

Review

Non-Oxidative Coupling of Methane Catalyzed by Heterogeneous Catalysts Containing Singly Dispersed Metal Sites

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Abstract: Direct upgrading of methane into value-added products is one of the most significant technologies for the effective transformation of hydrocarbon feedstocks in the chemical industry. Both oxidative and non-oxidative methane conversion are broadly useful approaches, though the two reaction pathways are quite distinguished. Oxidative coupling of methane (OCM) has been widely studied, but suffers from the low selectivity to C₂ hydrocarbons because of the overoxidation leading to undesired byproducts. Therefore, non-oxidative coupling of methane is a worthy alternative approach to be developed for the efficient, direct utilization of methane. Recently, heterogeneous catalysts comprising singly dispersed metal sites, such as single-atom catalysts (SAC) and surface organometallic catalysts (SOMCat), have been proven to be effectively active for direct coupling of methane to product hydrogen and C₂ products. In this context, this review summarizes recent discoveries of these novel catalysts and provides a perspective on promising catalytic processes for methane transformation via non-oxidative coupling.

Keywords: methane; non-oxidative coupling; single-atom catalysts; surface organometallic catalysts



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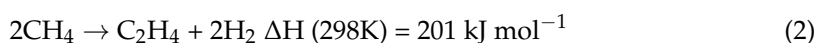
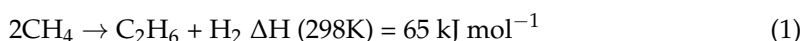
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1. Introduction

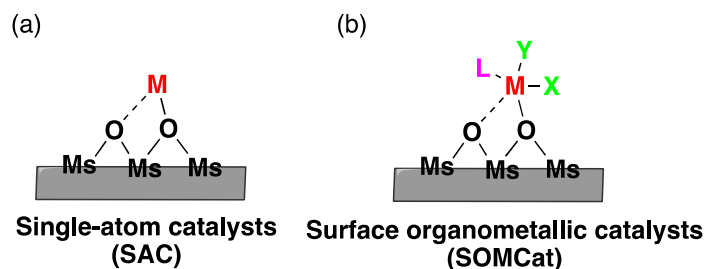
Methane (CH₄), the major component of natural gas or shale gas, is a significant energy resource and a basic raw gas for the C1 chemical industry [1–5]. The transformation of methane into various high-value chemicals, including hydrogen (H₂), oxygenates, olefins, and other hydrocarbons, is a critical technology for chemical and energy supply [6–14]. The conventional productions of valuable chemicals such as alkanes, benzene, methanol, carboxylic acids, etc., include indirect conversion of methane, which involves firstly dry reforming/wet reforming of methane to produce syn-gas (mixture of CO and H₂) and, subsequently, transformation of syn-gas into other materials [1,15–18]. Because such a two-step process requires high temperature and energy costs, it has drawn dramatic attention to the direct conversion of methane approaches as low-cost alternatives. Moreover, the process of ethylene production from methane coupling is a particularly essential way to utilize methane effectively, since ethylene is a highly important commodity chemical for many manufacturing products. Many excellent review articles have discussed the oxidative coupling of methane (OCM) to produce ethylene [19–24]. Low reaction temperatures of methane coupling have been achieved by involving oxidative agents; however, the selectivity to C₂ hydrocarbons is low due to over-oxidation leading to undesired products. Alternatively, non-oxidative coupling of methane (NOCM) to produce ethane (C₂H₆) or ethylene (C₂H₄) and hydrogen (H₂) (Equations (1) and (2)) is another critical method, as it utilizes the simplest C–C coupling process.



Different types of catalysts have been developed to achieve efficient non-oxidative methane coupling. Notably, the transformation of methane is challenging because of its chemical inertia [4,25]. Classical heterogeneous catalysts for NOCM include noble metal nanoparticles such as Pt- or Pd-based catalysts [26–28] and some bimetallic catalysts, such as Pt-Sn or Pt-Bi on supports [29,30]. However, these metal-based heterogeneous catalysts result in low yields to hydrocarbon products and intensive coke formation during NOCM, leading to the quick deactivation. The high temperature required for activating the C–H bonds of methane also causes the sintering of nanoparticles and further deactivation of metal catalytic sites. Mo-based catalysts are another promising heterogeneous catalyst for NOCM, but the selectivity towards C₂ hydrocarbons is not dominant [31–34]. In general, a multistep process is involved for NOCM via conventional catalysts [35]: (i) methane dissociation on metal particles, (ii) stepwise surface carbon–carbon bond formation, and (iii) formation of products through hydrogenation and desorption from catalysts. From an economic viewpoint, the practical catalysts achieving at least 25% selectivity of C₂H₆ and less than 20% coke formation would be available for commercial applications [36]. Therefore, new types of heterogeneous catalysts need to be developed for more efficient NOCM.

Recently, two new types of heterogeneous catalysts, namely, single-atom catalysts (SAC) and surface organometallic catalysts (SOMCat), have been found to be catalytically active for NOCM reaction. Since the last century, these two types of heterogeneous catalysts have been broadly studied and developed, presenting outstanding catalytic activity for various chemistry reactions [37–56].

There are many critical reviews regarding SAC and SOMCat that clarify their concepts and demonstrate their applications [57–61]. Here, a brief introduction to the SAC and SOMCat is illustrated. The “single-atom catalysts” are commonly described as materials consisting of isolated, dispersed metal atoms supported or embedded on a solid support (oxide, carbide, nitride, sulfide, etc.) [37,43,50,51,62–64], or even on the surface layer of a metal host; these are also called single-atom alloy catalysts [65–68]. The nature of the interactions between the metal center and the support surface can be different, involving covalent, coordination, or ionic bonds (Scheme 1a). Given the identification of SAC, the structure and the reactivity of that isolated atom could be tailored and rationalized through the rules of molecular chemistry (either coordination or organometallic chemistry). Differently from SAC, the “surface organometallic catalysts (SOMCat)”, which are developed on basis of the discipline of surface organometallic chemistry (SOMC) [38–40,52,57,69], are materials comprising the catalytically active sites formed via the reaction of organometallic complexes or coordination compounds with well-defined surfaces (oxides, metal nanoparticles, carbon, graphene, etc.). The metal sites of these supported organometallic compounds will form covalent or ionic bonds to the solid support while retaining at least some of the ligands in the original complexes that present the target functionalities (Scheme 1b). Thus, the formed SOMCat contains specifically active moieties (X and Y in Scheme 1b) based on the proposed mechanism derived from well-established steps in molecular chemistry and other necessary ligands (L in Scheme 1b) assisting in controlling the oxidation state, geometry, or d_n configuration of the metal within the catalytic cycle. Certain similarities present in SAC and SOMCat are (1) creating isolated metal atoms on surfaces, with preexisting ligands or without ligands; and (2) applying isolated single atoms in heterogeneous catalysis with elevated activity based on the understanding of elementary steps in molecular or coordination chemistry. Moreover, the SOMC methodology can be employed to prepare singly dispersed atoms by combining grafting of precursors on surfaces and removing all organic ligands through a thermolytic, nonoxidative procedure. Both SAC and SOMCat methodologies can be used to design catalysts containing certain active sites that are crucial for catalysis.



Scheme 1. Structures of (a) single-atom catalyst (SAC) and (b) surface organometallic catalyst (SOMCat). Note: grey rectangle indicates support materials; Ms is the metal atom in the support; O is the oxygen atom in the support; M is the catalytic active metal; X and Y indicate specifically active moieties; and L indicates the other necessary ligand. Reproduced with permission from ref. [61]. Copyright 2014 American Chemical Society.

Thus, in this review, we will summarize the essential examples of SAC and SOMCat, discovered recently, that present good catalytic performances of NOCM. We will also discuss our understanding of the NOCM mechanism via two types of catalysts. The combination of catalysis and theoretical studies will provide a perspective for the design and development of desired catalysts for direct transformation of methane to produce hydrogen and C₂ hydrocarbons.

2. Heterogeneous Catalysts Containing Singly Dispersed Metal Sites Active for Non-Oxidative Methane Coupling

As shown in Table 1, catalysts containing singly dispersed metal sites have been discovered to be efficiently active for non-oxidative coupling of methane.

Table 1. List of representative heterogeneous catalysts with singly dispersed metal sites active for methane non-oxidative coupling to produce hydrogen and C₂ hydrocarbons.

Catalysts ¹	T (°C)	Catalytic Performance	Ref.
0.5 wt% Fe@SiO ₂	1090	Conversion of CH ₄ = 48.1% Selectivity of C ₂ H ₄ = 48.4%	[70]
Fe@SiO ₂ ²	1030	Conversion of CH ₄ = 20–30% Selectivity of C ₂ hydrocarbons = 65%	[71]
Fe@CRS	1080	Conversion of CH ₄ = 6.9–5.8% Selectivity of C ₂ hydrocarbons = 86.2%	[72]
[Fe]CHA	700–800	Conversion of CH ₄ = ~2% Selectivity of C ₂ hydrocarbons = >90%	[73]
Pt ₁ @CeO ₂	975	Conversion of CH ₄ = 14.4% Selectivity of C ₂ hydrocarbons = 74.6%	[74]
[Ta]-SiO ₂	250–475	conversion of CH ₄ = 0.5% Selectivity of C ₂ H ₆ = 50% (>98% among hydrocarbons) Cumulative TON = 40	[75]
[W]-H@γ-Al ₂ O ₃ ¹	350	Conversion of CH ₄ = 0.6% Selectivity of C ₂ H ₆ = 93% Cumulative TON = 40	[76]

Note: ¹ Both @ and @ here mean singly dispersed metal sites. ² The catalyst Fe@SiO₂ was evaluated in a membrane reactor for the non-oxidative coupling of methane (NOCM) reaction.

2.1. Catalytic Performance and Structure of Single-Atom Catalysts

In 2014, Bao and co-workers reported the direct non-oxidative coupling of methane producing C_2 hydrocarbons (especially ethylene) catalyzed by the single iron atoms embedded in a silica matrix, $Fe@SiO_2$, at high efficiency [70]. This single-dispersed iron catalyst, 0.5 wt% $Fe@SiO_2$, was prepared by firstly fusing the mixture of ferrous metasilicate and commercial silica at 1700 °C after ball milling under high-purity Ar at 450 rpm for 15 h, sequential leaching with aqueous nitric acid, and drying at 80 °C. Studies of sub-angstrom-resolution high-angle annular-dark field (HAADF) scanning transmission electron microscopy (STEM) and in situ X-ray absorption near-edge spectroscopy (XANES) have shown that Fe species form singly dispersed sites bonded with two C atoms and one Si atom (Figure 1a), that is, the Fe atoms are singly embedded within the SiO_2 matrix during the activation under reaction conditions (90 vol% CH_4/N_2 , space velocity = 800–1000 $mL \cdot g^{-1} \cdot h^{-1}$) at 900 °C for 2 h. These isolated Fe atoms, coordinated by one Si and two C atoms, were also discovered to be the most stable structure through density functional theory (DFT) calculations. A maximum methane conversion of 48.1% was achieved at 1090 °C, the high selectivity of ethylene peaked at 48.4%, and the total hydrocarbon selectivity exceeded 99%, representing the fact that this transformation process of methane is atom-economical (Figure 1b). Such unprecedented efficiency of the catalytically initiation of CH_4 may have resulted from the high activity of the CH_4 association on low-coordinated iron sites [77,78]. More importantly, the conversion of methane into ethylene was stably catalyzed by lattice-confined single iron sites, presenting no apparent deactivation during the time study for up to 60 h (Figure 1b). The confined/embedded interaction between FeC_2 sites and the SiO_2 matrix led to a good stabilization of isolated metal atoms, preventing the aggregation and sintering of metal sites. The single-site nature was found to be essential to preventing coke formation, as the absence of iron nanoparticles or adjacent iron sites avoids the coke deposition resulting from catalytic C-C coupling and further oligomerization. The coke formation and oligomerization were also prevented by optimizing the reaction conditions, particularly the space velocity and the temperature. In addition, the conversion of methane and selectivity of C_2 products from the $Fe@SiO_2$ -catalyzed NOCM were significantly promoted by employing a hydrogen-permeable tubular ($SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$) membrane to separate hydrogen [71]. And more mechanistic and kinetic studies were also conducted to optimize the ideal reaction conditions of $Fe_1@SiC_2$ -catalyzed, direct, non-oxidative coupling of methane to produce C_2 hydrocarbons [79,80]. Furthermore, $Fe@CRS$ is another NOCM catalyst with silica (polymorph cristobalite)-supported active Fe sites synthesized by a similar fusing process [72]. X-ray adsorption spectroscopy (XAS) studies and computing simulations indicated that isolated iron carbides formed on silica are the active species for NOCM. By cofeeding 50% H_2 at 1080 °C, 6.9–5.8% methane conversion and 86.2% C_2 selectivity were achieved from NOCM via $Fe@CRS$ for 100 h.

In 2023, another catalyst of singly dispersed iron sites on zeolite $[Fe]MFI$ and $[Fe]CHA$ was reported to present high selectivity to ethylene and ethane from the non-oxidative activation of methane. Such Fe-based catalysts were synthesized via specifically developed direct hydrothermal synthesis techniques [73]. Compared to the MFI- or CHA-supported Fe_2O_3 nanoclusters formed using the impregnation method, single-Fe catalysts obtained 4–5-fold more selectivity to C_2 hydrocarbons (>90% for $[Fe]MFI$ and >99% for $[Fe]CHA$). The in situ X-ray absorption spectroscopy uncovered the isolated Fe^{3+} centers in the zeolite framework of fresh catalysts are reduced during the reaction to the active sites, including Fe^{2+} species and Fe (oxy)carbides dispersed in zeolite pores. Deactivated $[Fe]$ zeolites can be regenerated by burning coke in air.

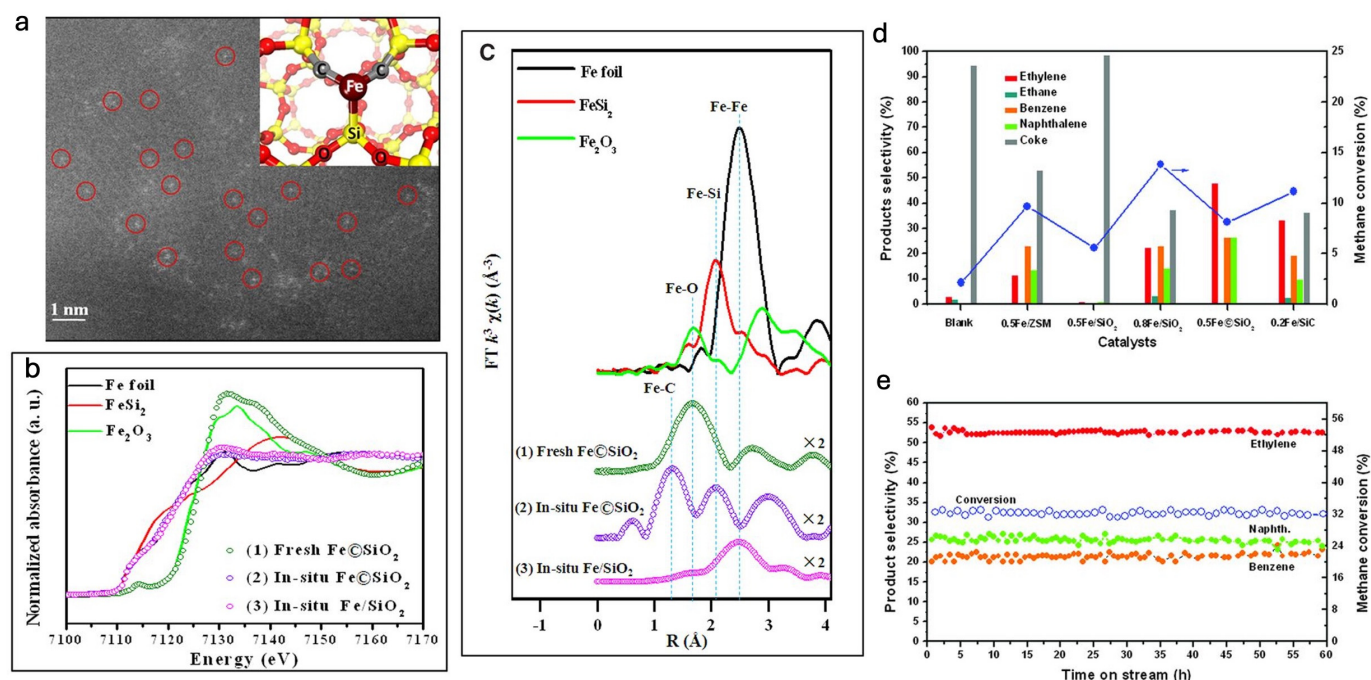


Figure 1. Structural features and reaction performance of 0.5 wt% Fe@SiO₂. (a) STEM-HAADF image of the catalyst after reaction, with the inset showing the computational model of the single iron atom bonded to two C atoms and one Si atom within the silica matrix. (b) In situ XANES upon activation and (c) Fourier-transformed (FT), k^3 -weighted $\chi(k)$ -function of the EXAFS spectra. Note: Solid lines denote reference samples of Fe foil, FeSi₂, and Fe₂O₃. Line 1 denotes the fresh 0.5% Fe@SiO₂. Line 2 stands for 0.5% Fe@SiO₂ and line 3 for 0.5% Fe/SiO₂ upon activation in 10% CH₄/N₂ at 1173 K for 2 h. R(Å): distance in angstroms. (d) Comparison of different catalysts at 1223 K and 4.84 L gcat⁻¹ h⁻¹. (Note: the blue dots and line mean methane conversion). (e) Long-term stability test of 0.5% Fe@SiO₂ at 1293 K and 14.5 L gcat⁻¹ h⁻¹. Reproduced with permission from ref. [70]. Copyright 2014 The American Association for the Advancement of Science.

Aside from Fe-based single-atom catalysts, other catalysts containing singly dispersed Pt sites were also explored to achieve an advanced catalytic performance for methane non-oxidative coupling. Wang and co-workers synthesized nanoceria-supported atomic Pt catalysts, namely, Pt₁@CeO₂, through high-temperature (1000 °C) calcination of Pt-impregnated porous ceria nanoparticles [74]. The combination of aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) [81], X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [82] analyses confirmed the atomic dispersion of Pt on a nano-CeO₂ support. Compared to the nanoparticulated Pt catalysts, the Pt₁@CeO₂ catalyst demonstrated a superior catalytic performance of methane under equivalent conditions, achieving 14% conversion of methane at 975 °C and ~75% selectivity toward C₂ products (ethane, ethylene, and acetylene). The catalyst also displayed good stability during NOCM up to 60 h. The atomic Pt sites were found to act as catalytic sites for the selective conversion of methane into C₂ hydrocarbons and to suppress carbon coking.

Recently, Emiel and co-workers also synthesized the isolated dispersed Pt/CeO₂ catalyst via flame spray pyrolysis under the harsh conditions of an NOCM reaction [83]. The sintering of isolated Pt sites during the reaction at 800 °C led to a loss in the yield of C₂ products. Interestingly, the redispersion of agglomerated Pt could be obtained using an in-situ regeneration strategy in oxygen. It was found that the isolated Pt centers were initial active species which then formed a CePt₅ alloy during the reaction, which also acted as an active phase for direct methane conversion. Another work by Fabio and co-workers [84]

also explored the sintering of surface Pt sites, which were initially singly dispersed on CeO₂, due to coking during the NOCM reaction. These results indicate the nature of active sites is essential for the non-oxidative coupling of methane under industrially relevant conditions, and this will motivate further research on catalyst development for this reaction.

2.2. Reaction Pathway of NOCM via Single-Atom Catalysts

The reaction pathways of NOCM catalyzed by single-iron-atom catalysts were proposed to involve an initial generation of methyl radicals on isolated iron sites and a sequential series of gas-phase reactions forming C₂ products [70]. The mechanism was found to include the C–H bond of CH₄, which was firstly cleaved over isolated iron sites, giving •CH₃; the formed •CH₃ species were then desorbed into the gas phase, forming C₂H₆ and C₂H₄ via coupling and further dehydrogenation. The observation of an ionization energy of 10.6 eV from online vacuum ultraviolet soft photoionization molecular-beam mass spectrometry [85,86] supports the notion that methyl radicals are formed and desorbed from isolated iron sites instead of catalytic C–C coupling on the surface due to the lack of adjacent iron sites.

Li and co-workers proposed an alternative surface reaction mechanism of NOCM on silica-embedded iron catalysts through computational modeling and simulations (Figure 2) [87]. The dissociated methyl groups preferred to transferring to adjacent carbon sites of the active center (Fe₁@SiC₂) rather than to desorbing into the gas phase under reactive conditions. Additionally, a key –CH–CH₂ intermediate was found for the formation of the main product (ethylene) through C–C coupling of migrated methyl and bonding with a hydrogen atom transferred from an adjacent Fe site. Overall, as shown in Figure 2, the C–H bond of CH₄ was firstly cleaved on iron sites and dissociated to CH₃ and H species adsorbed on the Fe atom. The formed CH₃ group quickly diffused to adjacent unsaturated C sites, resulting in –C–CH₃ and –Fe–H intermediate species (the CH₃ and H adsorbed on C and Fe sites, respectively), and the –CH–CH₂ intermediate was then formed from –C–CH₃ through two steps of hydrogen transfer. After obtaining another hydrogen atom from an adjacent Fe site, the –CH–CH₂ intermediate finally transformed to a CH₂CH₂ molecule. After desorbing the CH₂CH₂, the active sites (Fe₁@SiC₂) were regenerated by the activation of another CH₄ on the Fe–C dual site of Fe₁@SiC₂. Such a whole catalytic cycle (Figure 2) is considered to be a quasi-Mars–van Krevelen (quasi-MvK) surface reaction mechanism [88,89] involving withdrawal and regeneration the surface carbon atoms, which undergo methane activation; the combination of carbon species from methane and the active center; and the recovery of the active center via gas-phase carbon recourse. The highest activation barrier is 2.24 eV, associated with regeneration of the active center through the activation of a second methane and subsequent carbon insertion into the surface, while the barrier of the active center regeneration step in the gas-phase reaction mechanism is 3.23 eV. According to the energetic span model [90], the rate constant of the above surface reaction pathway is $1.63 \times 10^5 \text{ s}^{-1}$ at 1090 °C, which is >4000 times larger than the rate constant of the gas-phase reaction pathway. Thus, the lower barrier energy and faster rate indicate that the quasi-MvK surface reaction mechanism is more plausible than the alternative gas-phase reaction mechanism for the non-oxidative conversion of methane on Fe₁@SiC₂. Here, both Fe and C at the active site participate in the catalytic pathway, suggesting that synergetic interaction of dual site could be essential for the complicated reaction of methane non-oxidative coupling to produce C₂ hydrocarbons.

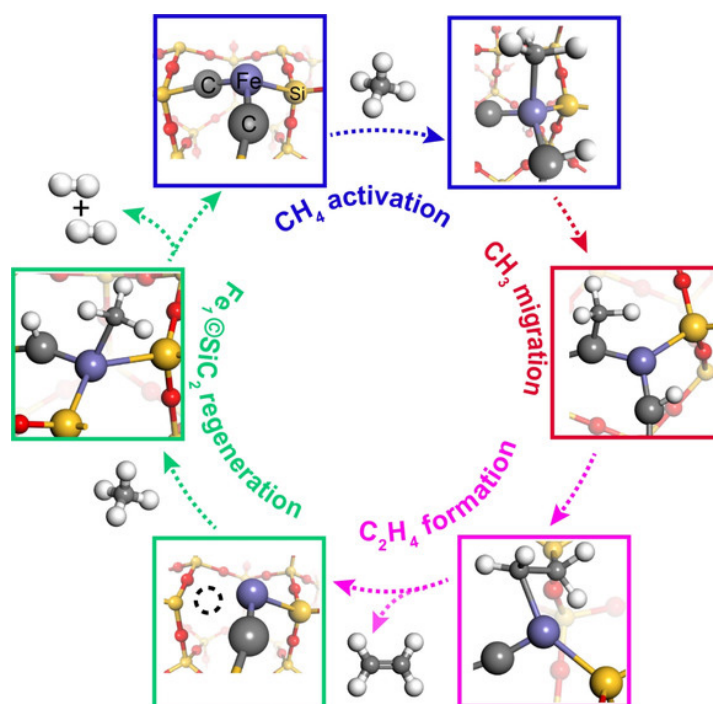


Figure 2. Illustration of quasi-Mars–van Krevelen mechanism of methane conversion at the $\text{Fe}_1\text{@SiC}_2$ active center. Reproduced with permission from ref. [87]. Copyright 2020 John Wiley and Sons.

In terms of platinum singly dispersed on ceria catalysts, both active platinum centers and the ceria support have been proposed to play important roles in the oxidative coupling of methane to produce C_2 products [74]. As the π -bonded ethylene and acetylene were observed from DRIFTS analysis of the $\text{Pt}_1\text{@CeO}_2$ catalyst after methane activation at 900°C , methane activation via single Pt sites could involve adsorbing C_2 intermediates possibly generated from catalytic coupling of two dehydrogenated C_1 adsorbates (such as $^*\text{CH}_3$ and $^*\text{CH}_2$). The CeO_2 could stabilize the single-atom Pt sites and also assist in the activation of CH_4 resulting from the synergetic effects between CeO_2 and Pt sites. These findings of synthetic functions from iron and platinum catalysts may lead to a promising way to develop more effective heterogeneous catalysts.

2.3. Catalytic Performance and Sites of Surface Organometallic Catalysts

The silica-supported single-site $[\text{Ta}]\text{--H}$ catalyst was the first example of a SOMC-based catalyst active for the non-oxidative coupling of methane to produce ethane and hydrogen, and was reported in 2008 [75]. The surface organometallic $(\equiv\text{SiO})_x\text{Ta}(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_{3-x}$, prepared by grafting $\text{Ta}(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_3$ [91] onto dehydroxylated commercial silica (at 500°C), was treated under H_2 at 250°C to form the silica-supported tantalum hydride $\text{SiO}_2\text{--}[\text{Ta}]\text{--H}$ [92,93]. Under a pressure of 50 bar, methane was converted into ethane and hydrogen was catalyzed by $\text{SiO}_2\text{--}[\text{Ta}]\text{--H}$ in a continuous flow reactor at $250\text{--}450^\circ\text{C}$. A high selectivity of ethane ($\geq 98\%$ among other hydrocarbons) was obtained, along with an equimolar amount of hydrogen (at 300°C). This supported tantalum catalyst also continuously obtained stable ethane selectivity of 50% at 300°C for more than 200 h, indicating good stability during NOCM at a moderate temperature. A maximum cumulative turnover number (TON) of 40 was achieved at 475°C after 147 h. Thus, this supported organometallic $\text{SiO}_2\text{--}[\text{Ta}]\text{--H}$ can achieve effective non-oxidative coupling transformation of methane into ethane and hydrogen at moderate temperatures. Based on spectroscopic studies (IR, SSNMR), the $\text{Ta}\text{--CH}_3$, $\text{Ta}(\text{H})(=\text{CH}_2)$ and $\text{Ta}\equiv\text{C}\text{--H}$ species may be plausible key reaction intermediates for NOCM (see mechanism discussed below).

In 2010, silica–alumina or alumina-supported single-site $[\text{W}]\text{--H}$ coupled with a membrane was reported to achieve a better yield than the $[\text{Ta}]$ catalyst [76]. Similarly to the

supported [Ta] catalyst, supported [W]–H catalysts were prepared from the H₂ treatment SiO₂–Al₂O₃ or γ -Al₂O₃-grafted W($\equiv$ CtBu)(CH₂t-Bu)₃ at moderate temperatures (150 °C) [94,95]. A high ethane selectivity (>99% among hydrocarbon) was produced from the non-oxidative coupling of methane via supported [W]–H in a classical fixed-bed reactor. A constant conversion and a high selectivity for ethane up to 10 days (TON = 35) confirmed that the supported [W]–H catalysts were more stable than their [Ta]–H counterparts. In addition, a Pd–Ag membrane was employed in a fixed-bed reactor to separate generated hydrogen, leading to methane coupling far beyond the thermodynamic equilibrium conversion, which was limited at a low temperature. Thus, a significant enhancement of the yield was achieved in the membrane reactor, giving TON = 40 after 2500 min (20 times higher than in a classical reactor under equivalent conditions). As methyl, tungsten methyl, carbene, and carbyne species were observed from spectroscopic analysis, the reaction pathway probably involves similar steps to those of other alkane metathesis reactions (see mechanism discussed below).

Single-atom iron catalysts active for the direct conversion of methane were discussed in the previous section. Here, another type of single-iron(II) site supported on silica was prepared via surface organometallic chemistry methodology, forming $\equiv$ SiO–Fe_n(OSi(OtBu)₃)_{2n–1}. It was further treated at 1020 °C in a vacuum, forming atomic dispersion of Fe sites [($\equiv$ SiO)₂–Fe] [96]. Such single-iron sites were confirmed via characterizations of IR spectroscopy, X-ray adsorption spectroscopy, and ⁵⁷Fe Mössbauer spectroscopy. This single-iron catalyst demonstrated a rapid initiation of methane coupling at 1000 °C, resulting in 15–22% selectivity towards hydrocarbons at 3–4% conversion, supporting the notion that iron sites facilitate faster initiation of radical reactions and adjust the surface reactivity. However, during that process, the Fe(II) sites were found to be quickly reduced and to form carburized Fe⁰ nanoparticles, accompanied by the deposition of coke and the formation of surface hydrosilanes and paramagnetic defects. Similarly to previous singly dispersed platinum catalysts, the loss of single-atom sites, e.g., those reduced into nanoparticle sites, led to the deactivation of catalysts for the coupling of methane into hydrocarbons. Thus, it is essential to design and develop heterogeneous catalysts consisting of singly dispersed metal sites that are effective and stable (at relatively high temperatures) in future research.

2.4. Mechanisms of NOCM via Surface Organometallic Catalysts

Similar catalytic working cycles of non-oxidative methane coupling via Ta- and W-catalysts were proposed (Figure 3a), as mentioned above [40,61,75,76], since the equivalent reaction intermediates [M]–CH₃, [M]=CH₂, and [M] $\equiv$ CH ([M] indicates metal centers) were observed from spectroscopic characterization (IR, SSNMR) of both supported [Ta]–H and supported [W]–H (Figure 3b). Firstly, metal hydride [M]–H was activated with methane via the σ -bond metathesis step, forming metal-methyl [M]–CH₃ and H₂ [97,98]. Metal methylidene hydride [M](=CH₂)(H) was then generated through α -H elimination from the CH₃ ligand. The hydride of this intermediate reacted with another methane, which produced hydrogen and metal methyl methylidene [M]–(CH₃)(=CH₂). Next, the metal-ethyl [M]–CH₂CH₃ was formed from the migration of the methyl ligand to the methylidene [99]. Finally, this ethyl species reacted with another methane via σ -bond metathesis to release ethane and regenerate catalytic sites. Note that another catalytic cycle was also proposed to involve the metal carbene species [M] $\equiv$ CH that formed through further α -H abstraction of [M](=CH₂)(H), along with the evolution of H₂, and then reacted with another methane to form [M](=CH₂)(CH₃). Several computational simulation works were conducted to further understand the authentic elemental reaction steps of non-oxidative methane coupling to produce ethane via SOMC-based catalysts.

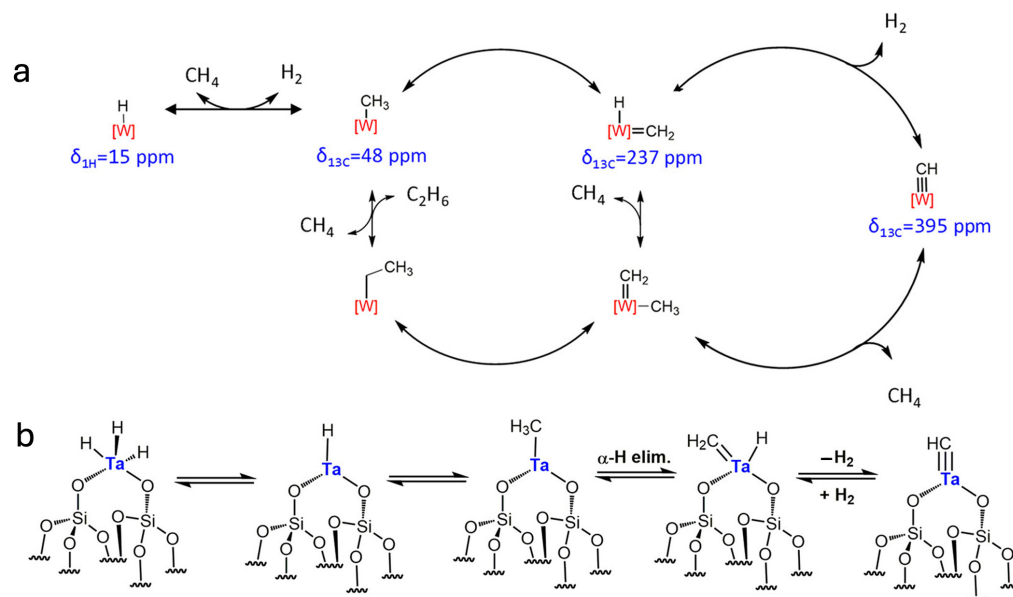


Figure 3. Proposed catalytic cycle of grafted [M]-H catalysts. (a) Detailed mechanism of coupling of methane to ethane, ethylene, and hydrogen using single-site [W]-H catalysts, including SS NMR signals. (b) Initiation reaction in the low-temperature activation of methane with a silica supported [Ta]-hydride. Reproduced with permission from ref. [61]. Copyright 2014 American Chemical Society.

The reaction mechanisms of silica-supported single-site tantalum (Ta)-catalyzed NOCM were firstly studied by DFT calculations [100], which investigated two catalytic cycles, namely, catalytic cycles A (CCA, Figure 4a) and B (CCB, Figure 4c), as well as other competing pathways, to reveal the potential energy surfaces for the reactions of interest. Here, CCA is the NOCM pathway through the supported metal-methyl species, [Ta]-CH₃, comprising five elementary steps: the C-H bond of CH₄ is firstly broken on [Ta]-CH₃ (3); the formed [Ta]-(H)(CH₃)₂ (4) is then changed to [Ta]-(CH₃)(=CH₂) (5) via H₂ elimination and is further transformed to [Ta]-(CH₂CH₃) (6) via intramolecular carbene insertion; then, another CH₄ is activated via 6, forming [Ta]-(CH₃)(H)-CH₂CH₃ (7); and finally, a CH₃CH₃ molecule is eliminated from 7, regenerating 3 active species. The two rate-determining states for the CCA route are (3 + CH₄) and TS-6-7 (Figure 4b), giving an energetic span of 66.0 kcal/mol. On the other hand, CCB is the NOCM catalyzed via the supported metal-hydride species, [Ta]-H, containing six elementary steps: [Ta]-(H)₂-CH₃ (8) is firstly formed through the addition of a CH₄ molecule on [Ta]-H (1) and then transformed to [Ta]-CH₃ (3) via H₂ elimination; another CH₄ molecule is activated on 3 through breaking the C-H bond to form [Ta]-(H)(CH₃)₂ (4); and the transformed [Ta]-(H)₂-CH₂CH₃ (10) finally recycles to 1 and eliminate an CH₃CH₃ molecule. And an energetic span of 74.1 kcal/mol was obtained from the CCB route with two rate-determining states, (9 + H₂) and TS-4-10 (Figure 4d). Thus, the turnover number of NOCM catalyzed by the supported methyltantalum (referring to energetic span [90,101,102]) was about 105 larger than that catalyzed by the supported tantalum hydride, indicating that the supported metal-methyl species [M]-CH₃ is predominantly responsible for the direct conversion of methane into ethane.

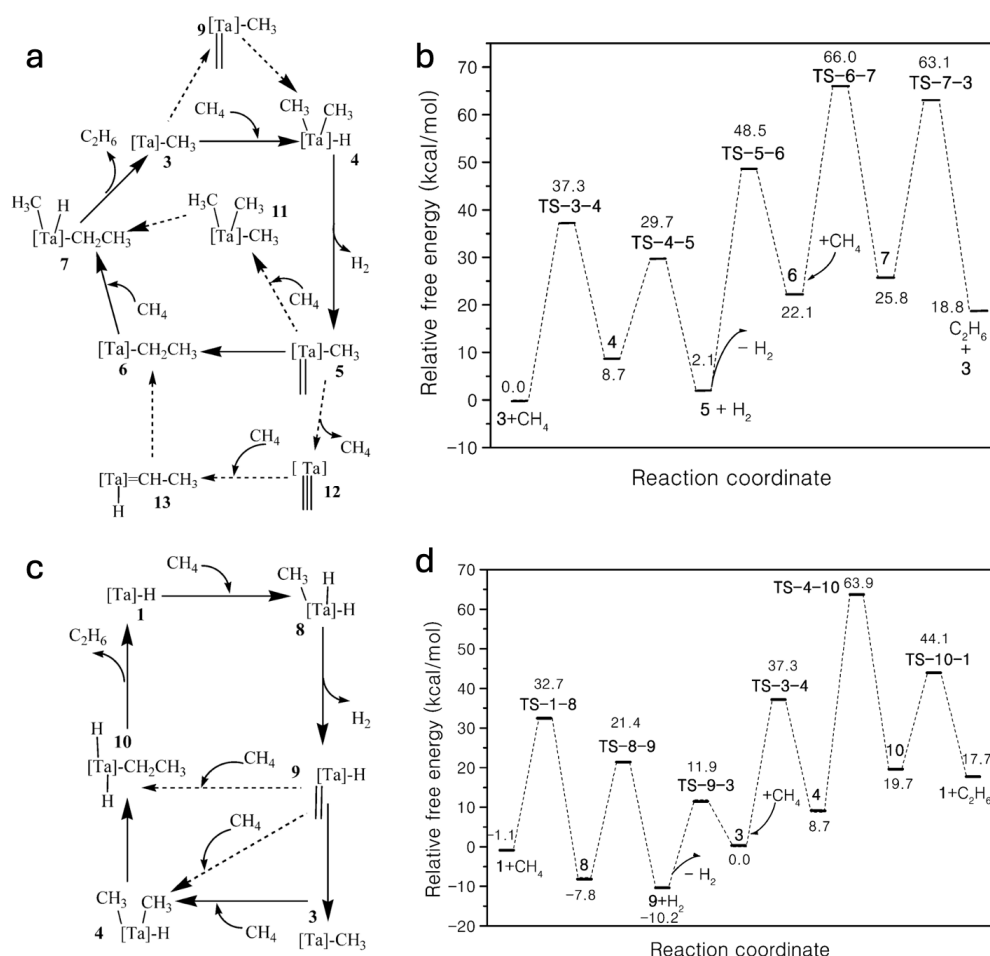


Figure 4. Catalytic cycles a (CCA) for silica-supported single-site tantalum-catalyzed NOCM (a) and relative free energy (723.15 k, 49.3 atm) profile for CCA (b). Catalytic cycles b (CCB) for silica-supported single-site tantalum-catalyzed NOCM (c) and relative free energy (723.15 k, 49.3 atm) profile for CCB (d). Note: Reaction pathways indicated with solid lines are catalytic cycles, and dotted lines are unfavorable pathways competing with these two catalytic cycles. [Ta] is used to represent the silica-supported Ta part for clarity. Reproduced with permission from ref. [100]. Copyright 2020: American Chemical Society.

More simulations with similar reaction pathways of NOCM via supported metal organometallic sites were performed on other metal centers, such as Nb and V [103]. Interestingly, compared to the silica-supported [Ta]-CH₃ catalyst, the silica-supported [Nb]-CH₃ catalyst had the potential to present an increasing turnover frequency (TOF) for NOCM by two orders of magnitude due to the smaller energetic span of CCA via [Nb]-CH₃. Thus, these theoretical studies involve useful approaches that guide the catalyst design process for efficient non-oxidative coupling of methane to produce C₂ products.

3. Conclusions

This review illustrates the heterogeneous catalysts comprising singly dispersed metal sites that present decent catalytic performance in terms of non-oxidative methane coupling to produce ethane or ethylene. More insights into the mechanism of NOCM via isolated catalytic sites were obtained through integral characterization investigations and computational simulations. It is known that: (1) the synergetic effect of dual catalytic sites or interaction between isolated metal sites and support potentially plays an essential role in the activity of NOCM; and (2) the catalytic species containing similar structures to critical intermediates generated during NOCM could be highly active for the conversion of methane

and the formation of ethane or ethylene. It is also proposed that the supported singly dispersed sites with transition/late metals (such as Nb, Zr, Mo, etc.) are potentially active for NOCM reactions. Moreover, the good stability of isolated metal sites during NOCM reactions is a critical factor to be thoughtfully considered. Although it is still challenging to maintain singly dispersed metal atoms during NOCM, especially during high-temperature processes, several potential approaches for SAC and SOMCat are explored herein to prevent the deactivation of these catalysts. Proper interaction between isolated metal atoms and support is essential for the stabilization of singly dispersed metal sites. For instance, good stability was achieved from NOCM via $\text{FeC}_2\text{@SiO}_2$ due to the embedded structure of the FeC_2 species in the silica matrix. The non-innocent or redox supports have the potential to stabilize the singly dispersed metal sites, avoiding the aggregation and sintering of metal sites. In addition, surface organometallic catalysts are also proposed to show good stability in NOCM because, based on the mechanism, the active species $[\text{M}]\text{-H}$ and $[\text{M}]\text{-CH}_3$ are able to activate the C-H bond of methane at a moderate temperature. And the significantly lower coke formation from NOCM via SAC or SOMCat is also beneficial for maintaining good activity of NOCM. However, it is still challenging to achieve the desired catalysts, which are composed of proper singly dispersed catalytic sites with high activity and good stability. Thus, a combination of practical studies and fundamental understanding may guide the design of ideal catalytic sites on SAC and/or SOMCat that are promising for efficiently catalyzing the non-oxidative coupling of methane to produce hydrogen and C_2 hydrocarbons.

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