Study of CoFe$_2$O$_4$@ Calixarene Core-Shell as a Novel Catalyst

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Abstract

The properties of CoFe$_2$O$_4$@Calix [8] Core-Shell as a novel catalysthasbeen investigatedto compare with well-known catalyst"Fe$_3$O$_4$@Silica". It has been shown that CoFe$_2$O$_4$ magnetite particle can be use as important catalyst inside the calix ring.In our previous papersgood resultshave been yielded and exhibited about the B$_n$N$_n$ ring properties and CoFe$_2$O$_4$@B$_n$N$_n$. In present work it has been shown there is anon-covalent attractionbetween CoFe$_2$O$_4$and calix [8] coated molecules. The Physical-chemistry properties such asenergy densities,potential energy densities,electron densities, ELF, LOL,eta index, elasticity ofelectron density and ECPforCoFe$_2$O$_4$@calix[8] shell have been calculated and simulated in related reactions for those groups-functionalized.

Keywords: CoFe$_2$O$_4$; Nano-particles; Electron density; calix [8]; Silica; SiO$_2$

Introduction

CoFe$_2$O$_4$ as the Cobalt ferrite crystallizes in a partially inverse spinel position represented as (Co$_2$x^{++}Fe^{3+}1-x)(Co^{2+}1-xFe^{3+}1+x)O$_4$ where x based on thermal condition. It is ferri-magnetic and exhibits a relatively magnetic hysteresis which distinguishes it from the other of the spinel ferrites. Magnetic measurements on nano-particles of cobalt ferrite dispersed in various solvents of organic compounds and nano-crystalline powders prepared by hydroxideprecipitationhave been investigated earlier. In magnetic fluids, it has been seen that for particlesabove threenano-meters the saturationmagnetization remains constant at about 30emug^{-1} that is extensively less than the bulk values [1-5].

Magnetic Nan-Oparticles(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 CoFe$_2$O$_4$ is animportant issue, and various effects can contribute for making it deviate from the bulk value, including the charges, the nature of the coating, also the synthetic technique. The electronic properties and ionic distribution of CoFe$_2$O$_4$ NPs were probed by X-ray absorption spectro scopies X-ray-magnetic-circular-di-chroism and X-ray-photoemission-spectroscopy-techniques known as the abbreviation XAC, XMCD and XPS respectively. Magnetite-particlesarealso of interests in medicinal andindustries application such as Magnetic-Resonance-Imaging (MRI) ororganic catalyst and nano-material synthesize [4-8].

The overall magnetic behavior and the hyper-thermic properties were evaluated by magnetometers and molecular modelling measurements, respectively. The results show that all of the investigated CoFe$_2$O$_4$ NPs have high magnetic anisotropyenergy, 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 CoFe$_2$O$_4$ NPs suitable for biomedical applications.Magnetic nano-particle exhibitsseveral unique propertiessuch as super-para-magnetism compared to bulkmaterial andparticularly, are used in the field of biologyand medicines.Magnetic nano-particle has attracted a great deal of researchinterests due to their distinctive properties and special application recently [5-9]. CoFe$_2$O$_4$, 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.The most applications require at least a magnetic-particle for dispersing in the non-magnetic matrixes. Thismatrix plays an important role for providing the meaning of particle dispersion for determining a physical property of a composite.

Recently, in thesol-gelsynthesis of $CoFe_2O_4$ particles, the gelsare built-up viaphysical and chemical binds between the chemical species.It has been introduced a different sol-gelroutes@ polyacrylamide gel route for preparing $CoFe_2O_4$ nano-particle.Due to lack of controls over the specific transformation of anano-particle, obviously super-paramagnetic particle has not been prepared from magnetite, i.e. Magnetite-nano-particle whichgenerallyloses their permanent magnetic properties in the lake of the external magnetic field [6-10]. The complex of metal-$CoFe_2O_4$@SiO_2-NH_2 nano-particlescould be recovered easily from aqueous through magneticseparation and reproducereadily by acid treatment. By this work it has been exhibited the amino-functionalized $CoFe_2O_4$@ calix[8] magnetic nano-particles compare to $CoFe_2O_4$@$SiO_2$is much more effective as recyclable adsorbent for the removal of heavy and alkali/earth metal ions in water and wastewater treatments. Silica shells chemically is stable and can be rapidly functionalized in the bio-conjugation purposes, in other words is biocompatible therefore $CoFe_2O_4$@SiO_2 as a silicacoated magnetite composite nano-particles have been synthesized by several groups. Catalysts have a very sensitivetreatment in technology and modern sciences as they increase reaction yield via reducingthe temperature in synthesisof the chemical product.There are two basic types of catalysis, heterogeneous, where the reaction accomplishes on the surfaces and the catalystsare in the solid phase.Homogeneous, where the catalyst is in one phase as reactant.The other important items of these matrixes are to act as a protection for magnetic nano-particlesagainst oxidation or corrosion especiallyin the metallicnano-particles. Among oxide matrixes such as alumina, silica, zeolites, titanic oxides, carbon-based, the silica can be a general suitable material for the matrixes because of inertness ofthe magnetic fields, its non-toxicity and easiness for forming crosslined networks structure [10-17]. The bridge between heterogeneous and homogeneous catalysts can be attained through the $CoFe_2O_4$ nanoparticle [17-25]. $CoFe_2O_4$exclusivelyis useful and important as the magnetic nano-particle which exhibit strong magnetic-moment and are seldom sustained outside of an external magnetic field. These kinds of nano-particle might be consistsofseveral materials such as nickel, cobalt, iron oxides, and ferritesand also alloys such as platinum/iron. $CoFe_2O_4$ MNPs of silica shells catalytic materials have the benefit for increasing surface area which causes for any increased reaction rate. Moreover, nano-particle might permit additional catalytic functionalitybecause of their unique properties. Several catalysis of magnetic nano-structurehas beeninvestigatedup to now,such as preparation of nano-composite materials consist of magnetic-(core) nano-particle which has been coated by various shells of other catalytically active nano-material [20-30].

Other type of catalyststhatare interest for organic compounds involves the using of organic molecules which are enabling forpreservationthe materialsin the end of any reactions for reusing [25-35]. In this work we have investigated the catalysis's properties of $CoFe_2O_4$ nano-particles @calix [8] instead of SiO_2 for comparing in chemical syntheses [36-47]. Recently extensive theoretical and experimental studies have been accomplished on boron-nitride-fullerenes for understanding their relative stabilities also

size dependence of important physical properties. In our previous works [48-61], it has been exhibited thesystemstabilities, NMR data, electronic properties, and chemical phenomenon.

Background & Methodology

Magnetic particles are suitable for aqueous transition and heavy metals due to their unique advantages of quick separation and their high surface areaunder external magnetic fields [62-65]. The surface modification, adsorption affinity, including covalentbinding and physical coating, has often been exploredforenabling specific complexationfor further facilitates [66-70]. Recently it have been exhibited which the amino-functionalized molecules demonstrated outstanding abilities for removing a wide variety of transition heavy metalions [71-76]. Although $CoFe_2O_4$@SiO_2has recently been investigated for potential biomedical applications [77-81], there is no work about the $CoFe_2O_4$@calix [8].

In this studywith the theoretical approaches magnetic an adsorbent has been developed via covalently grafting amino groupsover the surfaces of $CoFe_2O_4$@calix[8] nano-particles. Part of the systems including $CoFe_2O_4$@calix [8] nano-particles has been simulated with QM/MM methods and the investigation carried out by the Monte Carlo calculations.In this study, various force fields are donevia"Amber" and OPLSfor comparing the calculated energy of the $CoFe_2O_4$@ calix [8] nano-particles. Furthermore, a Hyper-Chem professional release-7.01program is used for any further calculations.Thedensity functional method is used for the high levelwhile the semi-empirical (pm_6) with pseudo=$Lanl_2$ and Pm_3MM for both of them respectively.Some accurate studies have indicated that in-accuracy of the low range exchange energies goes tothe large systematic errors for the prediction of molecular properties.

Geometries optimization and electronic calculations have been accomplished using the m06 functional of DFT. These approachessare based on solution of the Kohn & Sham [82] in the plane-waves sets with projector-augmented-pseudo-potentials. The Perdew & Burke [83] exchange-correlation and generalized-gradient-approximation GGA are also used for non-bonding calculation.

The charge transferring and electrostatics potentialsderived charges were also estimated using the Merz & Kollman [84]; [85,86]. The charges calculation methods based on MESP or molecular-electrostatics-potentials fitting are not wellsuited 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 [87,88]. The interaction energies or adsorbents energies between metals and $CoFe_2O_4$@calix[8]catalyst were done according to the equation as follows:

$$\Delta E_S \, (eV) = \left\{ E_C - \left(\sum_{i=1}^{n}(metal - CoFe_2O_4 - Calix[8])_i + \sum_{j=1}^{m}(CoFe_2O_4)_j + \sum_{v=1}^{q} calix[8]_v \right) + \sum_{k=1}^{p} metal - ion)_k \right\} + E_{BSSE} \quad (1)$$

That ΔE_S is the adsorbents energies. The electron-localization-function or ELF, localized-orbital-locator or LOL [89-91], electron

density of the Gradient-norm & Laplacian, values of orbitals wave-functions, electron spin densities, electrostatic-potentials from nuclear-atomic-charges,the exchange-correlation density, as well astotal 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 [89-91].

Density Electron Approach for Interaction between Mnps and Calix [8]

The kinetic energies densitiesare not defined individually, since the expected values of theoperators:

$$< \varphi \left| -\left(\frac{1}{2}\right)\nabla^2 \right| \varphi > \qquad (2)$$

Can be estimated by integrating kinetic energy densities from those alternatives definitions. One of the usual used definitionsis as follows:

$$k(r) = -\frac{1}{2}\sum_i \eta_i \varphi_i^*(r)\nabla^2 \varphi_i(r) \qquad (3),$$

Thelocal kinetic energies given below guarantee [89-91] hence the physical dataare more commonly used. The Lagrangian of kinetic energies densities, G(r)[97]are also known as positive definite kinetic energy densities.

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

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: $V_{nuc}(r) = \sum_A \frac{Z_A}{|r-R_A|}$ where $R_A$and Z_A denote position vector and nuclear charge of atom A, respectively, spherically averaged like-spin conditional pair probability havecorrelation with the Fermi hole and it has been suggested which the electron localization function (ELF).

$$ELF(r) = \frac{1}{1+[D(r)/D_{0(r)}]^2} \qquad (5)$$

Where
$$D(r) = \frac{1}{2}\sum_i \eta_i |\nabla\varphi_i|^2 - \frac{1}{8}[\frac{|\nabla\rho_\alpha|^2}{\rho_\alpha(r)} + \frac{|\nabla\rho_\beta|^2}{\beta(r)}]$$

and
$$D_{0(r)} = \frac{3}{10}(6\pi^2)^{\frac{2}{3}}[\rho_\alpha(r)^{\frac{5}{3}} + \rho_\beta(r)^{\frac{5}{3}}] \qquad (6)$$

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

*D*and D_0 terms can be simplified as

$$D(r) = \frac{1}{2}\sum_i \eta_i |\nabla\varphi_i|^2 - \frac{1}{8}[\frac{|\nabla\rho|^2}{\rho(r)}], \quad D_{o(r)} = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}\rho(r)^{\frac{5}{3}}$$

In which the kinetic energies terms in $D(\mathbf{r})$ is replaced by Kirzhnits types second-order gradients expansion, which are

$$\frac{1}{2}\sum_i \eta_i |\nabla\varphi_i|^2 \approx D_{0(r)} + \frac{1}{72}\frac{|\nabla\rho|^2}{\rho(r) + \frac{1}{6}\nabla^2\rho(r)} \qquad (7)$$

So that ELF is totally independent from the wave-function, and then can be used foranalyzing electron densities from X-ray diffraction data.Localized orbital locator orLOLis another item for locating high localization regions likewise ELF, which explained by Lu T [91].

$$LOL(r) = \frac{\tau(r)}{1+\tau(r)},$$

Where

$$(r) = \frac{D_{0(r)}}{\frac{1}{2}\sum_i \eta_i |\nabla\varphi_i|^2} \qquad (8)$$

for spin-polarized system and close-shell system are defined in the same way as in ELF. 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 regionfor detail. RDG is defined as

$$RDG(r) = \frac{1}{2(3\pi^2)^{\frac{1}{3}}}\frac{|\nabla\rho(r)|}{\rho(r)^{\frac{4}{3}}} \qquad (9).$$

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. $\rho^{pro}(r) = \sum_A \rho_A^{free,fit}(r-R_A)$. Where $\rho_A^{free,fit}$ is a pre-fitted spherically averaged electrons density of atom *A*.

Result and Discussion

Table 1: (a) All Electron Densities of non-bonded interactions for CoFe$_2$O$_4$@Silica shell, (b) CoFe$_2$O$_4$@calix[8] shell and(c) CoFe$_2$O$_4$ (isolate).

Atoms of CoFe$_2$O$_4$	Density of All Electron (10^{-3})			Density of Alpha(10^{-3})			Density of Beta (10^{-3})			Spin Density		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
Co(1)	0.28	0.32	0.12	0.14	0.16	0.06	0.14	0.16	0.06	0.0	0.0	0.1
Fe(2)	0.28	0.3	0.1	0.14	0.15	0.05	0.14	0.15	0.05	0.0	0.0	0.1
Fe(3)	0.16	0.28	0.12	0.08	0.14	0.06	0.08	0.14	0.06	0.0	0.0	0.1
O(1)	0.3	0.24	0.14	0.15	0.12	0.07	0.15	0.12	0.07	0.0	0.0	0.0

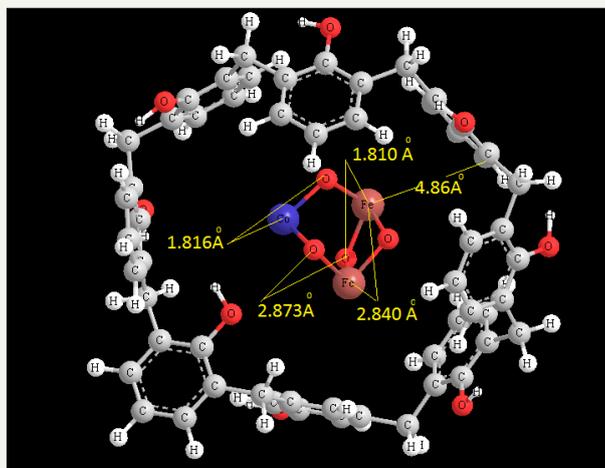| O(2) | 0.18 | 0.32 | 0.12 | 0.09 | 0.16 | 0.06 | 0.09 | 0.16 | 0.06 | 0.0 | 0.0 | 0.0 |
| O(3) | 0.3 | 0.22 | 0.16 | 0.15 | 0.11 | 0.08 | 0.15 | 0.11 | 0.08 | 0.0 | 0.0 | 0.0 |
| O(4) | 0.14 | 0.2 | 0.18 | 0.07 | 0.1 | 0.09 | 0.07 | 0.1 | 0.09 | 0.0 | 0.0 | 0.0 |

Figure 1: The non-bonded interaction between $CoFe_2O_4$ and Calix [8] shell.
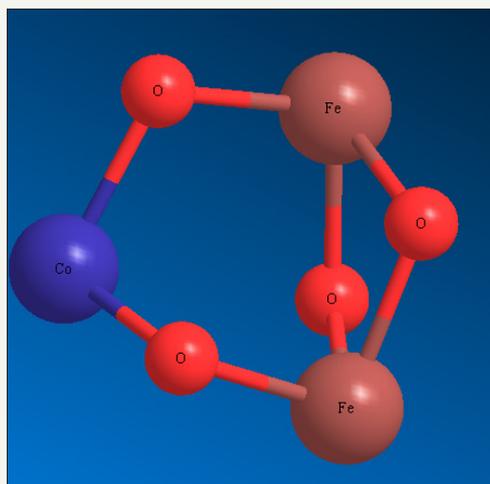
Figure 2: The optimized of $CoFe_2O_4$.
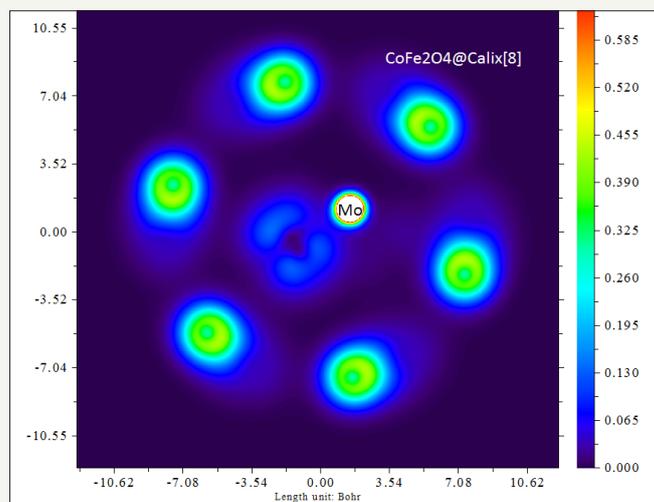

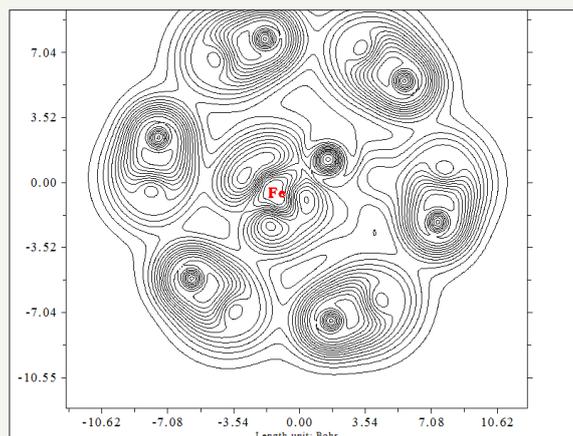**Figure 3**: Color field map of electro density including molybdenum & $CoFe_2O_4$ inside of Calix [8].

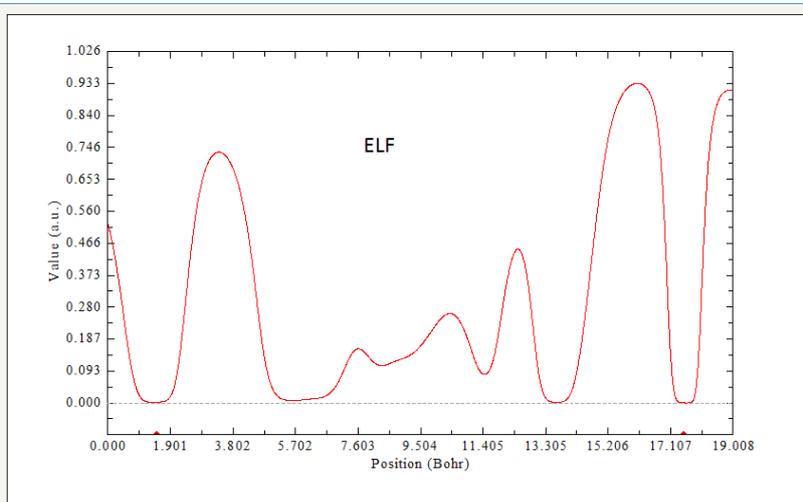**Figure 4**: Contour line map ofCoFe$_2$O$_4$-Calix [8]for LOL.

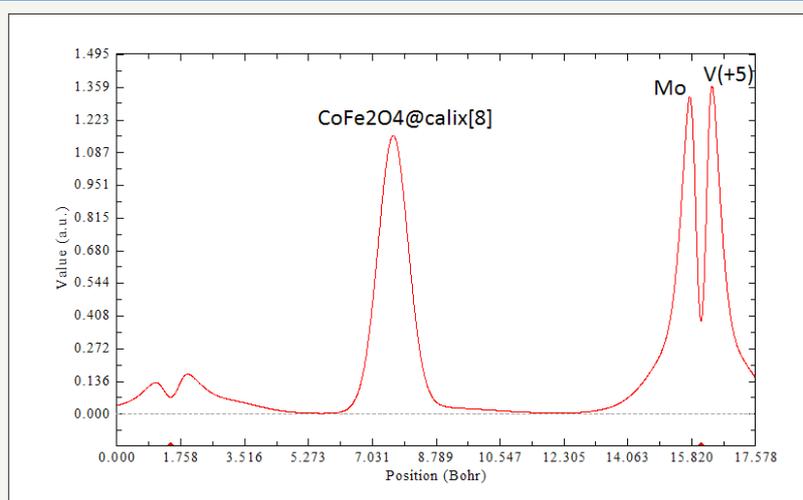**Figure 5**: ELF versus Position for CoFe$_2$O$_4$@calix[8] & Mo.

Figure 6: Pick Position for CoFe$_2$O$_4$@calix[8] Mo & V (+5).

Thisworkbasically focuses on the magnetic properties of CoFe$_2$O$_4$ in the non-bonded systems with calix[8] surfaces including "CoFe$_2$O$_4$@calix [8]". The CoFe2O4@calix[8]nano-adsorbent shown high adsorption affinities for aqueousion metalsspecially for cation of vanadium and molybdenum and the amino-CoFe$_2$O$_4$@SiO$_2$exhibited high adsorbent forvanadium and molybdenum ions, resulting from complexation of the metals ion with the surface amino groups.The metalloaded CoFe$_2$O$_4$@calix[8] nano-particles could

be recovered easily from aqueous solution bymagneticseparation. The data have shown in Figure 1-7 and Table 1. As it is indicated in Table 1, LOL is low and constant for Both $CoFe_2O_4$@silica, $CoFe_2O_4$@ calix[8] and $CoFe_2O_4$@calix [8]. ELF has a similar expression as LOL. The non-bonded interactions areshown in Figure 1-7.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 Table 1. The results of ELF and LOL indicate that the surfaces of silica and calix [8] are suitable to attach in aromatic and organic compounds in any scale from nano to micro or medium.
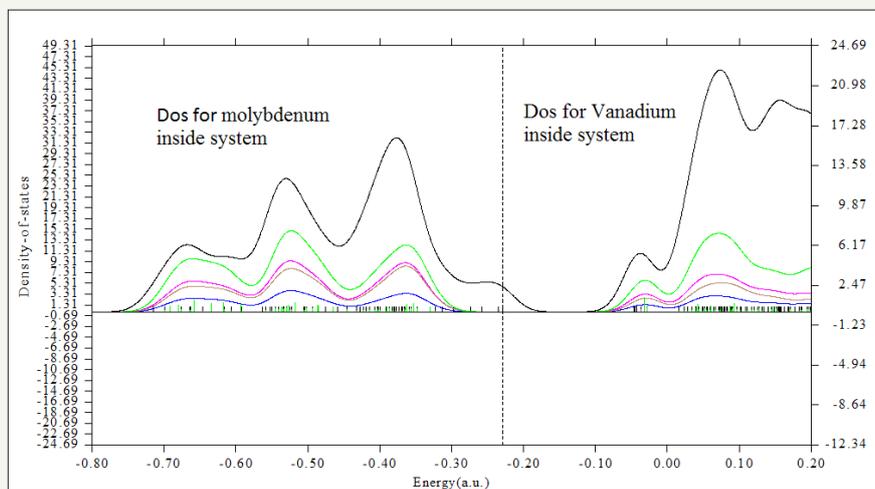

Figure 7: Density of state for energy absorption of Molybdenum and Vanadium in $CoFe_2$@Calix[8].

The interaction energy between two sides of $CoFe_2O_4$-silica and $CoFe_2O_4$-calix [8] are also calculated Table 1. This problem will removed by replacing the calix[8] instead of SiO_2 as a shell of $CoFe_2O_4$. 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 calix [8]rings is independent from acidic situations and hence for calix[8] comparing to SiO_2, the functions is not needed as an ideal shell composite to protect the inner magnetite core. Although $CoFe_2O_4$@SiO_2 or Silica-coated core–shell magnetite nanoparticles have recently been investigated for potentialbiomedical applications, by this work we exhibit the calix [8] is much useful for removing the earth/alkali metal from the aqueous solution Table 1. Relative adsorption energies of fourtransition metalons such as vanadium and molybdenum on $CoFe_2O_4$@calix[8]have investigated.

Conclusion

We think that calix[8] capabilities of magnetic substrates should be explored in the near future.Another interesting development is using the calix[8] on magnetic-nano-particle enables effective removal of transition metals such as vanadium and molybdenum metals based on catalysts forms important pharmaceutical products in the drug nanotechnology. Our Calculations indicate that the calix[8]is suitable surfaces for $CoFe_2O_4$such silica surfaces for removal metal ions such as vanadium cations and molybdenum.

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