>.  $\text{Fe}_3\text{O}_4$  is one of the most important electrical conductors within conductivities considerably higher comparison to  $\text{Fe}_2\text{O}_3$ <sup>3,4</sup> and this is imputed for exchange electron between two parts of the  $\text{Fe}^{(II)}$  and  $\text{Fe}^{(III)}$  centers<sup>1-3</sup>.

$\text{Fe}_3\text{O}_4$  family are ferromagnetic with remarkable curie temperature (858 K) and this ferromagnetism properties of  $\text{Fe}_3\text{O}_4$  appears because the spin electron of the  $\text{Fe}^{(II)}$  and  $\text{Fe}^{(III)}$  ions are coupled together in the octahedral structures and the spin of the  $\text{Fe}^{(III)}$  ion are coupled (anti-parallel to the former<sup>1-4</sup>) in a tetrahedral structure.  $\text{Fe}_3\text{O}_4$  is used in the water gas shift reaction as a catalyst in the “Haber process”

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is structured in the inverse-cubic-spinel-crystal<sup>4</sup>. Each of cubic-spinel-

cell contains “8” inter-penetrating oxygens within the tetrahedral sites<sup>4,5</sup> and has been occupied through “1/3” of the Fe atoms, such as diamond structures. The other iron atoms are placed at the octahedral situations with closest atoms arranged as string in six various directions<sup>5-7</sup>.

Fe<sub>3</sub>O<sub>4</sub> structures consist of the cubic-close-packed arrays of oxides which all of the Fe<sup>(2+)</sup> ions occupies “1/2” of the octahedral locations and the Fe<sup>(3+)</sup> splits equally along the other octahedral and tetrahedral locations<sup>1-7</sup>.

Cyclo-dextrin is extracted from the degradation<sup>5</sup> of starch by *Bacillus macerans*<sup>5,6</sup>, which for the first one has been isolated in the late 9<sup>th</sup> century<sup>5-8</sup>. Its abilities for forming complexes with various organic molecules were discovered immediately there after<sup>6-9</sup>. By developing the fields of Chemistry's Supramolecular<sup>8</sup>, its complexation properties have been tightly studied<sup>7-10</sup>. Usage of cyclo-dextrin and its derivatives are desirable in various areas of chemistry<sup>7-10</sup>, including the influencing of the organic molecules<sup>8-14</sup>. By this study the catalysis's properties of Fe<sub>3</sub>O<sub>4</sub> nanoparticles @ Cyclodextrins @ (12, 12) SWCNTs for comparing in the area of chemical synthesizes<sup>15-20</sup> have been investigated.

CNT or carbon nanotubes are representatives of Nano materials. CNT is a cylindrically<sup>21</sup> shaped-carbon-material<sup>22</sup> with the Nano metric diameter<sup>21-30</sup>. Their shapes which are in the structure of hexagonal-mesh<sup>23-28</sup>, look like a graphite<sup>26-30</sup> and these sheets

have wrapped and their two edges have attached together seamlessly<sup>31-35</sup>.

Although it is a common-place material using in pencil-leads<sup>31-33</sup>, their unique structures causes them for presenting a characteristic which had not observed with any other materials<sup>30-35</sup>. SWCNTs is classified<sup>33</sup> into (1): single-walled of carbon-Nano- tubes (CNTs), (2): double-walled carbon-Nano- tubes (CNTs), (3): multi walled carbon-Nano- tubes (CNTs) according to the number<sup>37</sup> of the layers in a rolled-graphite<sup>36-39</sup>.

The important attentions in this area are about the SWCNTs diameters, which are varying among (0.4 – 2) nanometer<sup>35-40</sup> while the lengths are in the order of microns (10<sup>-6</sup>m)<sup>32-40</sup>, but SWCNTs with the lengths in the order of centimeters have also been observed recently<sup>41-44</sup>.

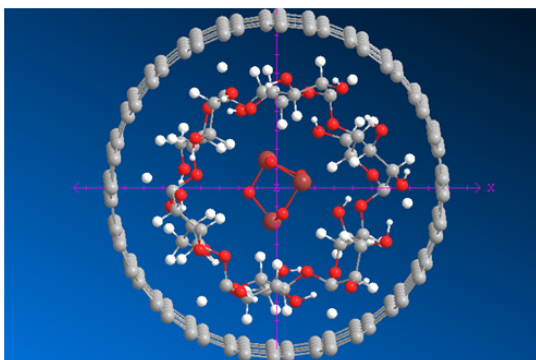
The extremities of the SWCNTs have been nearest with the lids<sup>46</sup> of the graphite sheets<sup>45-50</sup>.

#### Computational details

A section of our system for Fe<sub>3</sub>O<sub>4</sub>@ Cyclodextrins nanoparticles and Fe<sub>3</sub>O<sub>4</sub>@ (12, 12) CNTs have been simulated with QM/MM methods and the optimization were carried out<sup>51-55</sup> via the Monte Carlo approaches. These investigations with differences in the force fields are illustrated through comparing<sup>52-56</sup> the energies by the force fields of AMBER<sup>57</sup> and OPLS<sup>58</sup>. In addition, the software of Hyper-Chem professional version of 7.01 is used for further calculation.

In the noncovalent interaction of two parts of Fe<sub>3</sub>O<sub>4</sub> and Cyclo-dextrin, the density functional methods such as B3LYP are not suitable for describing the van-der-Waals forces in medium<sup>55</sup> ranges interaction. So, the QM/MM such as ONIOM method with three classes of (1): high, (2): medium, and (3): low calculations, has been used in this studies between two parts of Fe<sub>3</sub>O<sub>4</sub> and Cyclo-dextrin.

The ab-initio of DFT methods are used for the model of systems through definition of ONIOM<sup>53-56</sup> layers and the various semi-empirical<sup>55</sup> methods such as pm6 within pseudo=lanl2<sup>57</sup> order



**Fig.1: Non bonded interaction between Cyclodextrins (alpha) and Fe<sub>3</sub>O<sub>4</sub> Inside (12, 12)SWCNTs**

and the Pm3MM<sup>58</sup> for the second and third layers, respectively<sup>59</sup>.

The most general of density-functional-theory are inexpressive to exhibit the correlation<sup>56</sup> and exchange<sup>57</sup> energies for medium-range of non-bonded systems correctly. In addition, some of the recent works have exhibited the inexactitude of the medium-ranges exchange energies lead to the large principled error in prognostication of the molecular properties<sup>51-53</sup>.

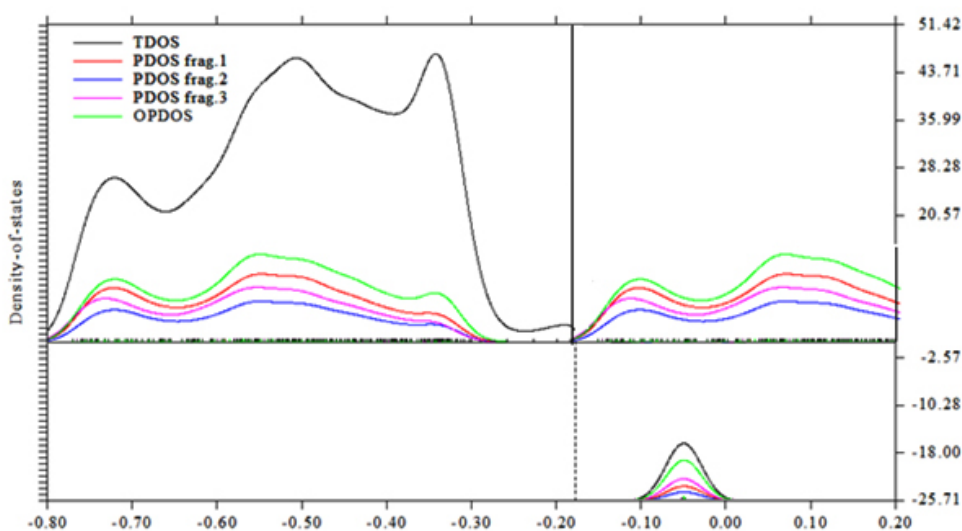
Electronic structure calculations and geometry optimization have been performed using the m06-DFT. This Functional theories are based on an repetition solution of the Kohn & Sham

equation<sup>53,54</sup> of DFT theory in the plane-wave sets including a projector-augmented-wave-pseudo potential<sup>50-54</sup>. The PBE<sup>55</sup> (Burke, Ernzerh &Perdew), XC (exchange/correlation) of the GGA (generalized-gradient-approximation) are also has applied. The calculation of the lattice- constant<sup>57</sup> and the atomic coordinate is made by the minimized the systems for the total energies.

The charges transfer<sup>56</sup> of electrostatics potentials derived<sup>57</sup> charges were also estimated using MKS(Merz-Kollman-Singh) and Chelp or chelpG<sup>56,57</sup>. The charges calculation method based on electrostatic-potentials fitting or MESP are not well befit for remedy of the bigger system.

**Table 1: All Electron Densities of non-bonded interactions for Fe<sub>3</sub>O<sub>4</sub>- Cyclodextrin ( $\alpha$  @ (12,12)SWCNTs**

Atom (number)	Density of all electron(10 <sup>-3</sup> )	Density of alpha (10 <sup>-3</sup> )	Density of Beta (10 <sup>-3</sup> )	Spin Density
Fe(1)	0.10	0.05	0.05	0.0
Fe(2)	0.20	0.10	0.10	0.0
Fe(3)	0.34	0.17	0.17	0.0
O(4)	0.30	0.15	0.15	0.0
O(5)	0.13	0.65	0.65	0.0
O(6)	0.36	0.18	0.18	0.0
O(7)	0.24	0.12	0.12	0.0



**Fig. 2: Density of states for Fe<sub>3</sub>O<sub>4</sub>@alphaCD@ (12,12)SWCNTs**

By these conditions, changes of the inner-most atomic-charge would not topped toward a remarkable changes of the MESP<sup>50-56</sup> for the molecules, which means that the precise value for the inner-most atomic-charge is not well specified out-side molecules . The agent atomic charge for a molecule might be calculated as the intermediate value over a few molecular conformations<sup>50-54</sup>.

In an overview of the effect of the basis sets and the “Hamiltonian” on the charges distributions would be found in the references<sup>56-58</sup>. The charges densities profile in this kind studies have been extracted from the ûrst principle calculations via an intermediate processing as explained in the references<sup>53,54</sup>. The interaction energies of these non-bonded interactions were calculated according to the equation as follows for all items:

$$\Delta E_s(eV) = \{E_c - \left( \sum_{i=1}^n (Fe3O4 - Cyclodextrin (\alpha, \beta \text{ and } \gamma))_i + \sum_{i=1}^n (Fe3O4 - SCyclodextrin (\alpha, \beta \text{ and } \gamma))_{i1} \right)\}$$

Where the “ $\Delta E_s$ ” are the stability energies.

Both electron densities of Laplacian and gradient, values of orbital-wave-functions, spin-electron densities, total potential of electrostatics (ESP), electrostatic potential from atomic charges of nucleus, ELF (localization-function for electron ), LOL (locator & orbital-localized), detailed by correlation

hole, as well as the correlation & exchange densities, Becke & Tsirelson, correlation- factor, and the expectation of ionization energies (local) using the Multifunctional<sup>55-57</sup> have also been applied in these kind studies. The contour lines maps were also drawn using the Multi-wfn software<sup>55-57</sup>. The contour lines corresponding to the VdW surfaces including of electron densities are defined by Bader and has been drawn in this study<sup>55-57</sup>. That is clearly useful for analyzing of distributions for the electrostatics potentials on VdW surfaces. Those contour<sup>55</sup> lines have also been drawn in the gradient-lines<sup>55</sup> and vector-fields-maps<sup>56</sup> by the equal option<sup>55-57</sup>. The relief<sup>62</sup> maps were applied for presenting the height values at the points. Shaded-surface<sup>61</sup> maps with and without a projection<sup>56</sup> is used in our representation<sup>56</sup> of height values at various situation<sup>60-62</sup>.

## RESULT AND DISCUSSIONS

### Monte-Carlo Approaches

The section of ab-initio methods are given by computation that is yielded from principals of theory phenomenon, without inclusion of the experiment information<sup>63,64</sup>. The important usual types of ab-initio optimization are called HF, while the primary approximations are called: central-field or CFA. An important method that eschews making the HF problems is popular as the name Quantum-Monte-Carlo<sup>7</sup>. Also in contrast to the molecular

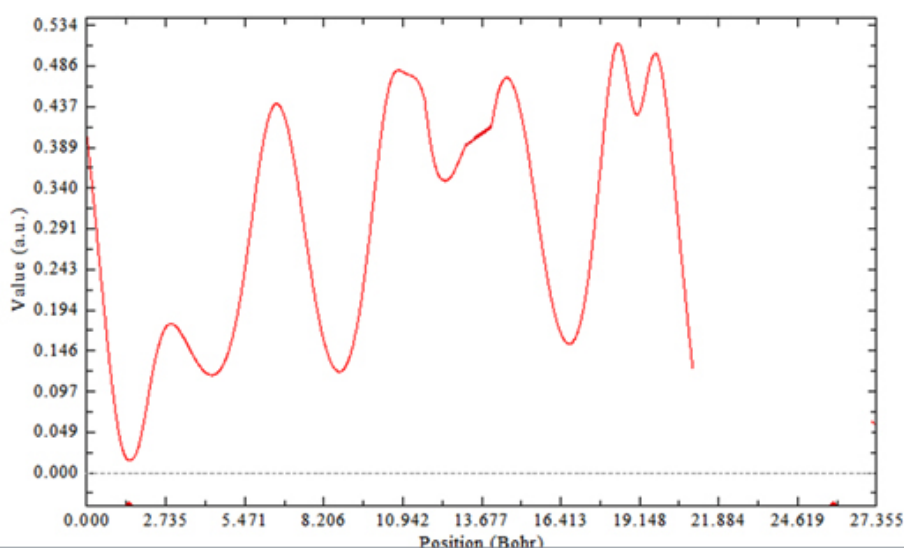


Fig. 3: Position of the first atom to end for Fe<sub>3</sub>O<sub>4</sub>@ CD @ (12,12)SWCNTs

dynamics methods which are totally definitive, the Monte Carlo simulation methods are based on using of stochastic significances. On those methods, the systems are included of M atoms which are given in a group of primary orients and interact together. Estimations of those primary configurations are then produced by this consecutive random displacement which works through variation of QMC, Green's functions and diffusion approaches. Those methods work via wave-functions and have evaluated the numerical integrals. Although those optimization might be much more time consuming, these are seems the most precise and suitable ways which are known up to now. An ab-initio calculation gives high quality results and then might yields increasingly high quanty results.

There are 3 levels for accomplishing of any QM/MM optimization in the "Hyper-Chem version 8.0" packages. Firstly sets up the structures of the

molecules with an appropriate starting geometry or coordinates. For the second step it should be chosen suitable optimization including its associated-choices. For the 3<sup>rd</sup> step it should be selected a kind of optimization with the related options. The MC simulation detects a so-called important phase-space region that is of the lowest energies. Because of fault of the force fields, these lower energies basin usually (in most cases) does not equal to the normal states, so the rank of native structures produced by the force fields themselves is low-order.

By this work, differences in the force-fields are investigated with comparison the energies optimization using force fields among the Amber, MM+, and OPLS of charmm. In addition, we investigated the polar solvents and the temperature effect (from 260K to 400K) for the stability of single wall of CNTs bonded to CGA or CFA by the various solvent. The QM or quantum mechanics

**Table 2: All Electron Energies of non-bonded interactions for Fe<sub>3</sub>O<sub>4</sub>- Cyclodextrin ( $\alpha$ @(12,12)SWCNTs**

Atom (number)	Lagrangian kinetic [G(r)]energy(10 <sup>-3</sup> )	Hamiltonian kinetic [K(r)]energy(10 <sup>-2</sup> )	Potential energy Density [U(r)] (10 <sup>-2</sup> )
Fe(1)	0.24	0.45	-0.32
Fe(2)	0.28	0.6	-0.42
Fe(3)	0.12	0.26	-0.60
O(4)	0.26	-0.14	-0.32
O(5)	0.32	-0.20	-0.56
O(6)	0.28	-0.10	-0.22
O(7)	0.10	-0.20	-0.80

**Table 3: Laplacian, ELF, LOL and Local information entropy of non-bonded interactions for Fe<sub>3</sub>O<sub>4</sub>- Cyclodextrin ( $\alpha$ @(12,12)SWCNTs**

Atom (number)	Laplacian of electron density(10 <sup>-1</sup> )	Electron localization function (ELF) (10 <sup>-3</sup> )	Localized orbital locator (LOL) (10 <sup>-1</sup> )	Local information entropy(10 <sup>-4</sup> )
Fe(1)	-0.12	0.62	0.25	0.12
Fe(2)	-0.16	0.42	0.36	0.14
Fe(3)	-0.28	0.38	0.16	0.46
O(4)	0.42	0.26	0.24	0.26
O(5)	0.32	0.16	0.12	0.26
O(6)	0.56	0.18	0.22	0.34
O(7)	0.26	0.22	0.10	0.10

**Table4: Average local ionization energy, RDG and ESP of non-bonded interactions for Fe<sub>3</sub>O<sub>4</sub>- Cyclodextrin (  $\alpha$  @ (12,12)SWCNTs**

Atom (number)	Reduced density gradient(RDG)	Average local ionization energy	ESP from nuclear charge (10 <sup>4</sup> )	ESP from electron charge (10 <sup>2</sup> )
Fe(1)	0.40	0.46	0.10	-0.42
Fe(2)	0.40	0.46	0.14	-0.48
Fe(3)	0.52	0.56	0.14	-0.42
O(4)	0.62	0.72	0.16	-0.42
O(5)	0.16	0.16	0.14	-0.42
O(6)	0.62	0.80	0.16	-0.42
O(7)	0.16	0.20	0.18	-0.64

**Table 5: Lambada2, Wave function value, Ellipticity of electron density and Eta index of non-bonded interactions for Fe<sub>3</sub>O<sub>4</sub>- Cyclodextrin (  $\alpha$  @ (12,12)SWCNTs**

Atom (number)	Lambada2 (10 <sup>-3</sup> )	Wave function value (10 <sup>-4</sup> )	Ellipticity of electron density	Eta index
Fe(1)	-0.16	0.42	0.48	-3.41
Fe(2)	-0.13	0.88	0.44	-2.54
Fe(3)	-0.15	0.67	0.23	0.53
O(4)	0.36	0.29	-0.46	1.41
O(5)	0.11	-0.43	-0.17	0.93
O(6)	0.34	0.33	-0.42	0.38
O(7)	0.23	-0.28	-0.17	0.76

calculation was carried out with the "Hyper-Chem 8.0" program.

This work basically accomplished on the magnetic properties of Fe<sub>3</sub>O<sub>4</sub> in the non-bonding systems of Cyclo-dextrin ( $\alpha$ ) and Fe<sub>3</sub>O<sub>4</sub>. The non-bonding interactions are exhibited in figs1- 3. As it is cleared in tables 1-10, the electrical<sup>55</sup> property can be yielded from changing in a non-bonding interaction. Potential energy, electron density, ELF, energy density<sup>55</sup>, Ellipticity, LOL, eta indexes and ECP of Fe<sub>3</sub>O<sub>4</sub>@Cyclodextrin (@ (12, 12) SWCNTs were calculated of each simulations (Table1-10)<sup>55-59</sup>.

### CONCLUSION

Fe<sub>3</sub>O<sub>4</sub> is Ferro-magnetic including a curie<sup>°</sup> temperature of the 858±0.5 K and these Ferro-

magnetism arises for "Fe<sub>3</sub>O<sub>4</sub>" because the spin of electrons for the FeIII and FeII in the octahedral location are in a coupled situations together and those spins of the Fe(III) ions in the tetrahedral locations are also coupled together but are in anti-parallel situations to the previous one. Fe<sub>3</sub>O<sub>4</sub> is used in the water gas shift reaction as a catalyst in the "Haber process". It has been emphasized this study have great potentials for developing the novel multi-functional catalysts with high selectivity and reactivity. The other amazing developments are using the (12,12) single wall Nano tube carbon over the magnetic nano-particles that causes useful removal of transition metals based catalyst in drug chemistry. These approaches should find relevant industrials applications in food additive, biopharmaceutical, fragrance and others.



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