

DFT study of the chlorine promotion effect on the ethylene adsorption over iron clusters



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ABSTRACT

This work explores how electronic perturbations induced by chlorine atoms can enhance the activity of iron toward ethylene. The metal clusters include Fe_n ($n=2-4$), in which each adatom (Cl) has an inclination to be adsorbed at the bridge site with electrostatic interaction. Ethylene adsorption over pure and chlorine-doped Fe_nCl_m ($n, m \leq 4$) clusters is analyzed using density functional theory (DFT) calculations, in π and di- σ adsorption modes. One of the interesting features is that the adsorption mode of ethylene changes by going from trimers to tetramers. Ethylene never orients toward di- σ mode for Fe–Fe bond in Fe_2 and Fe_3 series, while this orientation is preferred in tetramers. Our results demonstrate that the progressive change in the ethylene adsorption could not be sustained with increasing portion of chlorine in metal cluster. In this study, we attempt to provide a sensible justification for this phenomenon by the natural bond orbital (NBO) and quantum theory of atoms-in-molecules (QTAIM) analyses.

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1. Introduction

There have been increasing interests towards a molecular scale comprehension of binary alloy transition metal (TM) catalysts from both theoretical and experimental sides for many years [1–6]. The addition of controlled amount of certain nonmetallic in the frame of metallic systems gives a novel electronic structure that might be responsible for the promotional effect [7–10]. Particular issue in binary cluster studies derives from the fact that their properties such as chemical activity influenced by the type and composition of adatoms leading to the unique catalytic behavior of the alloy clusters [11–14].

The influence of chlorine on the carbon deposition reaction over transition metal species has been the subject of a number of investigations since 1959, in which Cullis et al. [15] reported that the hydrogen substitution by chlorine in reactant is followed by the changes in the carbon deposit. Other research teams have investigated the critical role of chlorine in some industrial reactions [16]. Goodwin and co-workers [17] have found the modifications in the performance of silica-supported ruthenium for the hydrogenation of carbon monoxide resulting from the presence of chlorine species in the reactant. Furthermore, there are a numerous reports empha-

sizing the effectiveness of chlorine on the transition metal catalytic behavior, by creating new sites on the surface of the catalyst [18] or enhancing the rate of hydrocarbon conversion [19]. In this communication, Baker and co-worker [20] have tried to gain an insight into essential factors regarding the promotional effect of chlorine on the catalytic activity of iron. They found that the charge transfer between adsorbed chlorine and the metal surface atoms results in the enhancement of the metal-ethylene bond strength and the C–C bond weakening in the olefin.

Iron can be considered as the most important metal among the transition metal elements used in the industry, because of its affordable cost and wide application in catalytic reactions, including hydrocarbon conversions [21–23], nucleation and growth of carbon nanotubes (CNTs) [24–31], and hydrogenation through Fischer-Tropsch (FT) synthesis [32,33]. In terms of olefin hydrogenation, the size effect of the metal particles in supported catalysts has been emulated by using small transition metal clusters on model oxide surfaces [34–36]. Iron clusters have been also applied to propose the reaction mechanism of hydrocarbon conversion, acetylene to benzene, at the level of theory in Salahub's group [37,38].

The subject of considerable interest when studying ethylene adsorption over transition metal cluster, whether as feedstock for carbon nanotube synthesis [39,40] or for hydrogenation of olefins [34,41–48], is developing a model in order to study many aspects related to activity of olefins. So, the inspection of ethylene interaction with metal clusters and evaluation of effective factors on

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improving the adsorption of C_2H_4 over them has required a lot of attention.

These observations were the motivation to realize how the presence of small portion of chlorine atoms is responsible for the promotion of ethylene interaction with iron cluster. In this study, it was interesting for us to find how the activity of iron clusters is greatly affected by the number of chlorine atoms. We hope to visualize the adsorption behavior of iron surface by using a metal cluster model.

In this work, our first priority is to establish a more qualitative description of the effect of chlorine on activity of bare iron clusters and the second one is to elucidate how ethylene behaves on the new doped cluster. So, we study the adsorption of C_2H_4 over the most stable pure Fe_n ($n=2-4$) and chlorinated clusters of Fe_nCl_m ($n,m \leq 4$) and report the results of detailed density functional theory (DFT) calculations. We also search for the essential factors that are accountable for the observed changes in activity of our clusters relative to bare iron clusters and the nature of chemical bonding in complexes through natural bond orbital (NBO) [49,50] and quantum theory of atoms in molecules (QTAIM) [51] analyses. It is hoped that this study will be able to provide a novel vision for using chlorine atom as catalyst promoter.

2. Method

Calculations of the geometry and electronic structure of clusters and inspection of their interacting systems have been performed at the framework of DFT level being implemented in the Gaussian 09 program [52]. Exchange-correlation functional consists of the combination of Becke's exchange [53] and Perdew-Wang's correlation functional [54], referred to as BPW91, within the generalized gradient approximation (GGA) [55]. The basis sets for all atoms have a triple- ζ quality augmented with two sets of polarization and one diffuse functions, 6-311+G**.

Binding (E_{bind}) and interaction (E_{int}) energies for each adsorption case have been calculating according to the expressions:

$$E_{bind} = E_{complex} - (E_{cluster} + E_{C_2H_4}) \quad (1)$$

$$E_{int} = E_{bind} - (\Delta E_{cluster} + \Delta E_{C_2H_4}) \quad (2)$$

where $E_{cluster}$, $E_{C_2H_4}$, $\Delta E_{cluster}$, and $\Delta E_{C_2H_4}$ are total energies of the bare cluster and ethylene, deformation energies of cluster and ethylene molecule, respectively, and $E_{complex}$ is the total energy of the system that consists of the two fragments. A negative E_{bind} and E_{int} values corresponds to a stable adsorption.

Natural bond orbital (NBO) has been employed to provide insight into the electronic structure of our systems and the essence of bonds. Applying NBO makes interpreting of the electronic perturbation induced by adatoms more comprehensible as a result of transforming the delocalized molecular orbitals into equivalent localized ones that recover the expected Lewis bond patterns, and showing non-Lewis delocalization within donor-acceptor interactions. In addition, quantum theory of atoms in molecules (QTAIM) analysis was carried out on optimized structures, using the AIM2000 [56] program, to reveal the nature of bonds.

3. Results and discussion

This section looks into the progression in the interaction tendency of iron clusters toward ethylene adsorption by the addition of chlorine atom to bare iron cluster. We achieve this objective by studying the interaction of ethylene with pure and Cl-doped clusters with varying constituent. Our studies encompass pure and chlorinated clusters ranging from dimer up to octamer, Fe_n ($n=2-4$) and Fe_nCl_m ($n,m \leq 4$). In this regard, we have examined

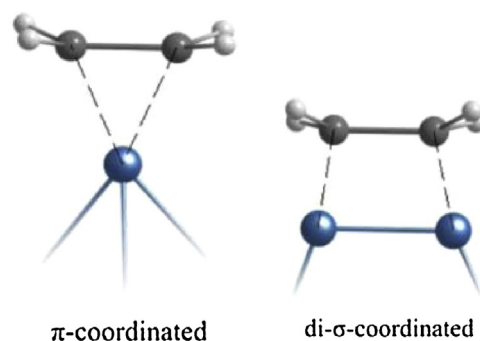


Fig. 1. π - and di- σ -coordinated ethylene over clusters.

two kinds of adsorption mode for ethylene over cluster, π - and di- σ -coordination, as shown in Fig. 1. Binding energy, binding sites, interaction energy, corresponding charge transfers, and vibrational frequencies for all interacting systems are evaluated and compared with those of bare clusters to understand the effect of addition of chlorine on the adsorption behavior of ethylene on iron clusters.

3.1. Structures and energies of Fe_n ($n=2-4$) and Fe_nCl_m ($n,m \leq 4$) clusters

First of all, we have investigated equilibrium geometries of metal and doped metal clusters as a matter of course. Geometry optimization procedure has been done without imposing any symmetry constraints. Vibrational frequency calculation carried out on all the optimized structures with the intention of specifying a stationary point. Their optimized geometric structures in the lowest energy state and the corresponding ground-state spin multiplicities are reported in Fig. 2. The results of optimization processing show that the iron skeleton of iron-chlorine cluster is nearly similar to bare iron. As you can see in this figure, chlorine atoms prefer to be adsorbed at the edge-site (Cl bridges over two iron atoms), and all the chlorines located in head-on (1-fold) site fall into the 2-fold one. Fe–Cl bond lengths are nearly 2.2–2.3 Å in all geometries, which clearly show a reasonable agreement with the theoretically and experimentally measured values for the iron surface [57]. Although a metal surface cannot be characterized completely by the small clusters, their behavior is not exceptional compared to these small aggregations of atoms. So, the metal clusters can be considered as a mimic of metal surfaces and this comparison, to some extent, makes us sure that our calculation at this level of theory is not in a wrong direction.

Another feature that is worth pointing out here is the characteristic of iron-chlorine bonds in new doped clusters. The electronegative element, Cl, gives rise to much electron affinity from the iron center, and the Fe–Cl bonds are expected to have a strong electrostatic character. In this regard, we have carried out the AIM calculation for Fe–Cl bond critical points. The obtained results, tabulated in supporting information (Table S2), show a depletion of electronic charge along the bond, and confirm the electrostatic nature of bonding interaction between Fe and Cl.

The second point at issue, with the purpose of lowest state discovering, is identification of spin multiplicity. So, we have attempted to identify the correct spin multiplicities by optimizing the geometry of each metal and metal-chlorine cluster for a series of possible multiplicities, until the lowest total energy is found. Then, the total energies are compared to find the most stable geometry. Our studies show that, the found spin multiplicities are close to the spin multiplicities of corresponding pure iron clusters. Moreover, spin contaminations were determined for chlorinated iron clusters to ensure the accuracy of our calculations to identify the lowest energy state (Table S1).

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