Methane activation on Fe4 cluster: a density functional theory study

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Keywords
activation, methane, cluster, density, functional, theory, study, fe4

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Methane Activation on Fe₄ Cluster: A Density Functional Theory Study

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Abstract

We report a comprehensive theoretical study on reaction of methane by Fe₄ cluster. This study gain insight into the mechanism of the reaction and indicate the Fe₄ cluster has strong catalytic effect on the activation reaction of methane. In detail, the results show the cleavage of the first C–H bond is both an energetically and kinetically favourable process and the breaking of the second C–H is the rate-determining step. Moreover, our study demonstrates that the different cluster size of iron can not only determine the catalytic activity of methane but also control the product selectivity.

Keywords Density functional theory; Methane; C-H cleavage; Fe cluster

1 Introduction

It is well known that finite clusters constitute a new state of matter with its own fascinating attributes.[1] Among all kinds of clusters, those consisting of transition metal (TM) elements are of particular interest due to their importance in heterogeneous catalysis on both their scientific and technological interests for industrial applications. Catalytic reactions of CH₄ with nano TM clusters are of considerable importance in many industrial processes. Among TMs, iron, the heaviest element with a significant cosmic abundance, is a desirable catalyst for activating the C–H bond in methane because it can decrease significantly the activation energy of C–H bond [2, 3]. Recent research shows that iron can reduce the C–H bond activation energy to about 8–20 kcal/mol, depending on the Ni/Fe mixture [3]. Although small iron clusters are crucial in the catalytic reaction of activation of the C–H bond, there are a few studies on methane activation by
iron alone, and most of these have focused on bulk iron or iron cations [4-10]. With regards neutral Fe clusters, Yamamoto's group used Mössbauer spectroscopy to monitor the reaction between Fe$_2$ and CH$_4$ [11]. Castro studied the interaction of methane with Fe$_4$ clusters and our group has investigated methane activation on Fe monomer and dimer by using density functional theory method [12, 13] The study of methane activation by neutral iron clusters which, beside its own importance, such as iron is one of the most economic affordable catalysts for methane activation reaction, may act as useful models for homogenous and heterogeneous catalysis.

The size dependence of reactivity of metal clusters has become a most fascinating and intriguing issue in modern cluster chemistry and has attracted much attention in both experimental and theoretical fields. It is well known the size of the active phase is one of the most important factors in determining the catalytic behaviour of a heterogeneous catalyst. For some TM clusters such as Pt clusters, the dimer through pentamer were found to be the most reactive, while larger clusters are much less reactive. For Pd clusters, Pd$_8$ and Pd$_{10}$ are the most reactive, while Pd$_3$ and Pd$_9$ activate CH$_4$ more slowly [14]. Research shows that the catalytic properties of small iron clusters show large variations with cluster size [1]. From activation of methane by iron cluster cations, Fe$_n^+$ (n=2-15): research find that there are barriers to the primary dehydrogenation reactions for all the clusters, except n=3 and 4, on the basis of thermochemistry [5]. Previously we have simulated methane activation on Fe monomer and dimer [13], and our results indicate that the iron dimer Fe$_2$ has a stronger catalytic effect on the activation of methane than the iron atom. Here we report methane activation by iron cluster Fe$_4$ tetrahedron, while the activation reactions of methane on Fe bulk solid are actually in investigation. Through the comparison of the activation mechanisms of methane by different size of iron clusters, even atomic scale, cluster and bulk solid iron, the study will provide useful information to tune the relative reaction
rates of the different steps during activation methane by controlling the catalytic iron size, which is very important for methane conversion from both scientific and industrial interests.

2 Computational methods

Density functional method of Perdew and Wang (i.e. BPW91) [15] method in conjunction with the 6-311+G* basis set [16] were employed in the structural optimization for all reactants, products, intermediates and transition states involved in the reactions of Fe₄ cluster with CH₄. The selected method has been widely applied to electronic structure calculations on systems containing transition metals, and has been proven to combine reasonable computational cost with sufficient accuracy for transition metal systems [17, 18]. Moreover, PW91 shows advantages in studying systems with periodic boundary conditions [19]. Frequency calculations at the same theoretical level were then performed to confirm whether the optimized species is a minimum or a saddle point.

AIM theory and NBO analysis which have been used to successfully determine intermolecular interactions of different systems were carried out on the basis of the optimized structures of Fe₄–CH₄ system in order to better clarify the nature of the intermolecular interactions [18, 20-27]. In the AIM analyses, the existence of a bond is indicated by the presence of a so-called bond critical point (BCP). The strength of the bond can be estimated from the magnitude of the electron density ($\rho$) at the BCP. Similarly, the ring or cage structures are characterized by the existence of a ring critical point (RCP) or cage critical point (CCP). RCP is saddle point inside ring, whose Hessian matrix presents two positive eigenvalues and it is characteristic of cyclic structures. As the name suggests, CCP is the point where the surrounding of electron density meet each other and is surrounded by ring critical points. Furthermore, the nature of the interatomic interaction
can be predicted from the topological parameters at the BCP, such as the Laplacian of electron
density ($\nabla^2 \rho_{\text{bcp}}$) and energy density ($H_{\text{bcp}}$). Generally, the sign of $\nabla^2 \rho_{\text{bcp}}$ reveals whether charge
is concentrated ($\nabla^2 \rho_{\text{bcp}} < 0$) as in covalent bonds (shared interaction) or depleted ($\nabla^2 \rho_{\text{bcp}} > 0$) as
in ionic bonds, H-bonds, and van der Waals interactions (closed-shell interaction). It is also
reported that if $\nabla^2 \rho_{\text{bcp}} > 0$ and $H_{\text{bcp}} < 0$, then the interaction is only partly covalent in nature [13].
Additionally, natural bond orbital (NBO) analysis was carried out to examine the interactions,
such as H-bonding and van der Waals force of the systems. The topological analysis of the
system was carried out via the AIMALL program [28].
To characterize the absorption strengths for methane on the Fe$_4$ cluster, the binding energy $\Delta E$
has been introduced, which is defined as the energy difference between the formed Fe$_4$–CH$_4$
complex and the corresponding monomers. Moreover, zero-point vibrational energy (ZPVE)
corrections and basis set superposition errors (BSSEs) calculations have also been considered,
where the Boys-Bernardi counterpoise technique has been employed to evaluate the BSSEs [29].
In order to confirm transition structures for some key reaction steps, intrinsic reaction coordinate
(IRC) calculations [30-31] have been performed to follow the reaction pathways. The
calculations presented herein have been carried out using the Gaussian 03 suite of programs [32].

3 Results and Discussions

3.1 Structural and energetic properties of Fe$_4$ and Fe$_4$–CH$_4$

To the best of our knowledge, we report here the first theoretical investigation on the methane
dehydrogenation pathway on Fe tetramer. Our goal is to study whether the low-energy magnetic
states of Fe$_4$ cluster is able to activate the C–H bonds of CH$_4$. Figure 1 lists the optimized
geometries of the various intermediates and transition states for the Fe$_4$–CH$_4$ system on the
BPW91/6-311+G* level. We start the discussion from the reactants of the reaction. For CH₄, in the ground state (GS), the C–H bond lengths are 1.097 Å, with H–C–H angle of 109.5 °. The GS of Fe₄ cluster is a distorted tetrahedron, with a multiplicity $M = 2S + 1 = 15$, where $S$ is the total spin. The magnetic moment of each Fe atom is $3.5 \mu_B$ with an average bond length of 2.352 Å. Using the DFT method, Gutsev and Bauchlicher [33] as well as Berski et al [34] also found a distorted tetrahedron for the GS of Fe₄, with $3.5 \mu_B$ at each atomic site and with similar bond lengths as those in the present study.

The total, relative energies, BSSE and ZPE corrections of reactants, intermediates, transition states and products are summarized in the supporting information (Table S1). We can see from Table S1 that Fe₄ cluster with $M = 13$ state is located 2.2 kcal/mol above the GS; it has a shorter average bond length of 2.296 Å. Calculational results [12] indicate that the $M = 17$, and $M = 11$ states were found 8 and 14 kcal/mol above the GS, respectively. Gutsev and Bauchlicher [33] as well as Berski’s study also show the same order for the excited states [34]. So, in this paper, we only consider the activation reactions of methane by Fe₄ cluster on its GS ($M = 15$) and its first excited state ($M = 13$).

The intermediates and transition states along the potential energy surfaces of GS ($M = 15$) are labelled as Cₙ (n=1, 2, 3, 4) and TSₙ (n=1, 2, 3) and those of the first excited state ($M = 13$) are labelled as Cₙ’(n=1, 2, 3, 4) and TSₙ’(n=1, 2, 3). The C1, GS of Fe₄–CH₄ complex, which was formed by the carbon atom of methane coordinated with a Fe atom of Fe₄, with bond length, Fe–C, of 2.442 Å. An adduct C1’, Fe₄–CH₄ with $M = 13$ state, is also formed by Fe–C interaction with the value of 2.597 Å. Subtracting the GS energies of Fe₄ and CH₄ from that of the C1, a binding energy, including the corrections of ZPE and BSSE of 2.0 kcal/mol is obtained, confirming a weak type interaction. With respect to Fe₄ ($M = 15$) of GS, C1’ is above
0.4 kcal/mol of the reactant asymptote \( (M = 15) \). But with respect to Fe\(_4\) of \( M = 13 \), its binding energy is 1.8 kcal/mol. From the bonding lengths and the binding energies we can draw a conclusion that the interaction between Fe\(_4\) and CH\(_4\) in C1 is stronger than that of C1', which is also supported AIM, mulliken atomic charges and NBO analysis.

As displayed in Figure 2, the interaction between Fe\(_4\) and CH\(_4\) can be confirmed by the existence of the bond critical point (BCP) of the Fe–C contact. The corresponding topological parameters at the BCP have been presented in Table 1. As mentioned above, the electron density \( \rho_{\text{bcp}} \) can be used to characterize the relative strength of the Fe–C contact, and we can see that the interaction between Fe\(_4\) and CH\(_4\) in C1 is stronger than that of C1', which is also consistent with the Fe–C contact distances shown in Figure 1. For the calculated Laplacians and energy densities at the BCPs, both of them are positive and negative, respectively. Therefore, the interactions between Fe and C atom are predominated by the electrostatic interactions as well as partial covalent characters in nature. Moreover, the C1 has more negative \( H_{\text{bcp}} \) than C1', implying that the strength of the Fe–C interaction of C1 is larger than that of C1'. Mulliken atomic charges show that there is small transference of electrons (0.19e in C1 and 0.18e in C1') from CH\(_4\) to Fe\(_4\) through the C–Fe bond. This charge does not lie on the Fe atom, whereas it is stabilized on the other three Fe atoms which are far from CH\(_4\) moiety. The Fe atom and H atoms have positive charge of 0.050e and 0.308e in C1 and 0.039e and 0.307e in C1', and the carbon atom has negative charge of -1.087e in C1 and -1.072 in C1', which can interpret that interaction between Fe\(_4\) and CH\(_4\) in C1 \( (M = 15) \) is stronger than that of C1' \( (M = 13) \). NBO analysis shows that the second-order interaction energies from the two donor orbits (\( \sigma(C–H) \)) to the acceptor orbits (\( n^*\text{Fe} \)) are 6.3 and 4.6 kcal/mol of C1 and C1', respectively, which is in agreement with the results of the binding energy, AIM and mulliken atomic charges analysis. The energies of singly occupied
molecular orbital (SOMO) orbital of the frontier orbits and the gap between HOMO and LUMO of some species of the system are shown in supporting information Table S2. The HOMO-LUMO gap in bare methane is 9.67 eV. But in the GS of Fe₄-CH₄ (C1), the gap becomes smaller with a value only 0.90 eV, which means that the interaction with Fe₄ activates the methane moiety. The gap of $M = 13$ state is even smaller with a values only 0.21eV. Normally, the higher HOMO energy is, the lower the LUMO energy is, and the narrower the LUMO-HOMO energy-gap is, the more chemically active the molecule is. We can see that C1' is more active than C1. In all, their weak interactions between Fe₄ and CH₄ of the two Fe₄–CH₄ complexes activate the methane moiety, and their interactions are the precondition of the activation reaction of methane on Fe₄ cluster. For the following discussions, we will focus on the activation reaction of methane by Fe₄ cluster on these two states.

3.2 Dehydrogenation of CH₄ on Fe₄

For the activation reactions of methane on TM tetramers, previously experimental and theoretical results indicated the most energetically favourable products are (TM)₄CH₂ and H₂ [17]. So in this paper, we mainly focus on the reaction pathways with production of Fe₄CH₂ and H₂. We have plotted in Figure 3 the CH₄ dehydrogenation pathways in the presence of $M = 13$ and $M = 15$ states of Fe₄. The first vibrational frequencies of the reactants, intermediates, transition states and products of these two states have been listed in Table 2. The number of imaginary frequencies can confirm whether there is a local minimum or a transition state.

For the activation reaction of methane on the catalyst Fe₄, firstly, two Fe₄–CH₄ adducts C1 and C1' are formed, which are -2.0 kcal/mol (C1) and 0.4 kcal/mol (C1') relative to the reactant asymptote ($M = 15$). The weak interactions between Fe₄ and CH₄ of the two Fe₄–CH₄ complexes activate the methane moiety, which are the precondition of the activation reaction of methane on
Fe₄ cluster. In TS1 and TS1', the bond lengths of C−H1 are 1.599 Å and 1.548 Å respectively, which are much longer than that of C–H (1.097Å) in gas phase. The AIM analysis indicates the formation of a Fe−H1 by the presence of the so-called bond critical point (BCP) and a three atoms ring, Fe−C−H1, is characterized by the existence of a ring critical point (RCP). The imaginary frequencies of TS1 (892i cm⁻¹) and TS1' (951i cm⁻¹) are assigned to the stretch mode of C–H for the breaking of the bond. From Figure 3 we can see that the first C–H bond of C1 and C1' will be broken if about 12.4 kcal/mol (via TS1) and 8.2 kcal/mol (via TS1') are provided, and consequently two stable intermediates (H–Fe₄–CH₃), C2 and C2', will be formed, which is 15.8 kcal/mol (C2) and 17.0 kcal/mol (C2') below the reactant asymptote. We can see that the intermediate CH₃Fe₄H is much more stable than those of the corresponding intermediates CH₃FeH and CH₃Fe₂H with the methane reaction of Fe atom and Fe dimmer at the BPW91 level [13]. Our results show that the breaking of the first C–H bond of methane in the presence of Fe₄ is both an energetically and kinetically favorable process. Moreover, from the potential energy surfaces we can see that the first C–H activation takes place most likely through a crossover between M = 13 and M = 15 potential surfaces.

As shown in Figure 3, to break the second C–H bond, the intermediate CH₃Fe₄H, C2 and C2' have to overcome a transition state with the energy barrier of 27.3 kcal/mol (TS2) and 25.4 kcal/mol (TS2') on M = 15 and M = 13 states, respectively. The AIM analysis (Figure 2) indicates the formation Fe−H2 by the presence of BCP. The bond lengths of the second C–H2 are 1.881 Å and 1.740 Å in TS2 and TS2', respectively, and the imaginary frequencies of TS2 (645i cm⁻¹) and TS2' (685i cm⁻¹) are assigned to the stretch mode of C–H bond, which indicate the breaking the second C–H bond, followed by an intermediate CH₂Fe₄HH (C3 and C3') with 10.0 kcal/mol and 8.1 kcal/mol below the reactant asymptote of the two states. The gaps of C3
(1.63 eV) and C3' (0.70 eV) show C3' is more active than C3. We can see that the intermediate CH2Fe4HH is much more stable than those of the corresponding intermediate CH2FeHH and CH2Fe2HH in reaction of methane on Fe atom and Fe dimmer at the BPW91 level [13]. The calculations also show the cleavage of the second C–H bond on Fe4 is more difficult than that of the first C–H bond.

The next step in the dehydrogenation is the formation of a complex H2FeCH2, in which the hydrogen molecules bond weakly to the Fe–CH2. For the transition states of dehydrogenation via TS3 and TS3', the AIM analysis shows the formation of a H1–H2 by the presence of the BCP and a three atoms ring, H1–Fe–H2, RCP. The imaginary frequencies of TS3 (832i cm⁻¹) and TS3' (773i cm⁻¹) are assigned to the stretch mode of H-H bond for the forming H2. As the following product C4 and C4', the disappearing RCP illuminates the breaking of the three atom ring, H1–Fe–H2, and disappearing BCP shows the breaking one of Fe–H comparing with the AIM analysis of TS3 and TS3'. The distance between the Fe and the two H atoms in the H2 unit is about 1.8 Å in C4 and 1.7 Å in C4', which is much longer than the calculated Fe–H value of 1.553 Å in gas-phase due to the Fe–H interactions. The bond distance between the two hydrogen atoms in the H2 unit is 0.822 Å in C4 and 0.877 Å in C4', which is slightly longer than the H–H bond of H2 in the gas phase, that is, 0.748 Å. Moreover, the Fe–C bonds around 2.0 Å in C4 and around 1.9 Å in C4' is also larger than the gas-phase value of 1.686 Å due to the interaction of Fe atom with the H2 unit. The energy barriers 27.4 kcal/mol for M = 15 state and 16.6 kcal/mol for M = 13 state, have to be overcome to form the H2FeCH2 complex through the transition states (TS3 and TS3'), which are 17.4 kcal/mol and 8.5 kcal/mol above the reactant asymptote. Once the intermediate H2Fe4CH2 is formed, the following steps involve the migration of H atom, combination of H atoms to form H2, and finally dissociation of H2. As the dehydrogenation
products, Fe₄CH₂ + H₂, are 15.3 kcal/mol and 9.2 kcal/mol above the reactant asymptote of M = 15 and M = 13, respectively, which means that methane dehydrogenation in the presence of Fe₄ cluster is endothermic.

From Figure 3 and discussed above we can see that among the three single steps, on M = 13 state, the one involving the breaking of the second C–H bond is the rate-limiting step. While for M = 15 state, the cleavage of the second C–H bond and H₂ elimination from the dihydrogen complex are difficult comparing with the cleavage of the first C–H bond. Here we will compare the activation reactions of methane on iron atom and dimer. For the methane activation on iron atom, our previous publication [13] suggests that the first C–H activation takes place most likely through a crossover between the triplet and quintet potential surfaces and the cleavage of the second C–H bond is neither an energetically and kinetically favourable process. Our study also explains the experimental observation HFeCH₃ complex rather than CH₃FeH₂ complex of by Fe–CH₄ system, while for Fe₄–CH₄ system, the products CH₃Fe₄H and CH₂Fe₄HH of can be obtained based on our calculations. For activation reactions of methane on Fe dimer, the cleavage of the first and second C–H bond are both facile, and H₂ eliminated from the dihydrogen complex is the rate-determining step, while for active reaction of methane by Fe₄ cluster, the first C–H bond cleavage is facile and the second C–H breaking is more difficult than that of by Fe dimer. We can see that the cluster size of iron can not only determine the catalytic activity of methane but also control their product selectivity. Furthermore, the activation reactions of methane on bulk solid are actually in investigation. The present studies serve as the probes for the activation mechanism of methane on small Fe clusters, providing an interesting contrast to the bulk solid.
4 Conclusions

Density functional theory (DFT) calculations have been carried out to explore the activation reactions of methane catalysed Fe₄ cluster with different spin states. Various intermediates, transition states, and products in the activation reaction are fully optimized at the BPW91/6-311+G* level. The potential energy surfaces (PES) corresponding to Fe₄ cluster with two states of \( M = 13 \) and \( M = 15 \) (the total multiplicity: \( M = 2S+1 \), \( S \) = total spin states) are examined in detail. Our calculational results show the barrier of the cleavage of the first C–H bond is only 8.2 kcal/mol on \( M = 13 \) state, and 12.4 kcal/mol on \( M = 15 \) state, which is both an energetically and kinetically favourable process. The results also suggest that the first C–H activation takes place most likely through a crossover between \( M = 13 \) and \( M = 15 \) potential surfaces. The cleavage of the second C–H bond is relatively difficult compared with that of the first one, and the barrier is 25.4 and 27.2 kcal/mol on \( M = 13 \) and \( M = 15 \) states, respectively. For \( \text{H}_2 \) elimination, the process on the PES of \( M = 13 \) state is feasible, with the activation barrier of 16.6 kcal/mol. Our calculational results show the cleavage of the first C–H bond is quite facile than that of the second C–H bond. The breaking the second C–H bond is the rate-limiting step. The relative energies of the intermediates \( \text{C}2 \) and \( \text{C}2' \) are -15.8 and -17.0 kcal/mol and \( \text{C}3 \) and \( \text{C}3' \) are -8.1 and -10.3 kcal/mol, on \( M = 15 \) and \( M = 13 \) states, respectively. So we can predict that the products \( \text{CH}_3\text{Fe}_4\text{H} \) and \( \text{CH}_2\text{Fe}_4\text{HH} \) can be obtained. In all, the study on one hand gains insight into that the strong catalytic effect of Fe₄ cluster in the activation reaction of methane, on the other hand, demonstrates that the size of iron cluster can not only determine the activity of methane activation but also control the product selectivity. With the aid of knowledge of reaction mechanism, the size effect can provide deep insights into for the conversion of reactants and for
the formation of different products. These insights will undoubtedly be helpful for the rational design of highly efficient catalysts.

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Captions

Figure 1 Optimized structures of transition states and intermediates of Fe₄ cluster activation reaction of methane of $M = 15$ and $M = 13$ states based on the BPW91/6-311+G* level (bond lengths in angstroms and bond angles in degrees, and the parameters in brackets are from the system with $M = 13$ state).

Figure 2 The molecular graphs of the intermediates and transition state of Fe₄ cluster activation reaction of methane, where the bond critical points (BCPs), ring critical points (RCPs) and cage critical point (CCP) are denoted as small green, red and blue dots, respectively.

Figure 3 Potential energy profiles of dehydrogenation and H elimination reactions of CH₄ and Fe₄ of $M = 15$ and $M = 13$ states based on the BPW91/6-311+G* level.

Table 1 The calculated topological parameters at the BCPs of the Fe₄–CH₄ system.

Table 2 Calculated first vibrational frequencies (cm⁻¹) and the vibrational mode assignments of Fe₄-CH₄ system of $M = 15$ and $M = 13$ states at the BPW91/6-311+G* level.
References


Figure 1
Figure 2
Figure 3
Table 1 The calculated topological parameters at the BCPs of the Fe₄–CH₄ system.

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<th>Complexes</th>
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*a Atomic numbering refers to Figure 1. The $\rho_{\text{bcp}}$, $\nabla^2 \rho_{\text{bcp}}$, $V_{\text{bcp}}$, $G_{\text{bcp}}$, and $H_{\text{bcp}}$ is electron density, the Laplacian of the electron density, potential energy density, kinetic energy density, and energy density at the BCP, respectively.
Table 2 Calculated first vibrational frequencies (cm$^{-1}$) and the vibrational mode assignments of Fe$_4$-CH$_4$ system of $M = 15$ and $M = 13$ states at the BPW91/6-311+G* level.

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