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Formation of Acetylene in the Reaction of Methane with Iron-Carbide Cluster Anions FeC_3^- under High-Temperature Conditions

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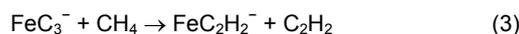
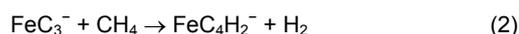
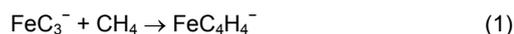
Abstract: The underlying mechanism for non-oxidative methane aromatization remains controversial due to the lack of experimental evidence for the formation of the first C–C bond. For the first time, the elementary reaction of methane with atomic clusters (FeC_3^-) under high-temperature conditions to produce C–C coupling product has been characterized by mass spectrometry. With the elevation of temperature from 300 K to 610 K, the production of acetylene, the important intermediate proposed in a monofunctional mechanism of methane aromatization, was significantly enhanced, which can be well rationalized by quantum chemistry calculations. This study narrows the gap between gas phase and condensed phase studies on methane conversion and suggests that the monofunctional mechanism probably operates in non-oxidative methane aromatization.

Methane aromatization has received significant attention spurred by the increasing demand of aromatics in chemical industry and the high availability of methane from natural gas, shale gas, and gas hydrate.^[1] A variety of silica-alumina zeolites modified with transition metal species, such as Mo, Fe, and Zn have been identified as promising catalysts for non-oxidative aromatization of methane to benzene^[2] under high-temperature conditions (typically more than 973 K). Considerable efforts have been devoted to uncovering the detailed mechanism of benzene formation. However, the reaction intermediates and active phase responsible for the cyclization to produce benzene remain controversial.^[3] Some researchers emphasized a bifunctional mechanism that the transition-metal carbide (M_xC_y) sites formed in the induction period activate methane and convert the resulting CH_x intermediates into ethylene,^[4] which reacts further to produce benzene at the Brønsted acid sites in the zeolites. An alternative monofunctional mechanism that both the activation of methane to form acetylene intermediate and the subsequent aromatization take place over M_xC_y sites was also proposed.^[5] Recently, single iron atoms embedded in a silica matrix (Fe@SiO_2) were reported to convert methane to benzene with

high selectivity.^[6] The methyl radical, generated through dehydrogenation by the single iron atom coordinated with one Si and two C atoms (SiFeC_2), was proposed as an important intermediate for the subsequent gas-phase formation of benzene. Identification of reliable mechanism of methane aromatization relies on the real-time detection of the intermediates generated in each elementary step.^[2a,7] However, detection of intermediates formed in elementary reactions is usually inaccessible in condensed-phase studies.

Gas phase study of the elementary reactions between methane and isolated transition metal carbide clusters (M_xC_y^q), the active species involved in non-oxidative methane aromatization, provides an important way to reveal mechanistic details relevant with surface chemistry.^[8] The reactions of M_xC_y^q clusters with methane have been extensively studied under room-temperature conditions.^[9] Little attention was paid to the reactions of M_xC_y^q clusters with methane under high-temperature conditions, which is important to narrow the gaps between the gas phase reactions and the related surface reactions. Herein, we report that the high-temperature reactions of iron carbide cluster anions (FeC_3^-) with methane produce acetylene, the important intermediate proposed in the monofunctional mechanism of methane aromatization. This is the first study of high-temperature reactivity of atomic clusters toward methane.

The FeC_y^- ($y = 2-5$) clusters were generated by laser ablation, mass selected, and then reacted with CH_4 in an ion trap reactor at temperatures from 300 K to 610 K (see Experimental Method in Supporting information).^[10] The FeC_3^- and FeC_5^- clusters show similar reactivity toward methane, whereas FeC_2^- and FeC_4^- clusters are inert (Figure S1). The reactivity of FeC_3^- is the main focus of this study and the time-of-flight (TOF) mass spectra for the reactions of FeC_3^- with CH_4 and CD_4 are shown in Figure 1. Upon the interaction of FeC_3^- with CH_4 at 300 K, a product peak assigned as FeC_4H_4^- was observed (reaction 1), whereas the other two products FeC_4H_2^- and FeC_2H_2^- were barely observable (Figure 1b). When the reaction temperature increased from 300 K to 610 K (Figure 1c,d), the relative intensities of FeC_4H_2^- and FeC_2H_2^- products, corresponding to reactions 2 and 3, respectively, increased significantly. The isotopic labeling experiment with CD_4 (Figure 1e) at 610 K confirmed the above reaction channels.



The pseudo-first-order rate constants (k_1) for $\text{FeC}_3^- + \text{CH}_4$ at different temperatures were measured (Figure S2) and shown in Figure 2. It can be seen that the temperature dependence of the rates is non-Arrhenius. The k_1 value is $1.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and increases by a factor of 2.8 when the temperature is ramped up to 410 K. However, the k_1 value increases slowly from 410 K to 575 K [$k_1(575 \text{ K}) = 1.2 \times k_1(410 \text{ K})$].

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From 575 K to 610 K, the k_1 value increases rapidly again [$k_1(610\text{ K}) = 1.4 \times k_1(575\text{ K})$]. The non-Arrhenius behavior can be interpreted on the basis of the quantum chemistry calculated cluster structures and reaction mechanisms in the text below. The branching ratios (BRs) of reactions 2 and 3 increase as the increase of the temperature while the BR of reaction 1 decreases (Figure 2b), suggesting the consecutive processes: $\text{FeC}_3^- + \text{CH}_4 \rightarrow \text{FeC}_4\text{H}_4^- \rightarrow \text{FeC}_4\text{H}_2^- + \text{H}_2$ or $\text{FeC}_2\text{H}_2^- + \text{C}_2\text{H}_2$.

It is noteworthy that almost all of the reported rate constants of cluster reactions with methane are greater than $10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ around 300 K,^[11] corresponding to facile activation and conversion of methane. In sharp contrast, the reaction rates of the current system $\text{FeC}_3^- + \text{CH}_4$ [$(2-8) \times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$] are very low. The elevation of temperature is thus required to enhance the reaction efficiency. The reaction system in this study can be more comparable to the condensed phase systems operated under high-temperature conditions.^[1d,12]

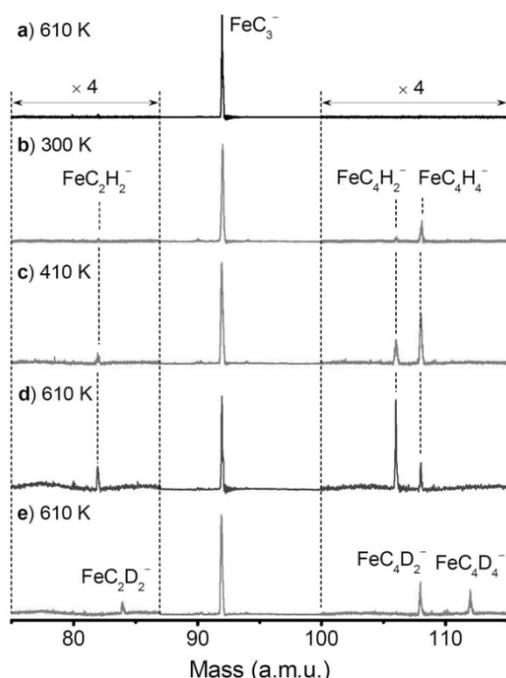


Figure 1. TOF mass spectra for the reactions of mass-selected FeC_3^- cluster with He at 610 K (a), with CH_4 at 300 K (b), 410 K (c), and 610 K (d), and with CD_4 at 610 K (e) for around 14.5 ms. The molecule density of reactant gases is about $2.4 \times 10^{15}\text{ molecule cm}^{-3}$.

Density functional theory (DFT) calculations were performed to study the structures and reaction mechanisms of FeC_3^- . In literature, cyclic (IS1) and linear (IS2) structures (Figure S4) with quartet spin multiplicities were separately proposed as the lowest-lying energy isomers of FeC_3^- .^[13] The gas phase ion chromatography experiments^[14] indicated that both cyclic and linear structures of FeC_y^- can be produced in the experiments. The adopted M06L functional (see Theoretical Method in Supporting Information) predicts that the quartet $^4\text{IS1}$ and $^4\text{IS2}$ structures are close in energy (0.14 eV) and the doublet $^2\text{IS1}$ and $^2\text{IS2}$ are above the $^4\text{IS1}$ and $^4\text{IS2}$ by 0.27 and 0.09 eV, respectively (Figure S4). As a result, both $^4\text{IS1}$ and $^4\text{IS2}$ can be produced by our experiment and $^2\text{IS1}$ and $^2\text{IS2}$ may also be populated through thermal equilibrium (Figure S5).

The potential energy surfaces (PESs) for methane activation by all of the four species ($^2,^4\text{IS1}$ and $^2,^4\text{IS2}$) were explored (Figures 3 and S7). High overall positive barriers ($>0.5\text{ eV}$) are

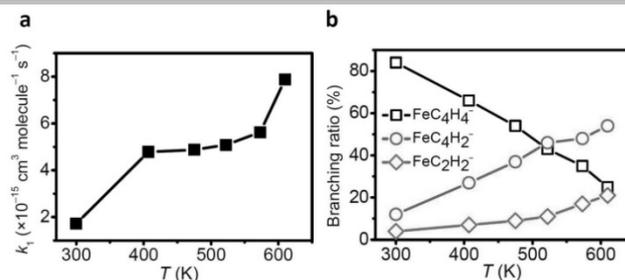


Figure 2. Rate constants (a) and branching ratios (b) at different temperatures.

encountered for C–H activation by the quartet species while the doublet species can activate methane more easily. The PESs starting from the linear structures ($^2,^4\text{IS2}$, Figure S7) can merge into the PESs from the cyclic structures ($^2,^4\text{IS1}$, Figure 3), so only the reaction mechanism of $\text{IS1} + \text{CH}_4$ is described below.

The reaction of $^4\text{IS1} + \text{CH}_4$ has a overall barrier of 0.58 eV that can be hardly overcome at 300 K (Figure S14). The observed reactivity in Figure 1b can be due to the doublet FeC_3^- . Figure 3 indicates that $^2\text{IS1}$ can trap CH_4 through the Fe atom with a binding energy of 0.20 eV. The reaction then proceeds through the mechanism of oxidative addition ($^2\text{I1} \rightarrow ^2\text{TS1} \rightarrow \text{I2}$) with a barrier of 0.05 eV, resulting in activation of the first C–H bond and formation of the Fe–H and Fe–CH₃ bonds. The intermediate I2 is more stable in the quartet than the doublet state, which results in a spin crossing process.^[15] After the spin conversion ($^2\text{TS1} \rightarrow \text{CP1} \rightarrow ^4\text{I2}$, see Figure S8), the reaction proceeds along the quartet surface. Upon a ring-opening isomerization ($^4\text{I2} \rightarrow ^4\text{I3}$), the C–C coupling takes place ($^4\text{I3} \rightarrow ^4\text{TS3} \rightarrow ^4\text{I4}$) and the $^4\text{TS3}$ is lower than $^2\text{IS1} + \text{CH}_4$ in energy by 0.03 eV. The C–C coupling step can release enough energy to overcome the barrier of the second C–H bond activation and generate the intermediate $^4\text{I5}$, in which Fe site is coordinated with two H atoms. The four-membered ring of $^4\text{I5}$ embraces the CH_2 moiety to form five-membered ring ($^4\text{I5} \rightarrow ^4\text{I6}$) and one of H atoms transfers from Fe atom to the carbon ligand to form $^4\text{I7}$, the most stable structure on the potential energy surface. The intermediate $^4\text{I7}$ has enough energy ($\sim 2\text{ eV}$) to relax ($^4\text{I7} \rightarrow ^4\text{I8}$) and then to activate the third C–H bond of CH_4 ($^4\text{I8} \rightarrow ^4\text{I9}$). After a structural rearrangement to break the Fe–C bond in $^4\text{I9}$, the fourth C–H bond can be activated to form intermediate $^4\text{I11}$, in which the Fe atom is four-fold coordinated with one C atom and three H atoms. Two of the three H atoms on Fe site can make a H_2 unit that can be evaporated to form product ions FeC_4H_2^- (P1, Figure S10, reaction 2).

In addition to the generation of dihydrogen, there is a competing reaction for C_2H_2 formation (reaction 3). After activation of the third C–H bond of methane to form intermediate $^4\text{I9}$, one H atom can transfer from the Fe site to a C atom of C_3 ligand to form a $[\text{C}_2\text{H}_2]$ unit in intermediate $^4\text{I13}$ ($^4\text{I9} \rightarrow ^4\text{I13}$), in which both of the two C atoms in $[\text{C}_2\text{H}_2]$ unit originate from the C_3 ligand. For further desorption of C_2H_2 molecule, the formed $[\text{C}_2\text{H}_2]$ unit in $^4\text{I13}$ should coordinate with Fe site ($^4\text{I13} \rightarrow ^4\text{I14}$). Therefore, the resulting intermediate $^4\text{I14}$ has enough internal energy to break $[\text{H}_2\text{C}_2-\text{C}_2\text{H}]$ bond to generate the intermediate $^4\text{I15}$ with isolated $[\text{HC}=\text{CH}]$ unit, which can be evaporated to produce the experimentally observed FeC_2H_2^- product ions (P2, Figure S11). The pathway for incorporation of the C atom from CH_4 into $[\text{HC}=\text{CH}]$ unit is also considered (Figures S12 and S13). From the intermediate $^4\text{I7}$, the H atom bonded with Fe can transfer to the adjacent C atom of $[\text{CH}]$ moiety to form intermediate $^4\text{I16}$ with two equivalent $[\text{CH}_2]$ units. Then, the third C–H bond of methane is activated to form intermediate $^4\text{I17}$, the

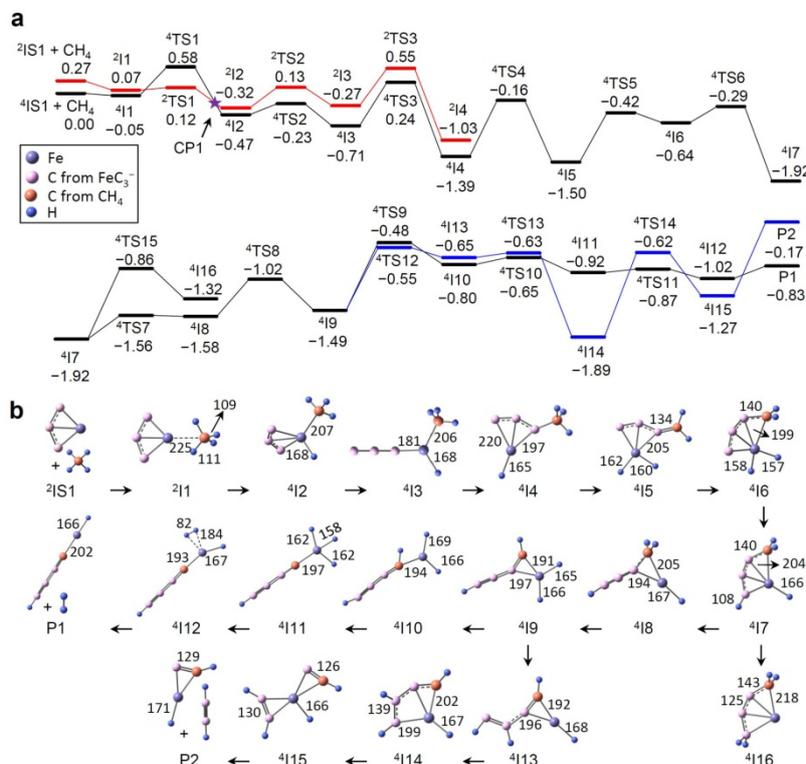
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structure of which is similar to that of 4I7 . Further transformation of 4I17 to generate $\text{HC}\equiv\text{CH}$ product follows the pathway similar to $^4I7 \rightarrow \text{P2} + \text{C}_2\text{H}_2$.

In the case that the reaction starts with $^2IS1 + \text{CH}_4$, all of the reaction intermediates, transition states, and the spin conversion point (CP1) are lower in energy than the separated reactants (Figure 3). In $^2IS2 + \text{CH}_4$ (Figure S7), the tiny positive barrier

(+0.08 eV) in activation of the first C–H bond can be surmounted by the kinetic energy and the vibrational energy of the reactants ($E_{\text{vib}} = 0.06$ eV at 300 K, see also Figure S14). As a result, the reactions 1–3 are thermodynamically and kinetically favorable at 300 K. The energy of $\text{FeC}_4\text{H}_2^- + \text{H}_2$ (P1, -0.83 eV) is significantly lower than that of $\text{FeC}_2\text{H}_2^- + \text{C}_2\text{H}_2$ (P2, -0.17 eV), which is qualitatively consistent with the higher branching ratio of FeC_4H_2^- over that of FeC_2H_2^- (Figure 2b).



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cations in the reactions with methane.^[16] The carbide cluster anions were reported to dehydrogenate methane to produce dihydrogen at room temperature facilitated by the dissociative CO adsorption^[17] or by the cooperation of two metal atoms,^[9f] while no C–C coupling product was observed. In this study, the production of C–C coupling product, acetylene, was evidently observed in the reaction of mononuclear iron carbide cluster anions FeC_3^- with methane under high-temperature conditions.

In condensed-phase studies of methane aromatization, a consensus that the formation of C_2H_x intermediates via C–C coupling is essential for further cyclization to produce aromatics has been reached.^[14,18] However, three different mechanisms were proposed for non-oxidative aromatization of methane based on the experimental identification of the intermediates. Most of the studies of the Mo/zeolites catalysts insisted on a bifunctional mechanism^[2c,19] that the Mo carbide phase converts methane into ethylene and then ethylene further goes through oligomerization into aromatics over the Brønsted acid sites embedded in the zeolites. A monofunctional mechanism, suggested by Mériaudeau,^[2b,5a] and Ha,^[20] emphasized activation of methane to acetylene, followed by aromatization into aromatics exclusively over Mo carbide phase.^[21] A gas phase mechanism, which is quite different from the above two mechanisms, was proposed for the catalytic system of Fe@SiO_2 in which methane is activated by the SiFeC_2 site to form gas phase methyl radical that undergoes series reactions to form ethylene and aromatics.^[6] Recently, the production of highly selective acetylene catalyzed by Fe@SiO_2 in a hydrogen-permeable membrane reactor was also reported.^[22] However, there is still a lack of experimental evidence for the formation of the first C–C bond to support the relevant mechanisms. In this study, by using a cluster mass spectrometer coupled with a high-temperature ion trap reactor, the elementary steps of methane activation and further transformation of the CH_x species into acetylene via C–C coupling over the active FeC_3^- cluster have been identified, implying that the monofunctional mechanism possibly operates over the surface of metal/zeolites and Fe@SiO_2 catalysts for non-oxidative aromatization of methane. Note that the single Fe atoms in both SiFeC_2 active site and FeC_3^- cluster (IS1) are three-fold coordinated.

In summary, the high-temperature conversion of methane to acetylene, an important intermediate for methane aromatization proposed in condensed-phase studies, mediated by mononuclear iron carbide cluster anions of FeC_3^- has been characterized. The detailed elementary steps involving methane activation and further transformation of CH_x into acetylene via C–C coupling exclusively occurring over the active cluster of FeC_3^- reveal a molecular level origin of the monofunctional mechanism for non-oxidative methane aromatization proposed in condensed-phase systems.

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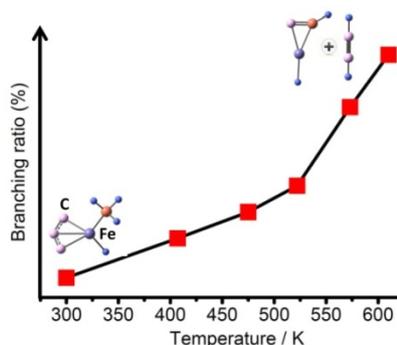
Keywords: methane transformation • metal carbide cluster • high temperature reaction • mass spectrometry • density functional calculations

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The generation of C–C coupling product of acetylene in the high temperature reaction of methane with atomic cluster species (FeC_3^-) has been identified, providing a molecular level origin of the monofunctional methanism for non-oxidative methane aromatization proposed in condensed phase systems.



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Formation of Acetylene in the Reaction of Methane with Iron-Carbide Cluster Anions FeC_3^- under High-Temperature Conditions

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