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Methane Activation: The Past and Future

Pei Tang[a], Qingjun Zhu[b], Zhaoxuan Wu[a], Ding Ma[a*]

[a] Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

[b] National Institute of Clean-And-Low-Carbon Energy, Future Science & Technology City, Changping District, Beijing 102209, P. R. China

Abstract

The conversion of methane to more valuable chemicals is one of the most intensively studied topics in catalysis. The direct conversion of methane is attractive because the process is simple, but unfortunately its products are chemicals that are more reactive than methane. The current status of this research field is discussed with an emphasis on C-H bond activation and future challenges.

1. Introduction

Methane is the main component in natural gas and methane clathrates, and with the depletion of petroleum reserves, it will become the most important hydrocarbon feedstock for the synthesis of fuels and chemicals. The development of hydraulic fracturing technology and the possible exploitation of shale gas has significantly increased the recoverable reserves and supplies of natural gas.[1] Consequently, chemical processes based on methane activation are getting more economically attractive. Nevertheless, because most of the methane is burned for heating and electrical generation and a tiny fraction is used as a fuel in vehicles, the carbon and hydrogen contents in this hydrocarbon resource are not utilized to their full potential in the chemical industry.[2] This is because methane, with the highest hydrogen to carbon atom ratio among the hydrocarbons, has four strong and localized C-H bonds (bond energy of 413 kJ/mol), and the absence of low energy empty orbitals and high energy filled orbitals make it difficult for methane to readily participate in a chemical reaction.

Presently, in industry methane is transformed into bulk chemicals by the indirect route. That is, methane is converted into syngas ($CO + H_2$) at an elevated temperature (> 973 K),[3, 4] and then the syngas is used to make a wide spectrum of hydrocarbons or alcohols with the use of catalysts.[5, 6] The process is energy intensive and the cost is high, and so it would be useful to lower the reaction temperature for the transformation of methane into chemicals. Ironically, the direct conversion of methane to derivatives, e.g., methanol, is thermodynamically feasible, but kinetically difficult.[7, 8] Moreover, methanol or some other products or intermediates are more reactive than the CH_4 reactant, and so the kinetic protection or the selective separation of the product is necessary, which leads to more challenges in the chemical process. However, much effort have been devoted to direct methane conversion to produce the desired chemicals in high yields in order to make the direct conversion process economically competitive with the indirect route. Many researchers have given examples how C-H bond conversion can be controlled with the use of catalysts and the correct reaction environment. The ultimate goal of these studies is the development of strategies to exploit methane resources more efficiently and cleanly.

The scope of this mini-review is limited to the one-step reaction of methane conversion. We restrict our discussion to reactions that have been clearly shown to involve C-H bond scission and the subsequent functionalization of the carbon atom in methane. The examples include reactions that are in the initial stage of fundamental study and those that have been used in industrial applications for years. We categorized our reactions into four types on the basis of the degree of C-H bond removal and the oxidation states of the carbon atom in the final product: 1) complete C-H bond removal from methane and partial oxidation of the carbon atom; 2) complete C-H bond removal from methane to give carbon black and hydrogen; 3) partial C-H bond removal from methane and further C-C coupling reaction to form chemicals such as C_2 hydrocarbons and aromatics; 4) partial C-H bond removal and their substitution by heteroatom functional groups. The examples discussed are chosen to illustrate how methane activity is controlled by the use of different catalysts, oxidants or the reaction environment. The detailed understanding of C-H bond activation in direct methane conversion is crucial for process development.

2. Complete C-H bond removal and the partial oxidation of carbon: production of CO and H_2

The complete oxidation of methane at low temperatures is thermodynamically favorable. More important is that the resulting mixture of CO_2 and H_2O is of less value in the chemical industry, whereas converting methane to syngas ($CO+H_2$) with an oxidant is much more attractive than the complete oxidation of methane.[9] These processes of converting methane to syngas are called the reforming of methane. The reforming of methane to syngas ($CO+H_2$) is the most important industrial process that utilize methane in large scale industrial applications at present. Syngas, which is a very versatile intermediate, can be used in methanol synthesis with $Cu/ZnO/Al_2O_3$ catalysts or in Fischer-Tropsch synthesis on Fe, Co or Ru catalysts to produce hydrocarbons.[6, 10] The first process has better atomic economy since the oxygen atom in CO is included in the product, whereas the oxygen atom of CO and some hydrogen atoms are wasted in form of water in Fischer-Tropsch synthesis.

There are three possible reforming processes for the conversion of methane to syngas: steam reforming shown in Equation 1, CO_2 reforming (dry reforming) shown in Equation 2, and partial oxidation of methane to syngas shown in Equation 3. These three reforming processes give different CO/H_2 ratios (1:1, 1:2 and 1:3) in the syngas.

Equation 1 $$CH_4 + H_2O \longrightarrow CO + 3\ H_2 \qquad \Delta H(298\ K) = 206\ kJ/mol$$

Equation 2 $$CH_4 + CO_2 \longrightarrow 2\ CO + 2\ H_2 \qquad \Delta H(298\ K) = 247\ kJ/mol$$

Equation 3 $$CH_4 + 0.5\ O_2 \longrightarrow CO + 2\ H_2 \qquad \Delta H(298\ K) = -36\ kJ/mol$$

Thermodynamics indicate that steam reforming and dry reforming hardly occur at low temperatures (< 450 K). Indeed, both the reactions of steam reforming and partial oxidation of methane to syngas favor the production of CO_2 and H_2 rather than CO and H_2 according to the thermodynamic equilibrium as shown in Figure 1. Also, high pressure reaction conditions neither favor the formation of CO and H_2 nor the conversion of methane.[11] The thermodynamic data of the reaction of partial oxidation of methane to syngas are shown in Figure 1. At high temperatures (1100 – 1300 K) and atmospheric pressure, with a proper catalyst, these three reforming reactions readily result in more than 90% methane conversion and more than 90% selectivity to CO and H_2. However, the high temperature reaction conditions mean that the costs are very high in the industrial operations.

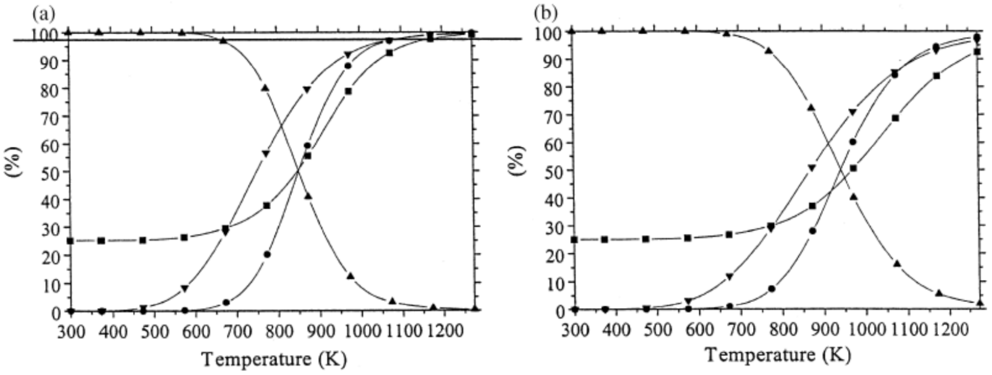


Figure 1 Thermodynamic equilibrium at: (a) 0.1 Mpa and (b) at 0.8 Mpa; (■) CH_4 Conversion; (●) [CO] Selectivity; (▲) [CO_2] Selectivity;(▼) [H_2] Selectivity.[3]

The steam reforming of methane is a well-established process in industry. This process is widely used to produce syngas for methanol synthesis, and hydrogen for ammonia synthesis and refining processes. About 48% of the hydrogen in the world is produced by steam reforming.[12] However, hot spots in the catalyst bed and the high temperature reaction conditions cause difficulties in the operation, and excess steam is needed to suppress the formation of coke.[11] In contrast, CO_2 reforming consumes two greenhouse gases (CO_2 and CH_4) to make the valuable syngas. This reaction not only mitigates CO_2 and CH_4 emission but also provides an effective way to utilize low grade natural gas resources consisting of CH_4 and CO_2, e.g., coal bed gas. Nerveless, the catalyst readily deactivates, and excess CO_2 has to be used to remove the coke.[4, 13] Interestingly, the reaction of partial oxidation of methane to syngas is the only methane reforming process that is exothermic with the optimal CO:H_2 ratio (1:2) in the reaction product, but this reaction still needs high temperatures (1100 - 1200 K) in order to obtain the CO and H_2. The main problems in the partial oxidation of methane to syngas are safety issues. First, a mixture of methane and oxygen is extremely dangerous in industrial application. Second, the partial oxidation of methane to syngas is only autonomous at high temperature, where the reaction is very difficult to control. Finally, hot spots formed in this autonomous oxidative process are difficult to handle and would result in local overheating.[3, 4] In addition to these issues, the stability of the catalyst is another factor that prevents this process from being industrialized. In order to overcome the catalyst deactivation problem, the catalysts are carefully designed, particularly in the choice and modification of the support and the addition of auxiliary metals.[6, 14] It was found that the metal crystallite size strongly affects the coke formation rate.[15] When the Ni particles are smaller than 1 nm, almost no coke is formed on the metal surface.[16]

It is interesting to note that all three reforming processes show similar orders of activity on different catalysts. Most of the initial researches focused on the noble catalysts of Rh, Ir, Pt, Ru and Pd, with Ru and Rh being the most active.[3] For the non-noble metals, Ni-based catalysts have the highest catalytic activity and its activity is even comparable to those of the noble metal catalysts in all three reforming process.[17] The similarities among these reforming processes[18] make it possible to combine two or three of these reforming reactions to adjust the final CO:H_2 ratio in the product as the three reforming reactions give different CO:H_2 ratios. These combined reforming reactions are called bi-/tri-reforming processs. For example, Olah et al. suggested that bi-reforming of methane to syngas with a CO:H_2 ratio of 1:2 is possible at high pressures, and this can be used directly in methanol synthesis.[19] The tri-reforming process is more economical if the exothermic partial oxidation process is combined with the endothermic steam reforming and CO_2 reforming, which can give a new reaction route to prevent hot spots and coke formation in the reaction.[20] In addition to the catalytic reforming reactions above, the non-catalytic homogeneous partial oxidation of methane for synthesis gas production, even though kinetically unfavorable, is also well-established and applied.[21]

3. Complete C-H bond removal: production of C and H_2

The thermocatalytic decomposition (TCD) of methane to pure hydrogen and solid carbon, shown in Equation 4, is another process for the transformation of methane with high selectivity. Unlike the reforming processes, the TCD process only produces solid carbon and hydrogen. Since no CO or CO_2 is formed, this implies a simple gas product separation process to give high quality hydrogen. Meanwhile, different types of carbon, such as amorphous carbons, carbon nanofibers, carbon nanotubes (see Figure 2) and layered carbon materials, can be produced depending on the operating conditions.[22, 23] The TCD process offers a convenient way to maximize the production of hydrogen gas from the methane molecule, and the many forms of value-added carbon products add importance to this process.

Equation 4 $$CH_4 \longrightarrow C + 2\,H_2 \qquad \Delta H(298\text{ K}) = 75.6\text{ kJ/mol}$$

The TCD reaction requires more than 1500 K to achieve a reasonable yield without a catalyst. However, both metal and carbon materials are active catalysts that can lower the reaction temperature. High product yields are obtained with carbon catalysts in the temperature range of 1100 - 1300 K while the reaction temperature range is 700 - 1100 K with metal catalysts.

The rate of methane decomposition activity on the transition metals follows the order: Co, Ru, Ni, Rh > Pt, Re, Ir > Pd, Cu, W, Fe, Mo.[22] Currently, most of the researches are focused on Ni- and Fe-based catalysts. The metal loading for the supported catalysts used in this process are usually more than 10% which is high compared to normal supported metal catalysts. For example, for Ni-based catalysts, the optimum loading of Ni was 40%, while the particle size of the Ni catalysts are pivotal for good activity.[24, 25] In the TCD process, although the production of solid carbon facilitates the gas separation, the drawback is that the large amounts of carbon formed cover and poison the catalysts as well as change the morphology and composition of the metal catalysts, which lead to severe deactivation of the catalysts.[22, 23, 25, 26] The choice of the support and the addition of promoters are widely used to enhance the tolerance of carbonaceous deposits.[22, 23]

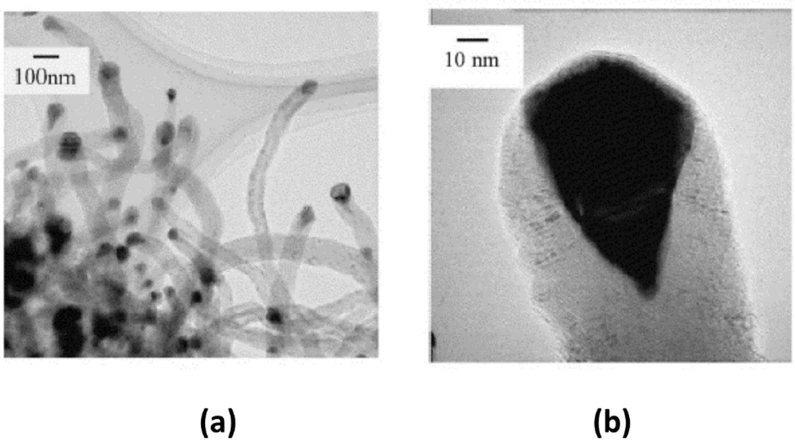


Figure 2 TEM images of carbon nano-fibers formed by the thermocatalytic decomposition of methane.[24]

Interestingly, carbon materials themselves can catalyze the TCD reaction. A different kinetics behavior was observed with carbon materials as compared with that of metal catalysts, illustrating the catalytic effect of carbon in the TCD reaction.[27]

Various carbon materials have been tested in the TCD reactions. Amorphous carbons (e.g., activated carbon and carbon black) are more active than well-ordered carbons (e.g., graphite and carbon nanotubes).[27-29] The carbon deposits produced in the reaction also dramatically reduce the surface area of the carbon catalyst, which lead to the deactivation of the catalyst. With activated carbon and carbon black, which are the most widely used catalysts, activated carbon shows a higher initial reaction rate and a faster deactivation rate than carbon black. It was suggested that the pores in activated carbon, especially the micropores, are readily blocked by the carbonaceous deposits, whereas the surface of carbon black is much more accessible to methane since the size of the carbon black particles are between 10 - 250 nm.[28, 30] Defects in the carbon materials are believed to be the active sites for the TCD reaction. In some cases, as the TCD reaction proceeds, the newly formed carbon is responsible for the activation of methane.[27, 30]

The TCD process is not industrially used because it is not yet economically competitive with the well-developed steam reforming process of methane. However, with the increasing demand of high quality hydrogen, the TCD process is getting more attractive as the pure hydrogen produced this way, with the absence of CO and CO_2, is suitable for fuel cells.[22, 23] The water splitting (2H2O=2H2+O2 ΔH=484 kJ/mol) is another important reaction to provide high-quality hydrogen. Firstly, that using solar energy to split water to hydrogen and oxygen is still far from the practical applications. Secondly, the electrolysis of water to high-quality hydrogen, although well established, also needs more energy than the TCD process. It is because that ΔH of this reaction is much higher than that of TCD reaction and this process costs electricity, the efficiency of which is limited by the electricity generation and transportation. Therefore, as methane has the highest H/C ratio in fossil fuel, we propose that the TCD process would play more and more important role in the production of hydrogen in the future. The reasons why this process is not applied on a large scale are: First, a continuous reaction process that is suitable for TCD industrial application has still to be developed. In the laboratory, a circulating fluidized bed is used to develop a continuous process, but this process requires the regeneration of the catalysts by oxidation, resulting in the release of large amounts of greenhouse gases (CO and CO_2).[31] Second, carbon market value is believed to be a key factor in the economics of the TCD process.[23, 32] If this process is industrialized, it will produce huge amounts of carbon each year. Therefore, to produce uniform types of carbon and to find suitable applications for these carbons are the key factors that govern the viability of the TCD process.

4. Partial C-H bond removal and C-C bond formation: production of hydrocarbons

4.1 Ethane and ethylene

Ethylene, a main building block in the chemical society, is now obtained by the pyrolysis of naphtha and dehydrogenation of ethane. The direct conversion of methane to ethylene would provide an alternative to these traditional processes based on petroleum and syngas.

In the oxidative coupling of methane (OCM) reaction, shown in Equations 5 – 6, methane is directly converted into ethane, ethylene and water in the presence of oxygen and a suitable catalyst. Ethylene, as one of the most important building feedstocks in polymer industry, could be converted to propylene or polymerized to polyethylene. Ethane could be easily converted to ethylene by a oxidative dehydrogenation process. This reaction has been extensively studied and reviewed in the literature.[33-36] Briefly, the reaction proceeds by a two-step process. First, oxidized catalyst sites abstract H from CH_4, and the resulting methyl radicals couple to form ethane. The existence of methyl radicals has been shown by synchrotron VUV photoionization mass spectroscopy.[37] In the second step, the ethane dehydrogenates to produce ethylene. A wide range of metal oxides are active for this reaction. Li-MgO and W-Mn-SiO_2 are the most widely studied catalysts. Some typical results are shown in Table 1. Despite much effort devoted to the OCM reaction, only a few catalysts can give a C_{2+} yield higher than 25% and selectivity to C_{2+} higher than 80%, which are the minimum criteria for its industrial application.[38]

Equation 5 $$2\ CH_4 + 0.5\ O_2 \longrightarrow CH_3CH_3 + H_2O \quad \Delta H(298\ K) = -42.4\ kJ/mol$$

Equation 6 $$2\ CH_4 + O_2 \longrightarrow CH_2CH_2 + 2\ H_2O \quad \Delta H(298\ K) = -67.4\ kJ/mol$$

The Li/MgO catalyst was shown to be very active in the OCM reaction by Lunsford et al. Lithium in the catalyst create surface defects and favor the formation of O^- which is believed to be responsible for the activation of methane.[33, 39] However, the Li/MgO catalysts are unstable at the reaction conditions, and deactivation occurs because of the loss of Li and sintering of the catalysts. Various dopants such as auxiliary metals and Cl^- are used to modify the Li/MgO catalysts to improve the stability and the selectivity towards C_2.[6, 39] The W-Mn-SiO_2 catalyst is also one of the most active catalysts in the OCM reaction. In this catalyst, Na is proposed to suppress the over-oxidation of methane and favor the migration of Mn and W to the catalyst surface. Both the Na-O-W and Na-O-Mn species are the active sites in this reaction. The near-surface concentration of Mn was correlated with CH_4 conversion and C_2H_4 selectivity. Concerning the W species, both tetrahedral WO_4 and octahedral WO_6 were found on the catalyst surface, and WO_4 was more active and selective for the reaction.[34, 40] Beside pure oxygen, other oxidants such as CO_2 have been used in the OCM reaction as well, although their C_2 yields are much lower.[41, 42]

Table 1. Some catalytic results of the methane coupling reactions

Catalysts	Reaction Conditions		Conversion	Selectivity(C_2)	References
	Reactants	Temperature			
Li-MgO	$CH_4 : O_2 = 2 : 1$	993 K	38%	50%	(32)
Na-W-Mn-SiO_2	$CH_4 : O_2 = 3 : 1$	1073 K	33%	60%	(33)
Modified La_2O_3	$CH_4 : O_2 = 4 : 1$	593 K	33%	55%	(34)
Modified Bi_2O_3	$CH_4 : O_2 = 2 : 1$	1223 K	44%	62%	(35)
Pd/ZrO_2	$CH_4 : S = 5.8 : 1$	1323 K	16%	19%*	(42)
Pt/SiO_2	Pure CH_4 then pure H_2	523 K	0.01%	64%	(44)
$\equiv(SiO)_2Ta$-H	Pure CH4	573 K	0.05%	98%	(45)

(*only the selectivity of ethylene is given)

As the main problem in the OCM reaction is that the activity of the ethane and ethylene products are much higher than that of methane in the oxygen atmosphere, a “soft” oxidant that has less oxidation ability may partly solve this problem. Recently, a process using S_2 as a mild oxidant to oxidize methane to ethane and ethylene was developed.[43] The thermodynamic data for S_2 and O_2 are shown in Figure 3. The metal sulfides used as the catalysts were like the metal oxides in the OCM reaction. The bond energy of the C-S bond is believed to play an important role in controlling the activation of methane. However, this mild oxidation process needs a higher reaction temperature than the traditional oxidation process using oxygen.

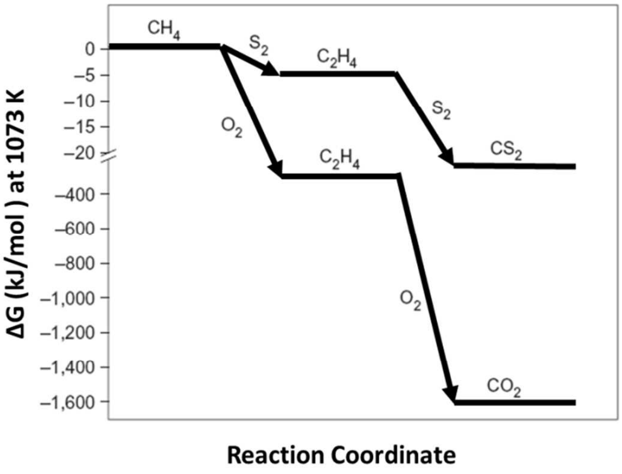


Figure 3. Thermodynamic calculations indicate that using S_2 as a mild oxidant can prevent the over-oxidation of methane as compared to using O_2 as the oxidant.

The non-oxidative coupling of methane (NOCM) reactions, shown in Equations 7 -8, to ethane and ethylene are thermodynamically unfavorable. However, due to the high selectivity and low reaction temperatures, this reaction still attracted much research attention. The reaction occurs by a two-step process. First, methane is chemisorbed on the surface of catalyst. Then the clearage of C-H bonds occurs, resulting in the formation of H_2 and H-deficient carbon species such as CH_X. When the CH_X coverage on the surface of the catalyst is high, C-C bond coupling occurs. In the second step of the reaction, hydrogen is introduced to promote the formation of the C-C bond by saturating the over-dehydrogenated CH_X, and thus cleaning the surface of catalysts for the next catalytic cycle.[38, 44]

Equation 7 $2\ CH_4 \longrightarrow CH_3CH_3 + H_2$ $\Delta H(298\ K) = 64.4\ kJ/mol$

Equation 8 $2\ CH_4 \longrightarrow CH_2CH_2 + 2\ H_2$ $\Delta H(298\ K) = 201.5\ kJ/mol$

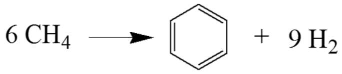
This reaction was first found to be active on Pt/SiO_2. At 523 K, methane can be transformed into higher hydrocarbons such as C_2-C_6 species by the two step reaction process. The selectivity to C_2 species is ca. 60%.[45] In addition to this isothermal process, methane can also form carbide and H_2 on noble catalysts at a higher temperature, and then successive hydrogenation can be used to convert these carbide species into higher hydrocarbons. The addition of a second metal such as Cu or Co can improve the catalytic activity, while a higher reaction pressure promotes the branching process and modifies the molecular weight distribution of the products.[38] Recently, SiO_2-supported tantalum hydride as a well-defined catalyst was used in this reaction. The reaction thermodynamics allows a high selectivity (> 98%) to ethane at 523 - 648 K.[46]

There are two problems with the NOCM process. First, thermodynamic limitation makes the activity extremely low. Second, the two-step process (at different reaction temperatures) is difficult to operate industrially. While the second issue needs engineering work, the development of a novel catalyst[47], use of membrane reactors,[48] and assistance of photo- and plasma-process can be used to promote NOCM to get better catalytic performance. [49, 50]

4.2 Aromatics

The methane dehydroaromatization (MDA) reaction was first reported in 1993.[51] As shown in Equation 9, in the absence of oxygen, methane can be converted into benzene with the release of H_2. All the carbon and hydrogen atoms in the methane molecule are utilized in the valuable chemicals obtained, resulting in 100% atomic use for both the carbon and hydrogen atoms. Benzene is an important solvent in industry and also the feedstock of phenol and p-xylene. Meanwhile, the high-quality hydrogen (absence of CO and CO2) produced at the same time of formation of aromatics could be used in fuel cell directly as well as in hydrogenation reaction where large amount of hydrogen was required. However, the formation of aromatic products from CH_4 in the absence of O_2 is not thermodynamically favorable at low temperatures (< 723 K). The equilibrium conversion of methane at 973 K is about 12%, with approximately equimolar amounts of benzene and naphthalene being the thermodynamically preferred products.[38, 52] Compared with the non-oxidative coupling of methane to C_2 species, a higher equilibrium conversion is obtained at the same temperature as shown in Figure 4.[38]

Equation 9



ΔH(298 K) = 531 kJ/mol

The reaction was first found to be active on Mo-ZSM-5.[51] A number of transition metal ions (Mo, Fe , V , W , Cr etc.) and supports (ZSM-5, mordenite, Y etc.)[53-55] were found to be useable constituents in this bifunctional catalyst system. Typically, with a Mo/ZSM-5 (4 - 6% Mo loading) catalyst, methane was converted to 50% benzene, 25 - 30% coke, 10 - 20% naphthalene and 5 - 10% C_2 with a conversion of 10 - 12% at 973 K.[38, 56]

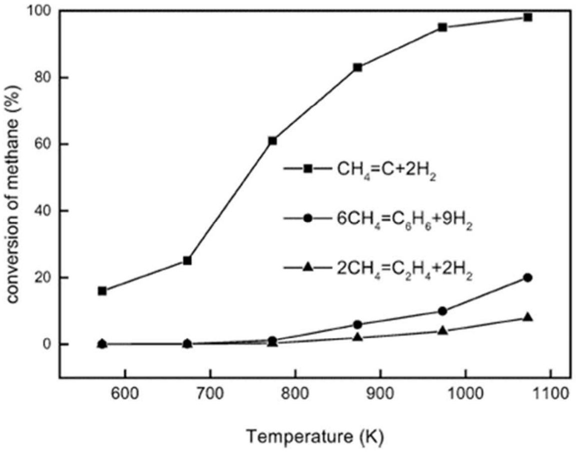


Figure 4 Thermodynamics of the direct conversion of CH_4 under non-oxidative conditions.[38]

Mo and ZSM-5 form a bifunctional catalyst to promote the MDA reactions.[57, 58] Molybdenum migrates into the zeolitic channel and exchange with the Brönsted acidic proton to form framework Mo-O-Al species.[59] Then, during the induction period, the carbonization of Mo-O-Al species occur to form molybdenum carbide,[60, 61] which is responsible for the activation of methane to CH_X.[62] On the other hand, the Brönsted acid sites that originated from the incorporation of aluminium into the zeolite framework is responsible for the following aromatization of the CH_X species, leading to the formation of various aromatics.[63, 64] The highest methane conversion and benzene formation rate were obtained when the zeolites possess the optimized Brönsted acidity. A good balance between the framework molybdenum species and Bronsted acid sites is needed for excellent catalytic performance. Clearly, too much Mo loading will consume a substantial amount of the Brönsted acidic sites, and in extreme situations, this can extract framework Al from the zeolite structure, resulting in the collapse of zeolitic structure and the inhibition of aromatization.[60]

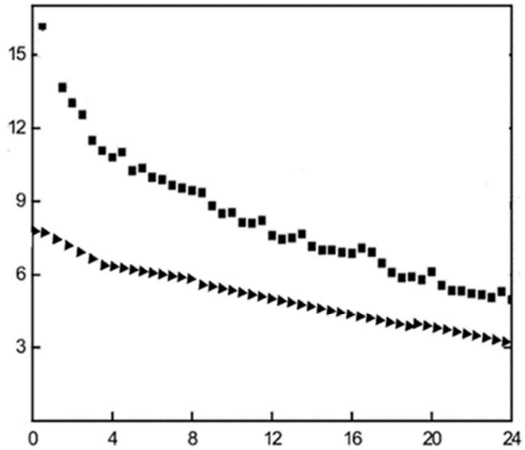


Figure 5 6% Mo-ZSM-5 catalysts gradually deactivate with time on steam.[38]
■ Methane Conversion ; ▲ Yield of BTX

Heavy carbonaceous deposition was observed in the reaction, which covers the active sites and blocks the channels of the zeolites to hinder the successive aromatization reaction, leading to significant catalyst deactivation, as shown in Figure 5.[53,65] The most efficient way to remove coke in this reaction is by hydrogenation, instead of the normally used oxygen regeneration. The hydrogenation regeneration benefits the stability of the active phase, molybdenum carbide.[66, 67] The yields of benzene and hydrogen from this MDA reaction have almost reached the thermodynamic equilibrium at reaction conditions. Hence, a careful design of reactors to separate the products is needed to break the thermodynamic equilibrium to obtain a higher product yield. Moreover, a fluidized bed to regenerate the catalyst and maintain the activity is needed to accomplish a continuous industrial processes.

4.3 Cross-coupling of methane with other hydrocarbons

In addition to the coupling reactions of OCM and MDA, the carbon atom in methane can also couple with the carbon atom of other hydrocarbon molecules, which is known as cross-coupling reactions. The most widely studied example in this field is the methylation reaction of aromatics with methane under an oxidative atmosphere. Zeolites can be used as the catalyst in the direct methylation of benzene and naphthalene. The methyl groups in the products are from methane, which was confirmed by ^{13}C labeling experiments. In this reaction, methane is activated by oxygen to form a methanol intermediate. Subsequently, methanol reacts with benzene to form toluene catalyzed by the acidity in the zeolite.[68] This is called oxidative methylation. The methylation of aromatics, especially benzene, is economically attractive since p-xylene is an important feedstock in the fiber industry. The methylation of ethylene to propylene is also possible. The oxidative cross-coupling process between ethylene and methane on Na-Li-MgO catalysts gave a propylene yield of 5% (based on ethylene).[69]

The methylation of olefins with methane under non-oxidative conditions has also been reported.[70] This occurs by a three-step process. Similar to the NOCM reaction, methane exposed to Ru/SiO_2 or Co/SiO_2 catalysts form CH_X at 600 – 800 K first. Then ethylene is added at a lower temperature. Finally, hydrogen is introduced and the hydrogenation facilitates the coupling of CH_X with adsorbed ethylene to form propylene. ^{13}C labeled experiments showed that the propylene products were formed from both the self-homologation of ethylene and methane incorporation into ethylene.

As methane is much less reactive than most of the other organic substrates at the reaction condition where methane can be activated, the organic substrates themselves are highly liable to be converted into other products. Therefore, the selectivity to the desired product is usually lower than 50%. More importantly, whether methane is incorporated into the final products should be investigated carefully.

5 Partial C-H bond fission and the introduction of heteroatoms: production of CH_3-X (X: halogens, -OH, $-NH_2$ etc.)

5.1 Reaction of methane and halogens

The activation of methane by halogenation is another important process to convert methane into more useful chemicals. The reaction is possible with all the halogens (F, Cl, Br and I), shown in Equations 10 - 13, and produce the corresponding halogenated methane and inorganic acid. The reaction between methane and F_2, which is corrosive and toxic, is extremely exothermic and the process is difficult to control. On the other hand, the equilibrium conversion between methane and I_2 is only 10% at 923 K, and iodomethane readily decompose to I_2 and hydrocarbons.[71, 72] Therefore, most of the researches have focused on the chlorination and bromination of methane.

Equation 10 $CH_4 + F_2 \longrightarrow CH_3F + HF$ ΔH(298 K) = -453 kJ/mol

Equation 11 $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$ ΔH(298 K) = -99.6 kJ/mol

Equation 12 $CH_4 + Br_2 \longrightarrow CH_3Br + HBr$ ΔH(298 K) = -29.0 kJ/mol

Equation 13 $CH_4 + I_2 \longrightarrow CH_3I + HI$ ΔH(298 K) = 52.9 kJ/mol

Olah et al. reported that 34% methane was converted with 96% selectivity to monochloromethane over supported noble metal and solid acid catalysts. In contrast, a methane conversion of 20% and a selectivity of 99% to monobromethane were obtained in the reaction between CH_4 and Br_2.[73] Metal oxides were also found to be promising catalysts in the reactions.[74, 75] The detailed reaction results are shown in Table 2. High yields of halogenated methane and their polar bond make them potential new platform molecules from methane chemistry. First, methanol and dimethyl ether are readily obtained by the hydrolysis of halogenated methane.[73] Second, halogenated methane can react with CO to produce acetyl halogen which is the precursor of acetic acid.[76, 77] Third, CH_3Cl and CH_3Br can be directly transformed into higher hydrocarbons using zeolitic materials.[72, 75, 78] However, although halogenated methane can be transformed into a series of useful chemicals at quite mild conditions with high yields, the severe corrosivity and toxicity of the reactants and products hinder the application of these chemical processes. In order to overcome these problems, the oxidative halogenation of methane, shown in Equation 14 - 15, was developed.

Equation 14 $CH_4 + 0.5\ O_2 + HBr \longrightarrow CH_3Br + H_2O$ ΔH(298 K) = - 166 kJ/mol

Equation 15 $CH_4 + 0.5\ O_2 + HCl \longrightarrow CH_3Cl + H_2O$ ΔH(298 K) = - 104 kJ/mol

Traditional supported noble metal catalysts are active for this reaction, such as Ru/SiO_2. In addition, $FePO_4/SiO_2$ was found to be a promising catalyst for the oxidative bromination of methane.[79-81] $LaCl_3$ was also an active catalyst in the oxidative chlorination of methane.[82] Interestingly, pulse experiments show that the Cl in $LaCl_3$ serve as a Cl reservoir in this reaction. Thus, La-O-Cl is believed to account for the catalytic cycle.[82] The conversion of methane is promoted by the doping of Co and Ce into LaCl3, but suppressed by a Ni promoter.[83] In these oxidative halogenation reactions, CO and CO_2 are the main byproducts. By careful control, a mixture of CH_3X and CO can be produced, which is a feedstock for the synthesis of acetic acid, from oxidative chlorination and bromination.[77, 84]

5.2 Introduction of other functional groups into methane

In addition to halogens, a number of other reaction types have also been developed to introduce functional groups (-OH, -COOH, $-NH_2$, $-NO_2$ etc.) to replace the hydrogen atoms in methane. Metal salts, homogeneous complexes, zeolites and supported metal catalysts are used to catalyze the methane conversion to the derivatives which are mainly C_1 oxygenates.

The partial oxidation of methane to methanol is an important technological and economical challenge to meet the enormous demand for methanol, which can be further transformed into a variety of bulk chemicals in industry. This reaction is thermodynamically favorable even at room temperature and exothermic as shown in Equation 16. This reaction route is particularly attractive from a fundamental point of view since natural catalysts such as methane monooxygenase (MMO) enzymes can activate methane and oxygen to produce methanol under mild conditions.[85] Zeolite supported metal catalysts are employed to mimic the function of methane monooxygenase to form the active di-iron or di-copper centers. Fe-ZSM-5, Cu-ZSM-5 and Cu-mordenite are founded to be able to activate methane under mild conditions.[86-88] Apart from these Fe/zeolites or Cu/zeolites, Zn-ZSM-5 catalysts could also convert methane to methanol and acetic acid under mild conditions.[89, 90] But the methanol yields in these mild conditions are so low that they are far from practical application.

Equation 16 $$CH_4 + 0.5\ O_2 \longrightarrow CH_3OH \quad \Delta H(298\ K) = -126.4\ kJ/mol$$

The difficulty in the selective oxidation of methane is that the methanol and formaldehyde are much more reactive than methane.[91, 92] By using carefully designed reactors and strict control of the reaction parameters, it is possible to get a reasonably high selectivity to methanol.[93] Beside zeolite based catalysts, oxide catalysts based on Mo-oxides and V-oxides were also promising catalysts for this reaction.[94, 95] Table 2 listed some typical results. N_2O and H_2 are promoters in partial oxidation reactions.[92, 96] The direct oxidation of methane to form oxygenates with more than one carbon is also possible. CH_3COOH can be obtained on Pt catalysts with the co-feeding of CO and O_2.[97] Moreover, by using Rh–$FePO_4$ as the catalyst, CH_3COOCH_3 can be produced from the reaction of N_2O, CO and methane.[98]

The hydrogen atoms in methane can also be replaced by N-containing groups, and some of those processes have been industrialized for decades. For example, CH_4 can react with NH_3 to produce HCN in the temperature range of 1373 – 1773 K over a Pt catalyst. The process is known as the Degussa process.[99] Under photocatalysis conditions, the product of methane and NH_3 is CH_3NH_2, indicating that the $-NH_2$ group can be introduced into the methane molecule as well.[100] Moreover, CH_4 can also react with concentrated HNO_3 to produce CH_3NO_2 at 573 – 823 K but the yield was below 20%.

Table 2 Some catalytic results of mono-substituted methane

Catalysts	Reaction Conditions			Yields		References
	Reactants	Pressure	Temperature	Products	%	
GaO_3/MoO_3	$CH_4 : O_2 = 7.6 : 1$	1.5 MPa	728 K	CH_3OH	0.7	(91)
Fe-ZSM-5	$CH_4 : O_2 = 5.5 : 1$	0.1 MPa	903 K	CH_3OH	3.5	(87)
Cu-Fe-ZSM-5	$CH_4 : N_2O = 4 : 1$	0.1 MPa	615 K	CH_3OH	0.6	(93)
Pt complex	CH_4 in oleum	3.5 MPa	493 K	CH_3OSO_3H	72	(108)
Fe-silicalite-1	CH_4 In 1M H_2O_2	0.3 MPa	343 K	CH_3OH	10	(98)
Pt/Al_2O_3	$CH_4 : Cl_2 = 1 : 3$	0.1 MPa	476 K	CH_3Cl	29	(72)
$ZrOF_2/Al_2O_3$	$CH_4 : Cl_2 = 1 : 4$	0.1 MPa	543 K	CH_3Cl	33	(72)
Rh/SiO_2	$CH_4 : O_2 = 4 : 1$ 40 wt.% HBr/H_2O	0.1 MPa	933 K	CH_3Br	32	(79)
Modified Ru/SiO_2	$CH_4 : O_2 = 1 : 1$ 40 wt.% HBr/H_2O	0.1 MPa	873 K	CH_3Br+CO	55	(76)

While most of the reactions for methane functionalization were performed in the gas phase, efforts have also been devoted to the activation of methane in liquid solution because liquid phase methane activation normally occurs at lower reaction temperature and with higher selectivity toward the desired product. Substantial progress has been made recently with the finding that Fe-ZSM-5 and Fe-Silicalite-1 can catalyze the oxidation of methane to methanol in the liquid phase with H_2O_2 as oxidant. The highest conversion of methane was about 10% at 323 K.[101] The addition of Cu as a promoter suppressed the over-oxidation of methanol, and the selectivity to methanol reached 90%. This result is the highest activity obtained to date in the oxidation of methane to methanol. Fe in the extra-framework positions of the zeolites was proposed to be the active species.[101] Further study showed that the catalytic activity of these catalysts can be further enhanced by introducing other trivalent cations (e.g., Al^{3+}, Ga^{3+}) into the framework to stabilize the active Fe species.[102] Moreover, Fe-Silicalite-1 is also a stable catalyst for at least 5 cycles.[103] This research highlighted the recent interest in using zeolites with strong solid acidity for the activation of methane.

In another system, CH_4 can also react with H_2 and O_2 to give methanol over a Au-Pd/TiO_2 catalyst. H_2O_2 formed in situ was proposed to be the actual oxidant for this reaction. However, although a relatively high selectivity was reported, the overall yield of methanol was very low.[104] The reaction was considered to proceed through a radical process, and methyl hydroperoxide may be a key intermediate, as evidenced by the existence of $\cdot CH_3$ and $\cdot OH$ radicals in the reaction.

Methane can be converted to CH_3COOH, CH_3OH and HCOOH in the presence of CO and O_2 by using $RhCl_3$ as the catalyst at 453 K in the aqueous phase although with very low methane conversion.[105] Other metal chlorides (e.g., $FeCl_3$, $CoCl_2$, $PdCl_2$) are also active in oxidizing methane to C_1 oxygenates with the oxidant of H_2O_2. $OsCl_3$ was found to be particularly active, giving 12 h^{-1} methane TOF (turnover frequency) and a remarkably high selectivity to C_1 oxygenates (61%). Os(IV) was proposed to account for the activation of H_2O_2 to form the active oxygen species and the subsequent oxidation reaction.[106] Another important progress is the use of Pd and Co salts to oxidize methane to CF_3COOCH_3, which is a methanol derivative, in the CF_3COOH phase.[107, 108] CF_3COOH is essential in the reactions since it captures the activated methyl groups and protects the CF_3COOCH_3 from over-oxidation. Moreover, $CaCl_2$ can catalyze the reaction of CH_4 and CO to CH_3COOH with $K_2S_2O_8$ as oxidant in CF_3COOH solution, and CH_3COOH was observed to be the only product with the yield of 11%. For the formation of CH_3COOH, the carbon of methyl group was from the CH_4 and the carbon of COOH was from the CO, as evidenced by the ^{13}C labeled experiments.[109] The reaction was believed to proceed through the radical mechanism.

Periana et al. reported a series of methane activation processes with considerably higher conversions and yields in oleum, as shown in Table 2. In oleum, $Hg(SO_4)_2$ catalyzed the methane to react with H_2SO_4 to form CH_3OSO_4OH, which is a methanol derivative. However, high concentrations of CH_3OSO_4H cannot be achieved due to the inhibition by other reaction products such as water and methanol.[110] It was also found that the reaction between CH_4 with H_2SO_4 can produce methyl bisulfate at 493 K over the catalyst of (bipyrimidine)$PtCl_2$, giving 90% methane conversion and 81% selectivity to the desired product.[111] These stable and highly efficient catalytic systems are known as Periana systems or Periana catalysts.[112] Furthermore, Au, I and Pd cations were developed to catalyze methane conversion.[113-115] The reaction mechanism is illustrated in Figure 6. The Pt-catalyzed methane activation process is an electrophilic C-H bond activation process. The methane reversibly forms the Pt^{II}-CH_3 species on the Pt complex, and then the Pt^{II}-CH_3 species are oxidized by H_2SO_4 to Pt^{IV}-CH_3. After the reductive functionalization, CH_3OSO_4H and Pt^{II} are generated.

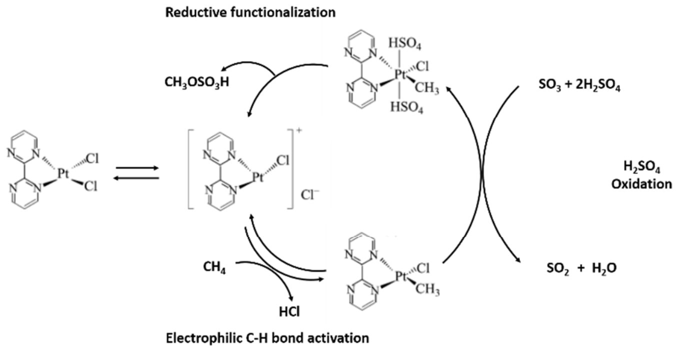


Figure 6 Mechanism for the “Periana system” for methane oxidation.[112]

The strong acidic environment is essential for maintaining the activity of the strong nucleophilic metal center in the Periana system. The products of water and methanol, with a much better nucleophilic ability than methane, block the oxidation step or compete with methane to block the methane activation step.[116] Based on the knowledge of Periana system, some researches were performed to simulate the structure of the Pt coordinated catalyst. N-heterocyclic carbene (NHC), a ligand similar to bipyrimidine, was used to catalyze the activation of methane. The Pd(II) NHC complex was proved to be active in oxidizing methane to CF_3COOCH_4 in CF_3COOH solution with $K_2S_2O_8$ as oxidant.[117] Graphitic carbon nitride is based on a covalent triazine framework. Its numerous bipyrimidine structures can coordinate to Pt to form a catalyst that function similar to the Periana catalyst.[118] These studies demonstrated that a wide range of transition metal catalysts with versatile ligands can be designed for methane conversion, although the strong acidic media used, relatively low methane conversion and expensive catalyst make the system difficult for industrial application.

6 Outlook for the future

This mini-review introduced diverse types of methane transformation processes that have been developed in the last few decades. The progress made are impressive, but an efficient, mild and well-controlled process for the direct conversion of methane in an economically attractive way remains a significant challenge for academia and industry in the goal of methane utilization to its full potential. The core of the art is to gain mechanistic insights into C-H bond activation over the different catalysts. As more strategies are developed to perform C-H bond scission and the subsequent substitution of functional groups or C-C bond coupling, a coherent picture of how the nature of the reaction environment affects the methane conversion and the desired product formation would emerge. Once the processes and factors controlling the activity and selectivity of catalytic methane activation are understood, it is anticipated that strategy designs, already demonstrated on a laboratory scale, can, if appropriately adapted and improved, lead to benign industrial methane utilization.

Although methane activation has been extensively researched for many decades, there is still an immediate need for scientists to explore new possibilities of methane chemistry, especially with the rapid development of shale gas as an available source of methane. Researchers in fundamental studies and reaction engineering have to be brought together. Here are a few research directions for methane conversion where we expect significant progress in the foreseeable future.

(1) In the vast majority of cases, a variety of oxidants have been used for the transformation of methane. In addition to the traditional oxygen, there are several mild oxidants such as H_2O_2 and halogens employed in the transformation of methane. However, few have found significant impact on the industrial scale. Many of the oxidants, such as the sulfur which is a “soft” oxidant, are candidates for future methane chemistry, yet their performances are largely unexplored.[43]

We suggest that other mild oxidants similar to S_2 should be studied for methane activation and see the controlled oxidative conversion of methane in a latest review by Hermans et al.[8]

(2) The presence of the oxidant is not a prerequisite for C-H bond activation, as proved by methane aromatization on Mo/zeolite catalysts. Non-oxidative routes should be carefully investigated both at low and high reaction temperatures. We anticipate that non-oxidative methane coupling to C_2 and other hydrocarbons will be a promising research field in the near future.

(3) Because many products, such as syngas and methanol, of the one-step reactions discussed in this review can be further transformed into more valuable chemicals, the combination of methane transformation and a subsequent reaction (second reaction) will be possible if hybrid catalysts, in which the active components of the different catalysts are arranged in a well-designed support system, are designed. In this case, the second reaction provides a thermodynamic driving force so that the first one-step methane route with a negative free energy can proceed. However, how to efficiently match the reaction parameter as well as how to effectively couple mass transport and heat transfer will have a significant impact on these types of combination reaction.

(4) The methane cross-coupling reaction discussed in section 4.3 is of particularly interest due to its various possible products. The direct addition of a methyl group from methane onto an organic substrate, such as ethylene and benzene, is of great industrial value.

(5) "Co-refinery" of oil/gas or coal/gas. Methane can be considered a hydrogen donor for important energy-related reactions such as the transformation of coal in one step and the hydrocracking of oil.[119, 120] As the dissociation of the C-H bond in methane occurs at 400 – 800 K on a metal catalyst, this temperature range is suitable for the hydrocracking reaction as well as the direct hydrogenation of coal to value-added products. Clearly, new catalysts and the related reaction engineering should be carefully strategized for the so-called "co-refinery" processes of oil/gas or coal/gas feeds. The concept can be extended to other system where hydrogen is important in the catalytic transformation.

(6) The activation of methane by a photocatalyst is worth trying. With solar energy as the most abundant energy source in nature and methane as the rising clean fossil fuel, how to successfully couple these two forms of energy is an interesting but challenging topic for scientists as well as energy policymakers.

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