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 owing 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$_y^-$) under high-temperature conditions to produce C–C coupling products 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, which was 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,C$_x$) sites formed in the induction period activate methane and convert the resulting CH$_2$ intermediates into ethylene,[4] which reacts further to produce benzene at the Brønsted acid sites in the zeolites. An alternative monofunctional mechanism in which both the activation of methane to form an acetylene intermediate and the subsequent aromatization take place over M,C$_x$ sites was also proposed.[5] Recently, single iron atoms embedded in a silica matrix (Fe@SiO$_2$) were reported to convert methane into 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.[6a,7] However, detection of intermediates formed in elementary reactions is usually inaccessible in condensed-phase studies.

Gas-phase studies of the elementary reactions between methane and isolated transition metal carbide clusters (M,C$_x^-$), 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,C$_x^-$ clusters with methane have been extensively studied under room-temperature conditions.[9] Little attention was paid to the reactions of M,C$_x^-$ 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$_y^-$) 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 Methods in the Supporting information).[10] The FeC$_2^-$ and FeC$_3^-$ clusters show similar reactivity toward methane, whereas FeC$_4^-$ and FeC$_5^-$ clusters are inert (Supporting Information, Figure S1). The reactivity of FeC$_y^-$ is the main focus of this study and the time-of-flight (TOF) mass spectra for the reactions of FeC$_y^-$ with CH$_4$ and CD$_4$ are shown in Figure 1. Upon the interaction of FeC$_2^-$ with CH$_4$ at 300 K, a product peak assigned as FeC$_2$H$_2$ was observed (reaction 1), whereas the other two products FeC$_2$H$_2$ and FeC$_3$H$_2$ were barely observable (Figure 1b). When the reaction temperature increased from 300 K to 610 K (Figure 1c,d), the relative intensities of FeC$_2$H$_2^-$ and FeC$_3$H$_2^-$ products, corresponding to reactions 2 and 3, respectively,
The molecule has an overall barrier of \(4 \times (2–8) \text{X} \text{s}^2\) molecule cm\(^{-4}\). The branches of reaction 1 decreases (Figure 2b), suggesting the consecutive processes: FeC\(_4^-\) + CH\(_4\) --\(\rightarrow\)FeC\(_4H\)\(^-\) --\(\rightarrow\)FeC\(_4H\)\(^2-\) + H\(_2\) or FeC\(_4H\)\(^2-\) + C\(_2\)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 FeC\(_4^-\) + CH\(_4\) \((2–8) \times 10^{-13} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\) 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.\(^{[14,12]}\)

Density functional theory (DFT) calculations were performed to study the structures and reaction mechanisms of FeC\(_4^-\). Cyclic (IS1) and linear (IS2) structures (Supporting Information, Figure S4) with quartet spin multiplicities were separately proposed as the lowest-lying energy isomers of FeC\(_4^-\).\(^{[13]}\) The gas-phase ion chromatography experiments\(^{[14]}\) indicated that both cyclic and linear structures of FeC\(_4^-\) can be produced in the experiments. The adopted M06L functional (see Theoretical Methods in the Supporting Information) predicts that the quartet \(1^4\)IS1 and \(1^4\)IS2 structures are close in energy (0.14 eV) and the doublet \(2^2\)IS1 and \(2^2\)IS2 are above the \(4^1\)IS1 and \(4^1\)IS2 by 0.27 and 0.09 eV, respectively (Supporting Information, Figure S4). As a result, both \(1^1\)IS1 and \(1^1\)IS2 can be produced by our experiment and \(1^1\)IS1 and \(1^1\)IS2 may also be populated through thermal equilibrium (Supporting Information, Figure S5).

The potential energy surfaces (PESs) for methane activation by all of the four species \((4^1\)IS1 and \(2^2\)IS2) were explored (Figure 3; Supporting Information, Figure S7). High overall positive barriers (> 0.5 eV) are 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 \((4^1\)IS2; Supporting Information, Figure S7) can merge into the PESs from the cyclic structures \((4^1\)IS1, Figure 3), so only the reaction mechanism of \(1^1\)IS1 + CH\(_4\) is described below.

The reaction of \(1^1\)IS1 + CH\(_4\) has an overall barrier of 0.58 eV that can be hardly overcome at 300 K (Supporting Information, Figure S14). The observed reactivity in Figure 1b can be due to the doublet FeC\(_4^-\).\(^{[15]}\) Figure 3 indicates that \(2^2\)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 \((1^1\)IS1 --\(\rightarrow\)TS1 --\(\rightarrow\)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--CH\(_2\) 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 \((TS1 --\(\rightarrow\)CP1 --\(\rightarrow\)I2; Supporting Information, Figure S8), the reaction proceeds along the quartet surface. Upon a ring-opening isomerization \((I2 --\(\rightarrow\)I3\), the C--C coupling takes place \((I3 --\(\rightarrow\)TS3 --\(\rightarrow\)I4) and the TS3 is lower.
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In eV) with respect to $\text{T}$. Further elimination products (reactions 2 and 3). Further are given. Bond

DFT calculated a) potential energy profiles and b) structures for FeC $\text{H}_2$. The isometric structures of FeC$^+$, FeC$^+$, and FeC$^+$ are given in the Supporting Information, Figures S4, S10, and S11, respectively. The transition states and some intermediates can be found in the Supporting Information, Figure S6. The zero-point vibration corrected energies ($\Delta$H in eV) for C $\text{H}_2$ are given. Bond lengths are given in pm.

Figure 3. DFT calculated a) potential energy profiles and b) structures for FeC$^+$ (IS1) + CH$_4$. The isometric structures of FeC$^+$, FeC$^+$, and FeC$^+$ are given in the Supporting Information, Figures S4, S10, and S11, respectively. The transition states and some intermediates can be found in the Supporting Information, Figure S6. The zero-point vibration corrected energies ($\Delta$H in eV) with respect to IS1 + CH$_4$ are given. Bond lengths are given in pm.

than IS1 + 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 IS5, in which Fe site is coordinated with two H atoms. The four-membered ring (IS5 embraces the CH$_4$ moiety to form five-membered ring (IS5–IS6) and one of H atoms transfers from Fe atom to the carbon ligand to form IS7, the most stable structure on the potential energy surface. The intermediate IS7 has enough energy (ca. 2 eV) to relax (IS7–IS8) and then to activate the third C–H bond of CH$_4$ (IS8–IS9). After a structural rearrangement to break the Fe–C bond in IS9, the fourth C–H bond can be activated to form intermediate IS11, 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$^+$ (P1; Supporting Information, Figure S10, reaction 2).

Along with the generation of dihydrogen, there is a competing reaction for C$_2$H$_2$ formation (reaction 3). After activation of the third C–H bond of methane to form intermediate IS11, one H atom can transfer from the Fe site to a C atom of C$_2$H$_2$ unit. The first C–H bond of CH$_4$ can release enough energy to overcome the barrier of the second C–H bond activation and generate the intermediate IS14 has enough internal energy to break [H,C$_2$–CH$_2$] bond to generate the intermediate IS15 with isolated [HC=CH] unit, which can be evaporated to produce the experimentally observed FeC$_2$H$_4$ product ions (P2; Supporting Information, Figure S11). The pathway for incorporation of the C atom from CH$_4$ into [HC=CH] unit is also considered (Supporting Information, Figures S12 and S13). From the intermediate IS7, the H atom bonded with Fe can transfer to the adjacent C atom of [CH$_2$] moiety to form intermediate IS16 with two equivalent [CH$_2$] units. Then, the third C–H bond of methane is activated to form intermediate IS17, the structure of which is similar to that of IS7. Further transformation of IS17 to generate HC=CH product follows the pathway similar to IS7–P2 + C$_2$H$_2$.

In the case that the reaction starts with IS1 + 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 IS2–CH$_4$ (Supporting Information, 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 the Supporting Information, Figure S14). As a result, the reactions 1–3 are thermodynamically and kinetically favorable at 300 K. The energy of FeC$_2$H$_4$ + H$_2$ (P1, −0.83 eV) is significantly lower than that of FeC$_2$H$_4$ + C$_2$H$_2$ (P2, −0.17 eV), which is qualitatively consistent with the higher branching ratio of FeC$_2$H$_4$ over that of FeC$_2$H$_2$ (Figure 2b).

The doublet FeC$_2$ can activate and transform methane at 300 K (Figure 1b) while the reaction efficiency is very low (on the order of 10$^{-6}$). The high energy barrier ($^{4}$TS$^\leftrightarrow$ IS3 = 0.95 eV) of the tight transition state $^{4}$TS3 ($\DeltaG_{(T=298)}^{\leftrightarrow} = +$ 0.56 eV) for C–C coupling is the bottleneck to form the H$_2$ and C$_2$H$_2$ elimination products (reactions 2 and 3). Further
more, the spin conversion in the C−H activation (\( \text{TS1} \rightarrow \text{CP1} \rightarrow \text{I2} \)) may also slow down the formation of \( \text{I3} \) that is the most possible candidate of the experimentally observed adsorption complex \( \text{FeC}_x\text{H}_y \) (reaction 1). The above two rate limiting processes (\( \text{I3} \rightarrow \text{TS3 and TS1} \rightarrow \text{I2} \)) can be enhanced by elevation of reaction temperature, which is consistent with the significant increase of rate constant from 300 K to 410 K (Figure 2a). Note that at 300 K, the quartet \( \text{FeC}_3^- \) is unlikely to contribute to the observed reactivity because very tiny percentage (10−8) of CH4 molecules have enough kinetic energy to overcome the high reaction barrier (0.55–0.58 eV; Supporting Information, Figure S14). At high temperatures (ca. 600 K), the quartet \( \text{FeC}_3^- \) may react with a fair amount of CH4 (0.03–0.09 %), which is consistent with a sharp increase of the rate constant from 575 K to 610 K in the experiment (Figure 2a).

During the gas-phase experiment, the adsorption complex \( \text{I3} \) can be stabilized through the collisions with the bath gas. Alternatively, it can transform to separated products (\( \text{I3} \rightarrow \text{FeC}_x\text{H}_y + \text{H}_2 \) or \( \text{FeC}_x\text{H}_y + \text{CH}_4 \)) or dissociate back to separated reactants (\( \text{I3} \rightarrow \text{FeC}_x^- + \text{CH}_4 \)). The temperature increase should always favor the formation of separated products and the total rate constant of reactions 2 and 3 increase during the entire temperature range (from 300 K to 610 K; Supporting Information, Figure S3). However, the increased temperature disfavors the stabilization of adsorption complex. As a result, reaction 1 can have a negative temperature dependence (from 410 K to 610 K in the Supporting Information, Figure S3). The coexistence of multiple species and the negative temperature dependence of the association reaction are responsible for the non-Arrhenius temperature dependence of the total rate constants shown in Figure 2a.

The gas-phase reactions of methane with transition-metal carbide cluster cations\(^{[9a,b,d,e]} \) (\( \text{TaC}_x\text{H}_y^+ \), \( \text{MoC}_x^+ \), \( \text{AuC}_x^+ \), and \( \text{CuC}_x^+ \)) and the anions\(^{[9,k]} \) (\( \text{FeC}_3^- \) and \( \text{Ta}_2\text{C}_3^- \)) have been previously studied by mass spectrometric experiments under room-temperature conditions. The generation of ethylene has been identified for many of the cations and the production of acetylene was only observed for the \( \text{TaC}_x^+ \).\(^{[90]} \) The cluster anions are generally much less reactive than the corresponding 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,\(^{[99]} \) 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 \( \text{FeC}_3^- \) with methane under high-temperature conditions.

In condensed-phase studies of methane aromatization, a consensus that the formation of \( \text{CH}_4 \) 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\(^{[20,10]} \) (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 \( \text{H}_2 \)\(^{[20]} \) 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.\(^{[9b]} \) 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\(_3\) 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 \( \text{FeC}_3^- \), has been characterized. The detailed elementary steps involving methan activation and further transformation of CH\(_3\) 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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**Conflict of interest**

The authors declare no conflict of interest.

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