

A Relative Study of Iron Versus Cobalt Nanostructures Concerning Their Efficacy in Chemical Reaction Promotion

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Abstract

The structural and electronic properties of nickel (Ni_n), iron (Fe_n), and cobalt (Co_n) clusters ($n = 2-10$) were investigated using density functional theory (DFT) within the generalized gradient approximation (GGA) as implemented in the SIESTA code. A search for low-energy configurations yielded novel stable structures. Key properties, including average bond length, binding energy, and Vertical Ionization Potential (VIP), were computed. The most stable geometries for $n > 6$ were found to be linear or planar. Maximum binding energy was observed for the Fe_{10} and Co_{10} clusters. VIP trends showed clear odd-even oscillations, indicating enhanced stability for the even-numbered Fe clusters (2, 6, 8, 10) and the odd-numbered Co clusters (3, 7, 9). This work provides a DFT-based analysis of the structural and catalytic characteristics of these systems.

Key Words: Density functional theory (DFT), Fe_n and Co_n clusters, Stability structure, vertical ionization potential (VIP), chemical catalysis.

1. Introduction

The physics and chemistry of nanoclusters have constituted a highly dynamic field of research over the past two decades. The hybrid character of these systems, which bridge the gap between molecular and bulk material properties, has driven significant theoretical interest in understanding the evolution from single atoms to clusters, molecules, and ultimately the solid state. In recent years, scientific inquiry has particularly focused on elucidating the structural, electronic, optical, and catalytic properties of metallic nanoclusters, which are of considerable importance due to their tunable nature for specific applications.

Mono- and bimetallic clusters at the nanoscale have attracted extensive attention owing to their unique and promising applications in areas such as optics, magnetism, and catalysis [1, 2]. This interest stems from their size-

dependent physical and chemical properties, which emerge from dominant surface effects. Among these, iron (Fe_n) and cobalt (Co_n) nanoclusters have been identified as particularly attractive catalytic materials [3-5]. The properties of bimetallic clusters are not solely determined by their size and morphology, but are also critically influenced by their atomic composition and arrangement [6]. Consequently, the novel structural and electronic configurations enabled by nanoscale dimensions are a subject of intense study [7], with some findings indicating that surface modifications can induce significant alterations in cluster characteristics [8].

The utility of iron and cobalt particles extends widely into organic chemistry and biomedicine. They serve critical functions in protein delivery [9] and have emerged as important agents in cancer therapeutics [10-12]. For instance, cobalt(II) chloride has been shown to enhance the *in vitro* expression of Hypoxia Inducible Factor-1 α in gingival-derived mesenchymal stem cells [13]. Iron nanoparticles are also employed in the catalytic oxidation processes, in studying the electrochemical behaviors of stable compounds, and in various other applications [14]. Furthermore, novel iron nanoparticles synthesized from *Beta vulgaris* extract have demonstrated efficacy as antimicrobials against Enterobacteriaceae, as anti-inflammatories, and as insecticides [15].

2. Detail of Calculations:

All calculations were performed within the framework of spin-polarized Density Functional Theory (DFT) [16]. For the exchange-correlation functional, the generalized gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerh of (PBE) was employed [17]. The initial optimization of the cluster geometries was conducted using a first-principles DFT methodology as implemented in the SIESTA code, which utilizes a basis set of numerical atomic orbitals [18]. These structures were further validated using the "clusters" module in the MATERIALS STUDIO software suite.

The calculations made use of a plane-wave basis set with a kinetic energy cutoff of 300 eV, applied uniformly across all systems studied. Integrations over the Brillouin zone were performed using Monkhorst-Pack k-point meshes. A self-consistent field (SCF) convergence threshold of 10^{-5} eV for the total energy was adopted. Geometry optimization was considered complete when the maximum force on any atom was below 0.005 eV/\AA , with a maximum ionic displacement tolerance of 0.05 \AA .

To ensure the identification of the global minimum energy structure, the geometric optimizations were initiated from a diverse set of initial candidate geometries, ranging from open, linear arrangements to close-packed configurations for the Fe and Co atoms. The final optimized electronic structure for each cluster was derived from the Z-matrices generated in the Q-Chem program output.

3. Results and Discussion:

1. Structural properties of clusters Fe_n and Co_n ($n=2-10$):

1.1 Structural characteristics:

The electronic structures of iron (Fe) and cobalt (Co) metal clusters have been reached, starting from the cluster consisting of two atoms to the cluster consisting of 10 atoms, using the simulated annealing application. Figure 1 show the most stable structures of the studied iron clusters, while Figure 2 show the most stable structures of the studied cobalt clusters

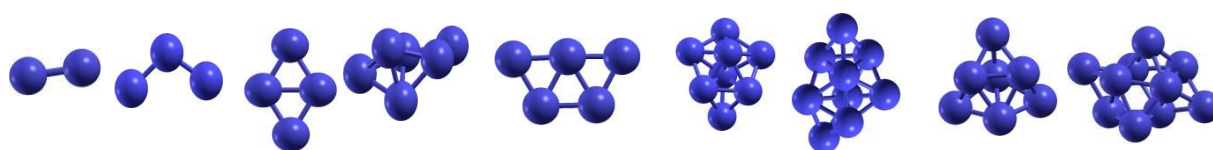


Figure 1. The most stable structures of Fe_n ($n=2-10$) clusters.

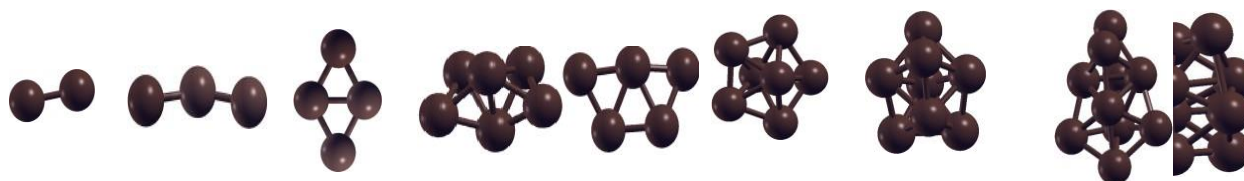


Figure 2. The most stable structures of Co_n ($n=2-10$) clusters.

Analysis of the optimized structures, as depicted in the two figures, reveals that the lowest-energy configurations for the diatomic and triatomic clusters are linear chains. The calculated average bond lengths for these clusters are 2.67 Å (Fe₂), 2.48 Å (Fe₃), 2.55 Å (Co₂), and 2.30 Å (Co₃). In contrast, the most stable geometries for the tetrameric and pentameric clusters (Fe₄, Fe₅, Co₄, Co₅) adopt a trapezoidal shape. The average bond lengths for the tetraatomic clusters are 2.57 Å for Fe₄ and 2.42 Å for Co₄.

The average bond length for each cluster was computed by summing all interatomic bond distances and dividing by the total number of bonds. These values were extracted from the optimized geometries using the XCRYSDEN program and are tabulated in Table 1.

Table 1. The average bond length for of iron (Fe_n) and cobalt (Co_n) clusters.

10	9	8	7	6	5	4	3	2	cluster	Average bond (Å) length
2.68	2.689	2.70	2.696	2.63	2.64	2.57	2.48	2.67	Fe	
2.57	2.58	2.53	2.49	2.55	2.45	2.42	2.30	2.55	Co	

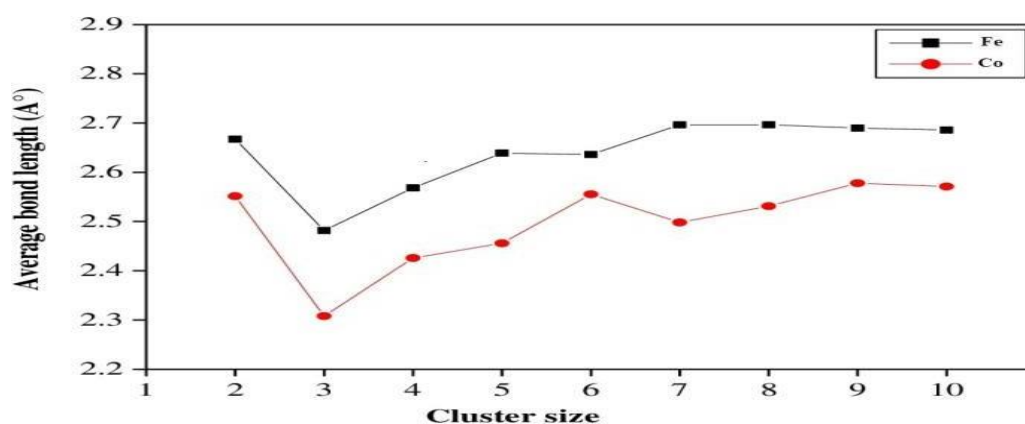


Figure 3. The average bond length of the Fe_n and Co_n (n=2-10) clusters

The data from Table 1 are presented graphically in Figure 3, which plots the average bond length of iron (Fe_n) and cobalt (Co_n) clusters as a function of cluster size (n = 2–10). The figure reveals a general trend of increasing average bond length with cluster size. The maximum values were recorded for Fe₈ (2.70 Å) and Fe₇ (2.696 Å) in the iron series, and for Co₆ (2.58 Å) and Co₁₀ (2.57 Å) in the cobalt series. Deviations from this overall trend were observed, marked by a decrease in bond length for the Fe₃, Fe₄, Co₃, and Co₄ clusters.

Analysis of Figure 3 indicates a correlation between bond length and stability, where a longer average bond length within a cluster appears to correspond to greater stability. Consequently, the data suggest that the iron (Fe_n) clusters are generally more stable than their cobalt (Co_n) counterparts.

1.2. binding energy:

The stability of the iron (Fe_n) and cobalt (Co_n) clusters was evaluated by calculating their binding energy. A strong correlation was observed between a cluster's geometry and its binding energy, reflecting the system's drive toward optimal stability. The results indicate that larger clusters generally exhibit greater stability. Furthermore, iron clusters are found to be more stable than their cobalt counterparts, as evidenced by their systematically higher binding energy values.

The binding energy per atom for a cluster of size *n*, $E_b(n)$, was determined from the total energy of the cluster and the energy of an isolated atom, using the following relationship:

$$E_{bin}(kn) = E_{tot}(kn) - nE_{at}(kn)/n \quad (1)$$

where it represents:

E_{at} is the energy of one atom in the free state, E_{tot} is the total energy of the cluster, n is the number of atoms in the cluster, kn is cluster code.

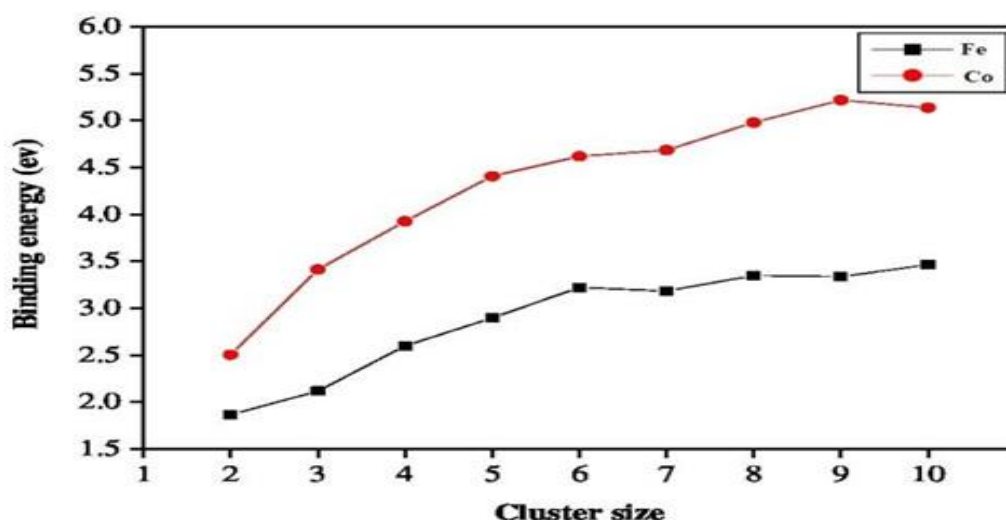


Figure 4: Binding energy of Fe_n and Co_n clusters as a function of cluster size

The binding energy values for the iron and cobalt clusters are presented in Figure 4.

The data reveal a general trend of increasing binding energy with cluster size for both metals. For instance, the binding energy rises from 1.86 eV for the Fe_2 dimer to 3.46 eV for the Fe_{10} cluster. A corresponding increase is observed for cobalt, where the binding energy escalates from 2.50 eV for Co_2 to 5.13 eV for Co_{10} .

vertical ionization potential (PIV):

The vertical ionization potential was calculated using the following relationship, based on the total energy difference between the optimized neutral cluster and the cation at the neutral geometry:

$$PIV = E(kn^*) - E(kn) \quad (2)$$

Where it represents:

$E(kn^*)$ is cation energy, $E(kn)$ is element energy.

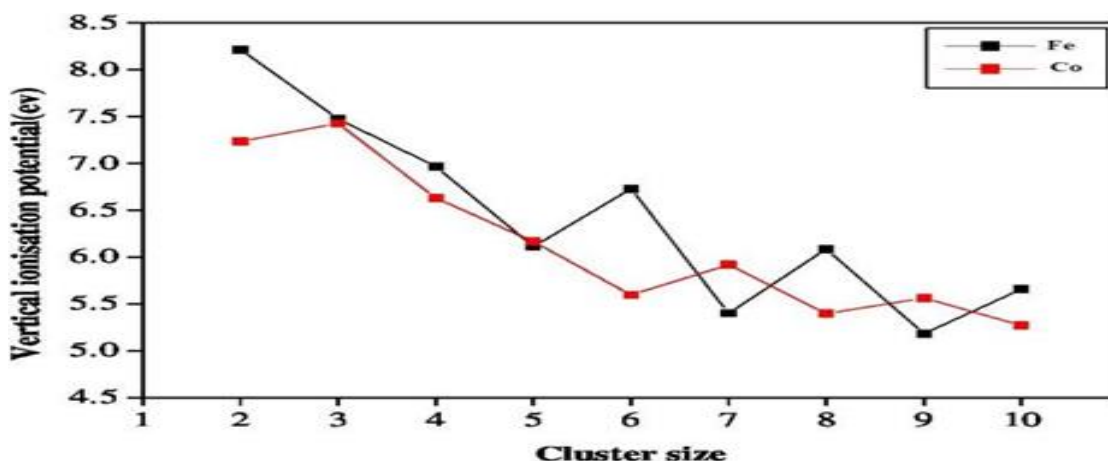


Figure 5: The vertical ionization potential of Fe_n and Co_n clusters as a function of cluster size

Figure 5 illustrates the vertical ionization potential (VIP) for iron (Fe_n) and cobalt (Co_n) clusters as a function of cluster size. A general decreasing trend in VIP is observed with increasing cluster size for both metals. The highest VIP values were recorded for the dimers, with Fe_2 at 8.21 eV and Co_2 at 7.23 eV. In contrast, the values for the decamers were significantly lower, at 5.65 eV for Fe_{10} and 5.26 eV for Co_{10} .

Notably, several clusters exhibited similar VIP values: Fe_3 and Co_3 (7.47 eV and 7.42 eV, respectively), and Fe_5 and Co_5 (6.11 eV and 6.16 eV, respectively). Furthermore, the VIPs for Co_7 (5.91 eV) and Co_9 (5.56 eV) were higher than those of their iron counterparts, Fe_7 (5.40 eV) and Fe_9 (5.18 eV).

The VIP is a key indicator of cluster stability, where a higher value corresponds to greater electronic stability. A comparative analysis reveals that iron clusters generally possess higher VIPs than cobalt clusters of the same nuclearity, suggesting that iron clusters are more stable. Consequently, cobalt clusters, with their lower ionization potentials, are predicted to be more chemically active and potentially more suitable as catalysts.

4. Conclusion:

This work presents a theoretical investigation of iron (Fe_n) and cobalt (Co_n) metal clusters to determine their structural and catalytic properties. The calculations were performed using the SIESTA program, which implements density functional theory (DFT) within the generalized gradient approximation (GGA).

The principal findings are summarized as follows:

- The electronic structure of both iron and cobalt clusters exhibits a significant dependence on cluster size.
- A positive correlation exists between cluster size and the average bond length. The systematically longer bond lengths observed in iron clusters suggest they possess greater stability compared to their cobalt counterparts.
- The binding energy demonstrates a positive correlation with cluster size. Given that higher binding energy corresponds to enhanced stability, this trend further confirms that iron clusters are more stable than cobalt clusters.
- An inverse relationship is observed between cluster size and the vertical ionization potential (VIP) for both metals; the VIP decreases as the cluster size increases. This trend confirms the superior stability of iron clusters over cobalt clusters, as indicated by their consistently higher VIP values. Consequently, the lower VIP of cobalt clusters implies higher chemical reactivity, rendering them more suitable for catalytic applications.

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