A Nano Catalyst of CoFe2o4@ B\textsubscript{18}N\textsubscript{18} as a Novel Material

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ABSTRACT

In this work the properties of CoFe2o4@ B\textsubscript{18}N\textsubscript{18} have been illustrated as a novel catalyst to compare with well-known catalyst “Fe3O4@Silica”. It has been shown that CoFe2o4 magnetite particle can be use as important catalyst inside the B\textsubscript{18}N\textsubscript{18} ring. In our previous papers amazing result about the B\textsubscript{18}N\textsubscript{18} properties have been calculated, exhibited (Struct. Chem., 23, 551-580, (2012); J. Phys. Chem A, 117, 1670-1684, (2013); J. Phys. Chem. C, 114, 15315,(2010) and discussed. In present work it has been shown there is a non-covalent attraction between CoFe2o4 and B\textsubscript{18}N\textsubscript{18} coated molecules. In the system of CoFe2o4@B\textsubscript{18}N\textsubscript{18} catalyst, the magnetic nanoparticles (MNPs) as a core part causes important change in the electronic structure of B\textsubscript{18}N\textsubscript{18} as a shell which some compounds are specific-sensitive functional groups for this system such as OH, CHO, NH\textsubscript{2} and were subjected to the some organic reaction. The Physical-chemistry properties such as energy densities, potential energy densities, electron densities, ELF, LOL, eta index, ellipticity of electron density and ECP for CoFe2o4@ B\textsubscript{18}N\textsubscript{18} shell have been calculated and simulated in related reactions for those groups-functionalized. Our Calculation indicates that the B\textsubscript{18}N\textsubscript{18} is much better surfaces for CoFe2o4 rather than silica surfaces.

Keywords: CoFe2o4, Nano-Particles, electron density, B\textsubscript{18}N\textsubscript{18} nano-ring, Silica, SiO\textsubscript{2}

INTRODUCTION

CoFe2o4 as the Cobalt ferrite crystallizes in a partially inverse spinel position represented as \((\text{Co}^{2+}\text{Fe}^{3+}\text{Fe}^{3+}-1)\text{(Co}^{3+}\text{Fe}^{3+}\text{Fe}^{3+}+x)\text{O}_4\) where x based on thermal condition. It is ferri-magnetic with a Tc approximately 520 degree and exhibits a relatively magnetic hysteresis which distinguishes it from the other of the spinel ferrites\textsuperscript{2,3}. Magnetic measurements on nano-particles of cobalt ferrite dispersed in various solvents of organic compounds and nano-crystalline\textsuperscript{2} powders prepared by hydroxide precipitation\textsuperscript{3-5} have been investigated earlier. In magnetic fluids\textsuperscript{5}, it has been seen that for particles above three nanometer the saturation\textsuperscript{3-4} magnetization remains constant at about 30 emu g\textsuperscript{-1} that is extensively less than the bulk\textsuperscript{5} values.

Magnetic nanoparticles (MNPs) have shown exceptional potential for several biological
and clinical applications. However, MNPs might be coated by the biocompatible shells for such applications. The aim of this study is to understand if and how the surfaces charges and coatings can affect the magnetic and electronic properties of Cobalt ferrite crystallizes. The role of the surfaces on the magnetic moments of a magnetic nano particle such as CoFe2O4 is an important issue, and various effects can contribute for making it deviate from the bulk value, including the charges, the nature of the coating, and also the synthetic technique. The electronic properties and ionic distribution of CoFe2O4 NPs were probed by X-ray absorption spectroscopies X-ray-magnetic-circular-dichroism and X-ray-photoemission-spectroscopy-techniques known as the abbreviation XAC, XMCD and XPS respectively. Magnetite-particles is also of interests in medicinal and industries application such as magnetic-resonance-imaging or (MRI), organic catalyst and nanomaterial synthesis.

The overall magnetic behavior and the hyper-thermic properties were evaluated by magnetometers and molecular modeling measurements, respectively. The results show that all of the investigated CoFe2O4 NPs have high magnetic anisotropy energies, and the surfaces charges and coating do not influence appreciably their electronic and magnetic properties. In addition, the citrate shell improves the stability of the NPs in aqueous environment, making CoFe2O4 NPs suitable for biomedical applications. Magnetic nanoparticle exhibits several unique properties such as super-para-magnetism compared to bulk material and particularly, are used in the field of biology and medicines. Magnetic nanoparticle has attracted a great deal of research interests due to their distinctive properties and special application recently.

CoFe2O4, is a well-known hard magnetic material with very high cubic magneto-crystalline anisotropy, high coercively, and moderate saturation magnetization. These properties make it a promising material for high-density magnetic recording.

CoFe2O4 nanoparticles have been widely synthesized using several ways, same as sol-gel, micro-emulsion, chemical coprecipitation, hydrothermal synthesis and microwave synthesis. Among those methods, the sol-gel routes are very attractive, within the main advantages including simple control for chemical composition. Recently, in the sol-gel synthesis of CoFe2O4 particles, the gels are built-up via physical and chemical binds between the chemical species. It has been introduced a different sol-gel polyacrylamide gel route for preparing CoFe2O4 nanoparticle. Due to lack of controls over the specific transformation of a nanoparticle, obviously super-paramagnetic particle has not been prepared from magnetite, i.e. Magnetite-nano-particle which generally loses their permanent magnetic properties in the lake of the external magnetic field.

The most applications require at least a magnetic-particle for dispersing in the non-magnetic matrixes. This matrix plays an important role for providing the meaning of particle dispersion for determining a physical property of a composite.

The other important items of these matrixes are to act as a protection for magnetic nano-particles against oxidation or corrosion especially in the metallic nano-particles. Among oxide matrixes such as alumina, silica, zeolites, titanic oxides, carbon-based, the silica can be a general suitable materials for the matrixes because of inertness of the magnetic fields, its non-toxicity and easiness for forming cross lined networks structure. Silica shells chemically is stable and can be rapidly functionalized in the bio-conjugation purposes, in other words is biocompatible. CoFe2O4 @SiO2 as a silica coated magnetite composite nanoparticles have been synthesized by several groups.

Recently, silica coated magnetite functionalized by γ mercaptopropyl-tri-methoxysilane has been successfully used for extracting Pb, Cd, Na+, K+, Mg2+, Hg2+ and Cu2+ in the wide pH ranges from water. The complex of metal- CoFe2O4 @SiO2–NH2 nanoparticles could be recovered easily from aqueous through magnetic separation and reproduce readily by acid treatment. By this work it has been exhibited the amino-functionalized CoFe2O4 @B,N magnetic nanoparticles compare to CoFe2O4 @SiO2 is much more effective as recyclable adsorbent for the removal of heavy and alkali/earth metal ions in water and wastewater treatments.
Catalysts has a very sensitive treatment in technology and modern sciences as they increase reaction yield via reducing the temperature in synthesis of the chemical product\textsuperscript{21,22}. There are two basic types of catalysis, (1) "heterogeneous\textsuperscript{22-23}, where the reaction accomplishes on the surfaces and the catalysts are in the solid phase. (2) "homogeneous\textsuperscript{23}, where the catalyst is in one phase as reactant\textsuperscript{24}.

The heterogeneous\textsuperscript{22} catalyst might be easily separated from the mixed solvent but because of their limited area of surfaces the reaction rate is restricted\textsuperscript{22}. Meanwhile homogeneous\textsuperscript{23} catalyst might react fast for providing a good rate (conversion rate) for the catalyst, but as they are solvable in the medium reaction, it might be a laboring processing for removing them of the reaction environment\textsuperscript{23}. The problem in removing homogenous\textsuperscript{23} catalytic materials from the reaction environment leads to problem of maintain the catalyst for repeating\textsuperscript{24}. The bridge between heterogeneous\textsuperscript{22} and homogeneous\textsuperscript{23} catalysts can be attained through the CoFe\textsubscript{2}O\textsubscript{4} nanoparticles\textsuperscript{25}. CoFe\textsubscript{2}O\textsubscript{4} exclusively is useful and important as the magnetic nano-particle which exhibit strong magnetic-moment and are seldom sustained outside of an external magnetic field\textsuperscript{25}. These kinds of nano-particle might be consist of several materials such as nickel, cobalt, iron oxides, ferrites\textsuperscript{26,27} and also alloys such as platinum/iron\textsuperscript{26}. CoFe\textsubscript{2}O\textsubscript{4} MNPs of silica shells catalytic materials have the benefit for increasing surface area which causes for any increased reaction rate\textsuperscript{28}. Moreover, nanoparticle might permit additional catalytic functionality because of their unique properties\textsuperscript{29}. Several catalysis of magnetic nano-structure has been investigated up to now\textsuperscript{30-32}, such as preparation of nano-composite materials consist of magnetic-(core) nano-particle which has been coated by various shells of other catalytically\textsuperscript{20} active nano-material\textsuperscript{23}.

Other type of catalysts that are interest for organic compounds involves the using of organic molecules which are enabling for preservation the materials in the end of any reactions for reusing\textsuperscript{31-32}. In this work we have investigated the catalysis’s properties of CoFe\textsubscript{2}O\textsubscript{4} nanoparticles @ B\textsubscript{n}N\textsubscript{m} instead of SiO\textsubscript{2} for comparing in the area of chemical synthesizes.

Recently extensive theoretical and experimental studies have been accomplished on boron-nitride-fullerenes for understanding their relative stabilities and also size dependence of important physical properties\textsuperscript{33-35}. (BN), are iso-electronic with carbon species, making them the goal of various research area and enhanced\textsuperscript{34} by this fact which B-N compounds have a stable crystalline phase near to graphite\textsuperscript{36-38}. Electronic properties of different BnN\textsubscript{m} rings and cages have been investigated theoretically\textsuperscript{39-45}. Despite those experimental and theoretical works, the structural synthesizes of B\textsubscript{n}N\textsubscript{m} rings and cages are still unknown.

Boron nitrides exist in several crystalline forms, such as hexagonal and cubic shapes. Due to the closely structures between C-C and B-N units, large efforts have been done recently to "BN” fullerenes, which has excellent properties like structural stability, heat resistance and insulation\textsuperscript{46-47}. As the thermodynamic mechanism of BN growth (from nuclei) is still not well known for those nanotubes, a comprehensive theoretical simulation continue to attract enhanced attention\textsuperscript{48}. Although those nanotubes are found to be non-chiral or chiral; however, most interests in the zigzag and armchair investigation are much less known about the chirality area of hexagonal boron nitride\textsuperscript{49}.

In our previous works\textsuperscript{50-69}, it has been exhibited the BN stabilities, NMR data, electronic properties, chemical phenomenon and the mechanism of tubes generating for the various structures of BN especially for the SWBNNT via multi-walled nanotube including chirality m, n (with n = 3-4 and m=5-7). The diagram generation for nano-ring of the B\textsubscript{n}N\textsubscript{m} (n = 15, 16, 18 and 20) are shown in the references of\textsuperscript{52-54}. In addition, we reported a unique stable structures\textsuperscript{52-54} with combinations of five and six loops same as a quasi B\textsubscript{n}N\textsubscript{m}H\textsubscript{6} shape for B\textsubscript{15}N\textsubscript{15} and B\textsubscript{18}N\textsubscript{18}, respectively. Those kinds of shapes have significant properties in the nano studies of CoFe\textsubscript{2}O\textsubscript{4} @ B\textsubscript{n}N\textsubscript{m} particles. The suitable stability and reasonable aromaticity of those structures have been confirmed by thermodynamic data, frequency optimization and NQR\textsuperscript{52-54}.

Hyperfine parameter and spin density, electrical potentials, electromagnetic properties and
isotropic-fermi-coupling-constant\textsuperscript{52-55} indicate the
stability of those rings through using non-bonded
interaction model between CoFe2o4 & B\textsubscript{18}N\textsubscript{18}. A novel
amino functionalized CCoFe2o4 & B\textsubscript{18}N\textsubscript{18} magnetic
nano-material with the core-shell structures has
been developed, for removing heavy metal ions
from the aqueous media. The elasticity of electron
density, electrical properties same as electron and
energy densities, kinetic and potential energies
densities, ELF or LOL, eta index and ECP for
CoFe2o4-B\textsubscript{18}N\textsubscript{18} core-shell systems have been
calculated and simulated in related reactions for
Amino-functionalized CoFe2o4 & B\textsubscript{18}N\textsubscript{18} magnetic.
The amino-functionalized CoFe2o4 & B\textsubscript{18}N\textsubscript{18} nano-adsorbent exhibited high adsorption affinities
for aqueous Fe (iii), Pb (ii), Ni (ii), Cu (ii) and Zn (ii)
ions, resulting from complexation by surface amino
groups.

**BACKGROUND & METHODOLOGY**

Magnetic particles are suitable for aqueous
transition and heavy metals due to their unique
advantages of quick separation and their high
surface area under external magnetic fields\textsuperscript{68-71}. The
surface modification, adsorption affinity, including
covalent binding and physical coating, has often
been explored\textsuperscript{70-75} for enabling specific complexation
for further facilitates\textsuperscript{72-76}.

Recently it have been exhibited which the amino-functionalized molecules demonstrated outstanding abilities for removing a wide variety of transition heavy metal ions\textsuperscript{77-79}. Both B\textsubscript{18}N\textsubscript{18} & SiO\textsubscript{2} are stable under acidic conditions, as compared with some other materials and functions for protecting the inner magnetite core\textsuperscript{80-82}.

Although CoFe2o4@SiO\textsubscript{2} has recently been
investigated for potential biomedical applications\textsuperscript{82},
there is no work about the CoFe2o4 @ B\textsubscript{18}N\textsubscript{18}.

In this study with the theoretical approaches
magnetic nano adsorbent has been developed via
covalently grafting amino groups over the surfaces of
CoFe2o4@ B\textsubscript{18}N\textsubscript{18} nanoparticles. Part of the systems
including CoFe2o4 @ B\textsubscript{18}N\textsubscript{18} nanoparticles has been
simulated with QM/MM methods and the investigation
carried out by the Monte Carlo calculations. In this
study, various force fields are done via “Amber” and
OPLS for comparing the calculated energy of the
CoFe2o4 @ B\textsubscript{18}N\textsubscript{18} nanoparticles. Furthermore, a
Hyper-Chem professional release-7.01program is
used for any further calculations.

For the non-covalent forces of B\textsubscript{18}N\textsubscript{18} and
CoFe2o4, the B3LYP & BLYP methods are unsuitable
for describing van der Waals\textsuperscript{83, 84} through medium-
range interaction\textsuperscript{84}. Therefore, the ONIOM\textsuperscript{*} methods
with three levels of tight (H), medium Hamiltonian (M),
and low (L) calculations have been accomplished in
these studies to estimate the non-bonded interaction
between B\textsubscript{18}N\textsubscript{18} and CoFe2o4.

The density functional method is used
for the high level while the semi-empirical (pm\textsubscript{s})
with pseudo=Lanl\textsubscript{2} and Pm\textsubscript{3}MM for both of them
respectively. Some accurate studies have indicated
that in-accuracy of the low range exchange energies
goes to the large systematic errors for the prediction
of molecular properties\textsuperscript{85-88}.

Geometries optimization and electronic
calculations have been accomplished using the
m06 functional of DFT. These approaches are based

<table>
<thead>
<tr>
<th>Atoms of CoFe2o4</th>
<th>Density of all electron(10\textsuperscript{-3}) (a)</th>
<th>Density of alpha ((10\textsuperscript{-3}) (b)</th>
<th>Density of Beta ((10\textsuperscript{-3}) (a)</th>
<th>Density of Beta ((10\textsuperscript{-3}) (b)</th>
<th>Spin Density (a) (c) (b)</th>
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</thead>
<tbody>
<tr>
<td>Co(1)</td>
<td>0.30 0.12</td>
<td>0.36 0.15 0.06</td>
<td>0.18</td>
<td>0.15 0.06</td>
<td>0.18 0.0 0.1 0.0</td>
</tr>
<tr>
<td>Fe(2)</td>
<td>0.28 0.10</td>
<td>0.34 0.14 0.05</td>
<td>0.17</td>
<td>0.14 0.05</td>
<td>0.17 0.0 0.1 0.0</td>
</tr>
<tr>
<td>Fe(3)</td>
<td>0.14 0.12</td>
<td>0.32 0.07 0.06</td>
<td>0.16</td>
<td>0.07 0.06</td>
<td>0.16 0.0 0.0 0.0</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.32 0.16</td>
<td>0.14 0.16 0.08</td>
<td>0.07</td>
<td>0.16 0.08</td>
<td>0.07 0.0 0.0 0.0</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.18 0.12</td>
<td>0.24 0.09 0.06</td>
<td>0.12</td>
<td>0.09 0.06</td>
<td>0.12 0.0 0.0 0.0</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.30 0.18</td>
<td>0.12 0.15 0.09</td>
<td>0.06</td>
<td>0.15 0.09</td>
<td>0.06 0.0 0.0 0.0</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.12 0.18</td>
<td>0.22 0.06 0.09</td>
<td>0.11</td>
<td>0.06 0.09</td>
<td>0.11 0.0 0.0 0.0</td>
</tr>
</tbody>
</table>
on solution of the Kohn & Sham equation in the plane-waves sets with projector-augmented-pseudo-potentials. The Perdew & Burke & Ernzerhof PBE exchange-correlation and generalized-gradient-approximation GGA are also used for non-bonding calculation.

The charge transferring and electrostatics potentials derived charges were also estimated using the Merz & Kollman & Singh, chelpG or chelp. The charges calculation methods based on MESP or molecular-electrostatics-potentials fitting are not well suited for the larger systems whereas several of the inner-most points are located far away from the centers at which the MESP are computed. In that position, variation of the inner-most atomic charges would not be towards the changing of the MESP outside of the molecules.

The charge-density profiles of this study have been estimated from the first principle calculation through an averaging process as described in the references. The interaction energies or adsorbents energies between metals and CoFe2O4 @ B18N18 catalyst were done according to the equation as follows:

$$\Delta E_s(eV) = \{E_c - [\sum_{i=1}^{n}(metal - CoFe_2O_4 - B18N18 - NH_2) + \sum_{j=1}^{m}(CoFe_2O_4) + \sum_{v=1}^{q}B18N18)] + \sum_{k=1}^{p}metal - ion\} + E_{BSSE} \ldots (1);$$

That is the adsorbents energies.

The electron-localization-function or ELF, localized-orbital-locator or LOL, electron density of the Gradient-norm & Laplacian, values of orbitals wave functions, electron spin densities, electrostatic-potentials from nuclear-atomic-charges,

Fig. 1: the non-bonded interaction between CoFe2O4 and B18N18 shell

Fig. 2: the non-bonded interaction between Fe3O4 and silica shell for binding to 3-aminopropyltrimethoxysilane (APTM)

Table 2: All Electron Energies of non-bonded interactions for CoFe2O4@Silica shell (a), CoFe2O4@B18N18 shell (b) and CoFe2O4 (isolate) (c)

<table>
<thead>
<tr>
<th>Atoms of CoFe2O4</th>
<th>Lagrangian kinetic [G(r)] energy(10^-3)</th>
<th>Hamiltonian kinetic [K(r)] energy(10^-3)</th>
<th>Potential energy Density <a href="10%5E-3">U(r)</a></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a) (b) (c)</td>
<td>(a) (b) (c)</td>
<td>(a) (b) (c)</td>
</tr>
<tr>
<td>Co(1)</td>
<td>0.32 0.14 0.30</td>
<td>0.60 0.58 0.54</td>
<td>-0.68 -0.52 -0.78</td>
</tr>
<tr>
<td>Fe(2)</td>
<td>0.33 0.12 0.31</td>
<td>0.62 0.66 0.62</td>
<td>-0.65 -0.64 -0.63</td>
</tr>
<tr>
<td>Fe(3)</td>
<td>0.23 0.16 0.30</td>
<td>0.38 0.72 0.68</td>
<td>-0.34 -0.37 -0.58</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.28 0.21 0.14</td>
<td>-0.32 -0.5 -0.43</td>
<td>-0.24 -0.59 -0.50</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.24 0.15 0.26</td>
<td>-0.14 -0.40 -0.46</td>
<td>-0.86 -0.68 -0.54</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.16 0.15 0.18</td>
<td>-0.44 -0.39 -0.44</td>
<td>-0.33 -0.63 -0.55</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.24 0.16 0.18</td>
<td>-0.14 -0.42 -0.42</td>
<td>-0.85 -0.63 -0.51</td>
</tr>
</tbody>
</table>
the exchange-correlation density, as well as total 
electrostatic potentials ESP), correlation-holes and correlation-factors, and the average local 
ionization energies using the Multi-functional-Wave-
function analyzer have also been calculated in this study.

### Density electron approach for interaction 
between MNPs and B$_{18}$N$_{18}$

The kinetic energies densities are not 
defined individually, since the expected values of the operators: $<\varphi | -\frac{1}{2}\sum_{i}\eta_i \partial^2 \varphi_i(r) + \nabla^2 \varphi_i(r) + \frac{1}{2} \frac{\eta_i}{\rho_{\alpha}} | \varphi_i(r) >$ (2) can be 
estimated by integrating kinetic energy densities 
from those alternatives definitions. One of the usual 
used definitions is as follows: $k(t) = -\frac{1}{2} \sum_{i} \eta_i \varphi_i(r) \Delta^2 \varphi_i(r)$ (3), the local kinetic energies given below 
guarantee hence the physical data are more 
commonly used. The Lagrangian of kinetic energies 
densities, $G(r)$, are also known as positive definite 
kine density.

$$G(r) = \frac{1}{2} \sum_{i} \eta_i |\nabla \varphi_i(r)|^2 = \frac{1}{2} \sum_{i} \eta_i \left[\left(\frac{1}{2} \frac{\partial \varphi_i(r)}{\partial x} \right)^2 + \left(\frac{1}{2} \frac{\partial \varphi_i(r)}{\partial y} \right)^2 + \left(\frac{1}{2} \frac{\partial \varphi_i(r)}{\partial z} \right)^2 \right]$$ (4)

K(r) and G(r) are directly related by Laplacian of electron density

$$\frac{1}{4} \nabla^2 \rho(r) = G(r) - K(r)$$

The electrostatic potential from 
nuclear/atomic charges can be calculated via:

$$V_{\text{nuc}}(r) = \sum_{A} \frac{Z_A}{|r - R_A|}$$

where $R_A$ and $Z_A$ denote position 
vector and nuclear charge of atom A, respectively.

Becke and Edgecombe have noted that 
spherically averaged like-spin conditional pair 
probability have  correlation with the Fermi hole and 
it has been suggested which the electron localization 
function (ELF) $\rho_{\alpha}(r) = \rho_{\beta}(r) = \frac{1}{2} \rho(r)$, $D(r)$ and $D_0(r)$ terms

$$D(r) = \frac{1}{2} \sum_{i} \eta_i |\nabla \varphi_i(r)|^2 - \frac{1}{8} \frac{\rho_\alpha^2(r)}{\rho_\beta(r)}$$ (5) 

for close-shell system, since $\rho_\alpha(r) = \rho_\beta(r) = \frac{1}{2} \rho(r)$, $D$ and $D_0$ terms

$$D(r) = \frac{1}{2} \sum_{i} \eta_i |\nabla \varphi_i(r)|^2 - \frac{1}{8} \frac{\rho_\alpha^2(r)}{\rho_\beta(r)}$$ (6) 

### Table 3: Laplacian, ELF, LOL and Local information entropy of non-bonded interactions for 
CoFe2o4@Silica shell (a),CoFe2o4@B$_{18}$N$_{18}$ shell (b) and CoFe2o4 (isolate) (c)

<table>
<thead>
<tr>
<th>Atoms of CoFe2o4</th>
<th>Laplacian of electron density(10$^{-1}$)</th>
<th>Electron localization function (ELF) (10$^{-1}$)</th>
<th>Localized orbital locator (LOL)</th>
<th>Local information entropy(10$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a) (c)</td>
<td>(a) (c)</td>
<td>(b) (a) (c)</td>
<td>(b) (a) (c)</td>
</tr>
<tr>
<td>Co(1)</td>
<td>-0.20 -0.26</td>
<td>0.41 0.46</td>
<td>0.14 0.22 0.13</td>
<td>0.14 0.15 0.25</td>
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<tr>
<td>Fe(2)</td>
<td>-0.25 -0.24</td>
<td>0.41 0.48</td>
<td>0.12 0.24 0.14</td>
<td>0.20 0.34 0.25</td>
</tr>
<tr>
<td>Fe(3)</td>
<td>-0.13 -0.27</td>
<td>0.13 0.25</td>
<td>0.63 0.12 0.17</td>
<td>0.4 0.16 0.18</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.79 -0.67</td>
<td>0.13 0.17</td>
<td>0.32 0.25 0.25</td>
<td>0.13 0.12 0.10</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.18 0.25</td>
<td>0.13 0.16</td>
<td>0.22 0.10 0.15</td>
<td>0.23 0.32 0.30</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.84 0.14</td>
<td>0.16 0.15</td>
<td>0.31 0.12 0.25</td>
<td>0.32 0.20 0.31</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.23 0.24</td>
<td>0.16 0.13</td>
<td>0.29 0.16 0.17</td>
<td>0.32 0.24 0.14</td>
</tr>
</tbody>
</table>
can be simplified as \( D(r) = \frac{1}{2} \sum_i \eta_i |\nabla \psi_i|^2 - \frac{1}{8} \left( \frac{|\nabla \rho|^2}{\rho(r)} \right) \), 
\( D_{0(r)} = \frac{3}{10} \left( \frac{3}{2} \right)^{2/3} \rho(r)^{5/3} \).

In which the kinetic energies terms in \( D(r) \) is replaced by Kirzhnits types second-order gradients expansion, which are 
\( \frac{1}{2} \sum \eta_i |\nabla \psi_i|^2 \approx D_{0(r)} + \frac{1}{72} \left( \frac{|\nabla \rho|^2}{\rho(r)} \right) + \frac{1}{6} \rho(r)^2 \). ... so that ELF is totally independent from the wave-function, and then can be used for analyzing electron densities from X-ray diffraction data.

Localized orbital locator or LOL \(^{38,99}\) is another item for locating high localization regions likewise ELF, which explained by Schmider & Becke \(^{99}\). LOL \( \tau(r) = \frac{\tau(r)}{1 + \tau(r)} \), where \( \tau(r) = D_{0(r)}^{1/2} \sum \eta_i |\nabla \psi_i|^2 \), ... for spin-polarized system and close-shell system are defined in the same way as in ELF \(^98\). LOL have similar approaches compared to ELF.

Notice that evaluating ESP is much more time-consuming than evaluating other functions. The ESP evaluated under default value is accurate enough in general cases. Reduced density gradient (RDG) RDG are a pair of very important functions for revealing weak interaction region \(^{96-98}\) for detail. RDG is defined as RDG \( \frac{1}{2}(3\pi^*)^{1/3} |\nabla \rho(r)| / \rho(r) \) \(^{96-98}\). Fortunately, it is found that weak interaction analysis under pro-molecular density is still reasonable. Pro-molecular density is simply constructed by superposing electron densities of free-state atoms and hence can be evaluated extremely rapidly. Where is pre-fitted spherically averaged electrons densities of atom A.

**RESULT AND DISCUSSION**

This work basically focuses on the magnetic properties of CoFe2O4 in the non-bonded systems with \( B_{18}N_{18} \) surfaces including “CoFe2o4@B_{18}N_{18}”. The CoFe2o4@B_{18}N_{18} nano-adsorbent shown high adsorption affinities for aqueous Na+, K+, Mg2+, and the amino- CoFe2o4@SiO\(_2\) exhibited high adsorbent for Fe (iii), Pb (ii), Ni (ii), Cu (ii) and Zn (ii) ions, resulting from complexation of the metals ion with the surface amino groups. The metal loaded CoFe2o4@B_{18}N_{18} nanoparticles could be recovered easily from aqueous solution by magnetic separation. The data have shown in ten figures and eight tables. As it is indicated in table 1, LOL is low and constant for Both CoFe2o4@silica, CoFe2o4@B_{18}N_{18} and CoFe2o4@B_{18}N_{18}. ELF has a similar expression as LOL.

The non-bonded interactions are shown in figs1-3. As it is indicated in tables 1-4, the electrical properties can be obtained from changes in the non-bonded interactions. Potential energy densities, ELF, LOL, electron densities, energy densities, eta index and ECP are shown in tables 1-4. The results of ELF and LOL indicate that the surfaces of silica and B18N18 are suitable to attach in aromatic and organic compounds in any scale from nano to micro or medium.

As it is shown in Figs.5-9, there are clear curves within a decreasing amount for electron

<table>
<thead>
<tr>
<th>Atoms of CoFe2o4</th>
<th>Reduced density gradient (RDG)(10^-1)</th>
<th>Average local ionization energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>Co(1)</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe(2)</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Fe(3)</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.4</td>
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</tbody>
</table>
density, energy density, ELF and LOL. The interaction energy between two sides of CoFe2O4-silica and CoFe2O4-B18N18 are also calculated. The potential energy difference between the two parts, are depicted in table 2.

It has been exhibited the BN compounds such as B_{18}N_{18} and amino-functionalized materials presented an ability for removing a wide range of earth/alkali. In contrast, the most usual used magnetic sorbents are based on iron oxide and unfortunately thus susceptible to leaching under acidic conditions. This problem will removed by replacing the B_{18}N_{18} instead of SiO_{2} as a shell of CoFe2O4. In addition, functional groups on the coating layer chemically adhering to the MNPs are also assailable to acid treatment. In contrast of SiO_{2} rings which is stable under acidic conditions the B_{18}N_{18} rings is independent from acidic situations and hence for B_{18}N_{18} comparing to SiO_{2}, the functions is not needed as an ideal shell composite to protect the inner magnetite core. Although CoFe2O4@SiO_{2} or Silica-coated core–shell magnetite nanoparticles have recently been investigated for potential biomedical applications, by this work we exhibit the B_{18}N_{18} is much useful for removing the earth/alkali metal from the aqueous solution.

Relative adsorption energies of four alkali and alkali/metal ions on CoFe2O4@B_{18}N_{18} have investigated. The adsorption data for Cu, Pb, Cd and so on were fitted to the Langmuir model according to the equation: \( q_e = \frac{q_m c_e}{1 + c_e b} \) where \( C_e \) (mmol/L) and \( q_e \) (mmol/g) are the aqueous concentration the adsorbed concentration at equilibrium adsorption, and, \( b \) and \( q_m \) are the coefficient of affinity and the adsorption capacity respectively.

**CONCLUSION**

We think that B_{18}N_{18} capabilities of magnetic substrates should be explored in the near future. Another interesting development is using the B_{18}N_{18} on magnetic-nanoparticle enables effective removal of alkali-earth/alkali metals based on catalysts froms important pharmaceutical products in the drug nanotechnology. Our Calculations indicate that the B_{18}N_{18} are suitable surfaces for CoFe2O4 such silica surfaces for removal metal ions such as Na+, Mg++,K+ and Ca++.

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