Computational Materials Science 146 (2018) 334–345

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Density functional theory study on the geometric and electronic structures of Fe_2O_2 and the reaction of $Fe_2 + O_2$

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ARTICLE INFO

Article history:
Received 19 September 2017
Received in revised form 6 November 2017
Accepted 14 November 2017

Keywords:
Density functional calculations
Broken-symmetry approach
Fe_2O_2
$Fe_2 + O_2$
Potential energy surface

ABSTRACT

Density functional theory calculations are performed on all possible structures of Fe_2O_2 using the hybrid B3LYP functional and the B3LYP functional combined with the broken-symmetry (BS) approach to obtain the most stable isomers. Based on the obtained stable isomers, the reaction mechanism of $Fe_2 + O_2$ toward rhombic $Fe_2(\mu\text{-}O)_2$ is considered. The BS-singlet state of the rhombic $Fe_2(\mu\text{-}O)_2$ **2.1** is found to be the ground state of all Fe_2O_2 isomers. The $^9A''$ state of the open-cycle $(\eta^1\text{-}O)Fe_2(\mu\text{-}O)$ **2.11** and ^3A state of the near-linear OFeOFe **1.4** are found to have the second and third lowest energy states, which are higher than the ground state **2.1** by 109.7 and 120.0 kJ mol^{-1}, respectively. The lowest-lying energy states of the bare Fe_2O_2 clusters do not favor three-dimensional structures, but favor the linear and planar structures. Numerous electronic states are found for the symmetric optimized rhombic **2.1**. The energy ordering of the BS-singlet ground state and the four lowest-lying states (^9A_g, BS-septet, BS-triplet, and BS-quintet) at the B3LYP and BS-B3LYP levels agrees with the energy ordering obtained at the CCSD(T) level. The characteristic frequencies calculated for the stable isomers are similar to the previous theoretical and experimental studies. The singlet and nonet energy surfaces calculated for the reaction of $Fe_2 + O_2$ toward rhombic $Fe_2(\mu\text{-}O)_2$ suggest that the reaction adiabatically proceeds with spin inversion from the nonet to singlet state and is expected to be fast because the reaction takes place with a very low barrier relative to that of the reactants (or without any activation energy). The NBO analyses show that the Fe—O bonds in the intermediates and final product exhibit both ionic and covalent characteristics and have highly polarities because of large charge transfer from Fe to O.

1. Introduction

Iron oxide clusters have been widely studied because of their importance in the technological system. The interaction between iron and oxygen is one of the most important chemical processes to understand corrosion, biological oxygen transport, and several catalytic processes [1–4].

Many theoretical and experimental studies have been performed on both small and large iron oxide clusters [5–18].

Recently, systematic high level *ab initio* all electron study of iron monoxide clusters (FeO, FeO^+, and FeO^-) has reported energetics, spectroscopic parameters, and dipole moments, which are in good agreement with experimental values [5]. The generation and structural characterization of FeO_2, FeO_2^+, and FeO_2^- have been studied by mass spectrometry method combined with high level *ab initio* MO calculations [6]. The formation of Fe_mO_n (m = 2–53) clusters has been studied using mass spectrometry combined with hybrid DFT calculations [7]. The GGA-DFT study on Fe_nO_2 and $Fe_nO_2^-$ (n = 2–8) [8] and the DFT-based first principles molecular dynamics (MD) calculations for Fe_nO_m (n = 1–5, m = 1–6) [9] have elucidated their structural and magnetic properties. The electronic and geometric structures of the ground state $Fe_{12}O_{12}$ cluster and the hollow cages $(FeO)_{12}$ have been studied using the GGA-DFT method [10]. The oxygen chemisorption on the $Fe_{12}O_{12}$ cluster surface has a total energy that is similar to that on the hollow cages $(FeO)_{12}$.

Reactions between iron oxide clusters ($Fe_{1-2}O_{1-3}$ [11,12], $Fe_{1-2}O_{1-6}^{+/-}$ [13,14], FeO_{1-3}, and $Fe_2O_{4,\,5}$ [15]) and CO have been studied both experimentally and by using DFT. The bare Fe_2O_3 cluster has been shown to form ideal catalysts for CO oxidation and NO reduction. Mass spectrometry and hybrid DFT studies [16] on reactions of neutral iron oxide clusters (Fe_mO_n, m = 1–2, n = 0–5) with methanol (CH_3OH) have suggested the complete catalytic cycles for the heterogeneous reaction of CH_3OH to CH_2O facilitated by an iron oxide catalyst. Electron microscopy and X-ray diffraction observations have shown that the nanospindles, nanotubes, nanotires, and nanospindles are periodically generated in $\alpha\text{-}Fe_2O_3$ nanostructure [17].

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https://doi.org/10.1016/j.commatsci.2017.11.027

Hybrid DFT studies on the diiron enzyme [18], which possesses the abilities of oxygen transport and storage, and oxidation of organic substrates at the active sites, have proved that the oxidized state of the enzyme is in a μ-1,1-coordination mode with a protonated bridging ligand, and the computed spectral data for the μ-1,1-coordination mode correlate well with the experimental data.

Several experimental and theoretical studies on diiron dioxide clusters such as Fe_2O_2, $Fe_2O_2^+$, and $Fe_2O_2^-$ have also been reported [8,9,13,14,19–26]:

In matrix-isolation studies using infrared (IR) and hybrid DFT calculations, one of the $Fe + O_2$ reaction products in low-temperature Ar matrices have been reported to be the rhombic $Fe_2(\mu\text{-}O)_2$ [19,20]. DFT calculations have predicted a slightly distorted rhombic $Fe_2(\mu\text{-}O)_2$ in the $^3A_2$ state as the most stable state. Photoelectron spectroscopic studies have suggested that the rhombic structure of Fe_2O_2 should stable [21].

B3LYP calculations for eight isomers of neutral Fe_2O_2 have predicted that the ground state of Fe_2O_2 should be the $^7B_{2u}$ state of the rhombic $Fe_2(\mu\text{-}O)_2$ with D_{2h} symmetry [22]. The B3LYP calculations have suggested that the observed frequencies originate from the rhombic ring structure. Rhombic $Fe_2(\mu\text{-}O)_2$ and the peroxide isomers have been studied using the B3LYP functional combined with the broken-symmetry (BS) approach [23]. The planar four-member ring structures have been found to be more stable than the non-planar ones, and the rhombic dioxide $Fe_2(\mu\text{-}O)_2$ with antiferromagnetically ordered electrons on the iron centers has been found to be the global minimum. A number of PBE calculations [8,13,14,24], as well as a DFT-based first principles MD study [9], have also predicted that the ground state of Fe_2O_2 has a rhombic structure with antiferromagnetic ordering on two iron centers.

In contrast, HF/LanL2DZ calculations have suggested that the ground state structure of Fe_2O_2 is the quasi-rhombic triplet state, which is energetically more stable than the rhombic geometry [25]. The local magnetic moments on the iron atoms have been found to be inequivalent because of the different environments, which leads to the distinct spin localization.

The geometric structures of iron oxide cluster cations have been recently studied via ion mobility mass spectrometry experiments combined with B3LYP calculations [26]. The experimental collision cross section for $(FeO)_2^+$ has been assigned to the linear isomer through comparisons between experiments and calculations, and the energy of the linear isomer has been found to be more stable than that of the rhombic isomer. It has been suggested that a larger basis set is needed to determine the most stable isomer of the cluster ions containing transition metal atoms.

In the present study, the possible stable isomers of Fe_2O_2 are examined with the B3LYP functional using the BS approach, and their structural and electronic properties are studied. The calculations provide for evaluating their relative stabilities and the details of reaction energy surfaces for the $Fe_2 + O_2$ system on the basis of the stabilities.

2. Computational details

All of the calculations are performed using the Becke three-parameter Lee-Yang-Parr exchange-correlation functional (B3LYP) [27,28] as implemented in the Gaussian 09 program package [29]. The Pople triple split 6-311+G(d) basis set [30–32] is adopted for all atoms.

All of the Fe_2O_2 isomers studied herein are schematically illustrated and labeled in Fig. 1. First, the geometric and electronic structures of the clusters are optimized with symmetry constraints for several spin states (singlet, triplet, quintet, septet, and nonet). The stability of the obtained SCF solutions are checked, and stable solutions are obtained by breaking all the symmetries using the “Stable = Opt” and “SCF = NoSymm” keywords in Gaussian 09 [29] if any unstable is found. Re-optimization of the geometries is performed using the stable solutions as the starting point. This sequence of procedure is called the BS approach [33,34], and it is repeated to find the optimal geometries and stable BS solutions. Further, the geometries of the lowest-energy isomers obtained within the symmetry constraints, are fully optimized without symmetry constraints, and the stability of the subsequently obtained solutions is checked. Based on the stable isomers of Fe_2O_2 obtained by full optimization, the reaction energy surfaces of the $Fe_2 + O_2$ system toward the rhombic $Fe_2(\mu\text{-}O)_2$ are obtained. Stationary points along the reaction channel are identified and transition states are confirmed to contain a single imaginary frequency. Intrinsic reaction coordinate (IRC) [35,36] calculations are performed on all possible transition states to confirm connections between the corresponding minima.

All geometry optimizations are performed with a self-consistent-field (SCF) convergence limit of 10^{-8} a.u. on the total electronic energy. The vibrational frequencies are calculated and analyzed to ensure the optimized geometries are minimums. The bond populations and charge distributions are obtained by natural bond orbital (NBO) [37–39] and Mulliken population [40] analyses. Finally, CCSD(T) [41–45] single point energy calculations are performed for the B3LYP and BS-B3LYP optimized geometries.

The BS approach is well-established and has been successfully applied to several transition metal systems to obtain a qualitatively correct description of structural and magnetic properties [23,46–53]. The descriptions obtained using the BS-DFT approach have been shown to be comparable to either experimental data or high level calculations (such as MRCI and full CI) [54,55]. Hybrid functionals, especially the hybrid B3LYP functional combined with the BS approach, have shown to yield the most reliable magnetic exchange couplings [23,47,48,50–53].

3. Results and discussions

3.1. Structures, energies, and vibrational frequencies of Fe_2O_2

Fig. 2 shows the lowest energy structures of linear, planar, and three-dimensional Fe_2O_2 optimized with the symmetry constraints. The symmetry-constrained geometries are fully optimized without symmetry constraints, and the obtained geometries are shown in Fig. 3.

For the four linear isomers of Fe_2O_2 optimized with symmetry constraints, the vibrational analyses predict that the linear isomers **1.1**, **1.2**, and **1.3** in the lowest-energy BS states have more than one imaginary frequency; thus, these isomers are found to be unstable. In contrast, linear isomer **1.4** has the lowest energy in the BS-triplet state, for which the vibrational analysis finds no imaginary frequency. The lowest-energy state of **1.4** is found to be stable. Furthermore, the full optimization of **1.4** results in the C_1 structure similar to that obtained with the symmetry constraint ($C_{\infty v}$). The major changes that help to stabilize the fully optimized structure of **1.4** are the slightly smaller O1—Fe1—O2 and Fe1—O2—Fe2 angles. Similar to **1.4**, the recently reported, detailed DFT studies on cyanide Co_nCN and bimetallic CuV_n clusters have also found that the most stable structure of neutral Co_2CN and CuV_2 clusters is linear configuration [56,57].

In the symmetry optimization of planar Fe_2O_2 isomers, the rhombic $Fe_2(\mu\text{-}O)_2$ D_{2h} **2.1** has the lowest energy in the BS-singlet state. The full optimization of **2.1** predicts the same results as the symmetry optimization. Therefore, the BS-singlet state of **2.1** is found to be the ground state for all of the Fe_2O_2 isomers.

The $Fe_2(\eta^2\text{-}O_2)$ **2.4**, $Fe_2(\mu\text{-}\eta^2{:}\eta^0\text{-}O_2)$ **2.6**, and *cis*-$Fe_2(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2)$ **2.8**, optimized with C_{2v} symmetry, have the lowest energies