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Direct conversion of methane to fuels and chemicals

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ABSTRACT

Direct selective conversion of methane to C_2-hydrocarbons, methanol or aromatics represents a formidable challenge to catalysis. This has become more and more evident over the last decades of intensive research and no breakthrough technology has so far been developed. A large number of approaches based on catalysis and reaction engineering has been proposed and the present contribution focuses on some of these approaches.

1. Introduction

Large resources of natural gas have made methane and also the NGL components (ethane and propane) important raw materials for the chemical industry. Steam cracking and catalytic dehydrogenation are the commercial processes for production of olefins from ethane and propane and promises to remain so. During the last years there has been a renewed interest in processes for olefin production from NGL components, in particular oxidative dehydrogenation of ethane [1]. However, conversion of ethane and propane will not be discussed in the following.

Although methane is an excellent raw material for production of fuels and chemicals, the main use is as fuel for power generation and for domestic and industrial use (Fig. 1). However, large amounts of natural gas are located in remote areas where gas transportation in pipelines is not an obvious solution. Conversion of methane to more easily transportable products (gas to liquids (GTL)) is therefore an interesting option.

Methane can be converted to chemicals and fuels in two ways, either via synthesis gas or directly into C_2 hydrocarbons or methanol. Today, almost all commercial processes for large scale natural gas conversion involve synthesis gas although other processes for converting methane also exist as indicated in Fig. 1. Steam reforming is the dominant process for production of synthesis gas [2]:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \quad -\Delta H^\circ_{298} = -206\ \mathrm{kJ/mol} \tag{1}$$

An alternative way of producing synthesis gas from methane is the direct partial oxidation. Partial oxidation would give a H_2:CO ratio of 2 in the ideal reaction.

$$CH_4 + \frac{1}{2}O_2 \rightleftarrows CO + 2H_2 \quad -\Delta H^\circ_{298} = 36\ \mathrm{kJ/mol} \tag{2}$$

Autothermal reforming and combined reforming are processes based on the two reactions above. The choice of technology for production of synthesis gas depends strongly on the downstream application. As shown above steam reforming gives a very H_2 rich synthesis.

The most important large volume products from methane via synthesis gas have been ammonia and methanol (Fig. 1). Synthetic fuels (hydrocarbons) can also be produced from synthesis gas by the Fischer–Tropsch synthesis (GTL technology). During the last years a large research effort has been devoted to the Fischer–Tropsch technology. Several demonstration plants [3,4] have been built and even new plants for large scale production of liquid hydrocarbons by the Fischer–Tropsch synthesis are in operation [5] and others are in construction.

60% or more of the capital cost of GTL plants is associated with the reforming of methane to synthesis gas. A large incentive therefore exists for the development of processes for direct conversion of methane without going through synthesis gas as an intermediate. The present survey focuses on different process proposals for direct conversion of methane without going via synthesis gas as an intermediate. Processes where methane is used as a co-reactant, are not included and the same holds for the direct use of methane in fuel cells (SOFC).

2. Direct conversion of methane

Methane is a very stable, symmetrical molecule. Methane has a melting point of −182.5 °C and a boiling point of −161.5 °C. The C–H bonds are strong (425 kJ/mol) and it contains no functional group, magnetic moment or polar distribution to facilitate chemical

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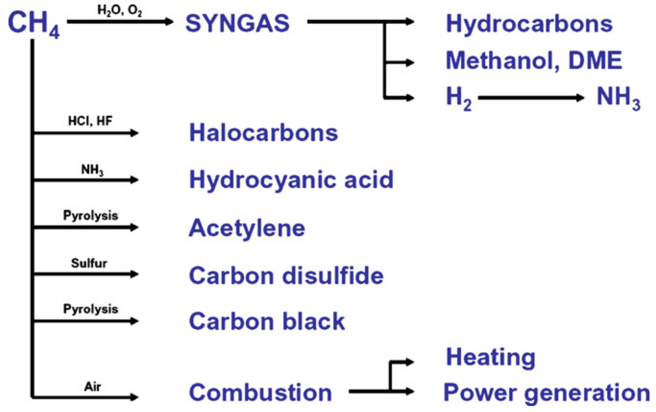

Fig. 1. Methane in industrial processes.

attacks. Activation of methane by splitting of the C–H bond will require high temperatures and/or the use of oxidations agents. Catalysis will have to play an important role in most processes for methane conversion.

Despite a large research effort on the direct conversion of methane during the last years, no breakthrough processes have been developed. The problems associated with the direct conversion of methane arise from both kinetics and thermodynamics. High temperatures are required for activation of methane and at such conditions radical reactions in the gas phase are dominating. The strength of the C–H bond in methane is stronger than in the possible products, meaning that the products will be more reactive than methane (the C–H bond strength in methanol: 389 kJ/mol). It means that the challenge in methane conversion is related to selectivity rather than reactivity. In order to circumvent theses problems several different approaches based on catalysis and reaction engineering have been proposed and tested. In the following some of these approaches are described:

1. Thermal and catalytic pyrolysis of methane.
2. Oxidative coupling of methane.
3. Partial oxidation of methane to methanol and formaldehyde.
4. Different processes (plasma, halogenation, photocatalysis, membranes, etc.).

The number of possible products from the direct conversion of methane is limited to a few components such as C_2 hydrocarbons, benzene (aromatics), methanol, formaldehyde and carbon in addition to synthesis gas.

2.1. High temperature pyrolysis of methane

Equilibrium calculations [6] indicate that the thermal decomposition of methane at high temperatures may give ethylene, acetylene, benzene and hydrogen as the main products provided that the reaction can be stopped before carbon is formed. In fact, methane can be converted directly to acetylene by pyrolysis or thermal coupling [6,7] with high yields. The reaction is highly endothermic and the heat must be supplied at high temperatures (Fig. 2). Acetylene and hydrogen are the main products (Fig. 3) [7]. Excessive carbon formation can be avoided using short reaction times and low partial pressures of methane preferably by hydrogen dilution of the feed. Rapid quenching of the reaction mixture is also very important as indicated in Fig. 3. High yields of acetylene (~90%) are obtainable at extreme conditions of temperatures (>2000 K) and short reaction times ($<10^{-2}$ s). A review of the chemistry and the process concepts is given elsewhere [6].

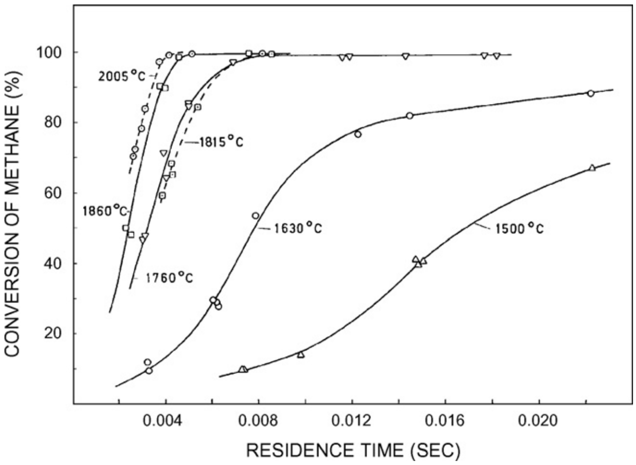

Fig. 2. Conversion of methane during pyrolysis of methane. CH_4:H_2 = 1:1, P_{tot} = 100 mmHg, solid lines: i.d. = 7 mm, cold finger quench; dotted lines: reactor i.d. = 10 mm, direct water quench [7].

The reaction mechanism consists of complex radical reactions in the gas phase. The overall reaction can be described as a stepwise dehydrogenation at high temperature:

$$2CH_4 \rightarrow C_2H_6 + H_2 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_2 + H_2 \rightarrow 2C + H_2 \qquad (3)$$

Due to the relative rates of the reactions above, it is not possible to produce high yields of ethene by thermal decomposition [6]. The chemistry is well established and the challenge is therefore on the engineering part for the pyrolysis of methane.

Many processes for acetylene production have been developed and even operated commercially with some success. These include the use of an electric arc (Huels, DuPont), regenerative techniques (Wulff process), flame techniques, incomplete combustions with O_2 (BASF, SBA, Tsutsumi) and an admixture with hot combustion gases [6,8]. The differences between the process concepts which have been proposed, are mainly due to the way heat is supplied and removed from the reactor.

A reaction scheme for direct production of ethylene or liquid hydrocarbons from natural gas has recently been proposed and even tested in a small pilot plant [9,10]. The process avoids the syngas step and it does not produce wax. Methane is converted to acetylene in an internal combustion cracker in the same way as for the BASF process. The temperature is high enough to convert much of the methane and all other hydrocarbons to acetylene and

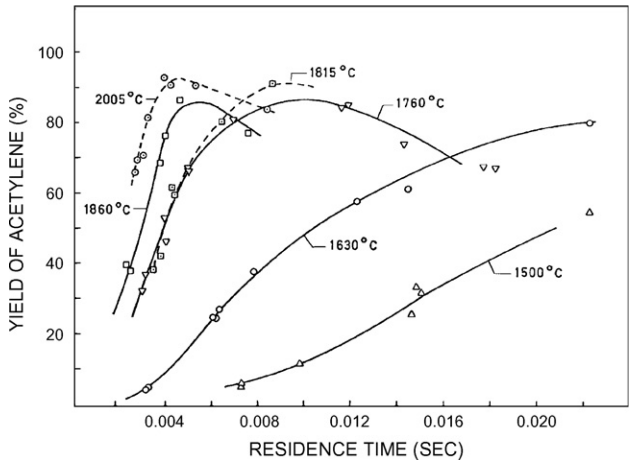

Fig. 3. Yields of acetylene from pyrolysis of methane. CH_4:H_2 = 1:1, P_{tot} = 100 mmHg, solid lines: i.d. = 7 mm, cold finger quench; dotted lines: reactor i.d. = 10 mm, direct water quench [7].

Table 1
Catalytic performance of HZSM-5 supported Re and Mo catalysts. Temperature: 973 K (950 for 4% Mo); pressure 0.1 MPa (0.3 MPa for 5% Re) [16].

Catalysts	Time (h)	Conversion of CH_4 (%)	Selectivity C_2's (%)	Selectivity benzene	Selectivity naphthalene	Selectivity coke
5% Re	2(6)	7(6)	4(6)	48(56)	11(10)	33(23)
2% MoO_3	1	6	4	50	n.a.	43
2% Mo	2(6)	9(5)	3(4)	57(62)	15(9)	15(15)
4% Mo	2(6)	10(8)	2(5)	65(69)	18(9)	3(1)

hydrogen (and CO_x). Steam is added to reduce the coke formation and for safety reasons acetylene is hydrogenated to ethylene [9]. Ethylene may be oligomerized to heavier products. Aviation fuels are obtained if the oligomerization is carried out at low pressure whereas high pressure operation gives diesel fuels. The product stream from the oligomerization reactor passes a stabilizer that produces the liquid product and a recycle stream of light hydrocarbons. The same idea has also recently been put forward by others [11]. It does not, however, remove the main difficulties associated with the production of acetylene.

IFP has also successfully built and operated a pilot reactor for methane pyrolysis at 1473 K [12]. Using 50% hydrogen dilution, IFP reports a selectivity of acetylene and ethylene of 32 and 23%, respectively at a conversion of 31%. However, the process also gives high selectivities for benzene (15%) and coke + tars (18%).

2.2. Catalytic pyrolysis of methane

Methane can also be converted over a catalyst to benzene, toluene, naphthalene and H_2 (dehydroaromatization) at lower temperatures than used for the thermal decomposition [13], but the theoretical yields are limited to equilibrium. The equilibrium conversion for CH_4 at 1 atm and 700 °C is about 12% with about half of the methane going to benzene and half to naphthalene. At 800 °C the equilibrium conversion would be 24% [14].

Several bifunctional catalysts are known to promote this reaction. The catalysts are typically zeolite based systems and the trend in the reported activity of the metal is $Mo > W > Fe > V > Cr$. Mo/HZSM-5 is the most well-known system and it has been studied extensively since the pioneering work by Wang et al. [15]. Some typical experimental results are shown in Table 1. Following the work of Wang much attention has recently been given to this route.

The mechanism of the reaction seems to involve the conversion of CH_4 to C_2H_4 (C_2H_2) on molybdenum carbide or oxycarbide and further conversion of C_2H_4 (C_2H_2) to aromatic products over the acidic sites within the channels of the zeolite. Recent studies using ^{95}Mo NMR have demonstrated that the carburized molybdenum species originating from the exchanged Mo species, are the active centers [17]. Catalyst deactivation arises from the formation of carbonaceous (coke) deposits. Coke and large hydrocarbons are formed on the external surface inhibiting the formation of complexes inside the pores. Several methods have been proposed for increasing the catalyst stability such as post-steam-treatment [18], adding CO/CO_2 to the feed stream [16] although different results have been obtained by CO/CO_2 addition [19], selective silanation of the external acid sites on HZSM-5 by means of large organosilane molecules [20,21]. It has also been claimed that by careful design of the catalyst precursor, the activity and stability can be increased without adding extra CO_2 [22]. A pilot-plant study has also been carried out in order to demonstrate the technology [23].

Several groups have used hydrogen selective transport membranes for coupling of methane. H_2 can thereby be removed by oxidation eliminating the thermodynamic constraints. Theoretical studies of the system have shown promising results [24]. A marked enhancement of the conversion of methane as well as of the formation of benzene, toluene, naphthalene and hydrogen was observed when a membrane was used together with Mo/HZSM-5 [25]. However, the synthesis and operation of membranes are not straightforward.

2.3. Two-step methane homologation (low temperature coupling of methane)

This process involves methane decomposition in the first step followed by hydrogenation of the surface carbonaceous species in the second step to obtain C_{2+} hydrocarbons [26,27]. Thermodynamics prohibits the direct formation of ethane from methane and in order to circumvent the thermodynamic limitation, van Santen and co-workers [26] operated the process at two different temperatures. Methane decomposition was carried out on silica-supported transition metal catalysts (Ru, Rh, Co) at 700 K followed by hydrogenation of the surfaces species at lower temperatures (373 K). The hydrogenation products obey the Schulz–Flory distribution. Three different types of carbonaceous species are formed on the surface during methane decomposition: C_α (highly active carbidic phase), C_γ (graphitic) and C_β (amorphous carbon). The active carbidic phase was held primary responsible for the formation of higher hydrocarbons whereas amorphous carbon was highly unreactive.

The two step process has also been studied at isothermal conditions [27] and recently several fundamental studies of the low temperature coupling of methane have been carried out. Based on surface science studies a mechanism involving surface methylidene (CH) and vinylidene (CCH_2) species have been proposed at the relevant temperatures (400 and 700 K). Chemisorption of methane on Ru surfaces involves the formation of methylidene and vinylidene species together with hydrogen. The vinylidene species are directly hydrogenated to ethane while the methylidyne species can either be hydrogenated to methane or transformed to vinylidene species.

2.4. Oxidative coupling of methane

In oxidative coupling CH_4 and O_2 reacts over a solid catalyst to form C_2H_6 and C_2H_4. Since the early work of Keller and Bhasin [28] a large number of papers have appeared during the last two decades on this subject. In fact, it was one of the main research topics in catalysis 15–20 years ago. The main problem in oxidative coupling is that the active sites in the coupling catalysts also activate the C–H bond in C_2H_6 and C_2H_4 resulting in the formation of CO_2 by combustion. The overall reaction is illustrated in Fig. 4. The single-pass yield of C_2 products is usually limited to about 25% at a C_2 selectivity of about 80%. SrO/La_2O_3 and $Mn/Na_2WO_4/SiO_2$

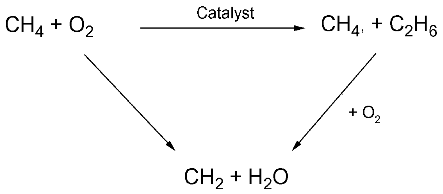

Fig. 4. Overall reaction scheme for the oxidative coupling of methane.

Table 2
Performance of some selected catalysts for oxidative coupling of methane [29].

Catalyst	T (K)	X_{CH_4} (%)	S_{C_2} (%)[a]	Y_{C_2} (%)[b]
Li/MgO	1013	37.8	50.3	19
BaF_2/Y_2O_3	1023	36.1	62.1	22.4
Rb_2WO_4/SiO_2	1123	32	78	25
La_2O_3–CeO_2	1048	22.3	66	14.7
Na_2WO_4/SiO_2	1123	44	52	22.9

[a] Selectivity towards C_2H_6 and C_2H_4.
[b] Yield of C_2H_6 and C_2H_4.

are examples of some of the best catalysts reported. It does not seem likely that it will be major improvements in the C_2 selectivity at reasonable conversions in the near future. In fact, it has even been predicted that an upper theoretical limit is yields of C_2 of about 30% at 1 atm [30–32]. The performance of some coupling catalysts is given in Table 2.

Oxidative coupling is an exothermic reaction and the formation of carbon oxides not only reduces the selectivity, but the heat of reaction is increased. Heat management is therefore also an important engineering problem.

The reaction follows a heterogeneous–homogeneous mechanism as indicated in Fig. 5 [33]. Methane is activated on the catalyst surface forming methyl radicals. The methyl radicals enter the gas phase where they couple to ethane. The gas-phase radicals may also participate in the formation of CO and subsequently of CO_2. The mechanism in Fig. 5 includes two different pathways. One pathway leads to the formation of oxygenates and the other to the formation of hydrocarbons. At high conversions a third reaction pathway becomes important, the decomposition of C_2H_4 to oxygenated species. It has been verified by isotopic labelling that CO_2 comes from CH_4 at low conversions whereas CO_2 at high methane conversion mainly comes from C_2H_4 [14].

The challenge in oxidative coupling is to find a catalytic material where the secondary reaction of C_2H_4 is inhibited while the activation of CH_4 is still functioning. Several approaches have been proposed, among others the use of membranes where methane and O_2 are separated and the use of cyclic reactors where the oxygen is supplied from the catalyst (no gas-phase O_2 present).

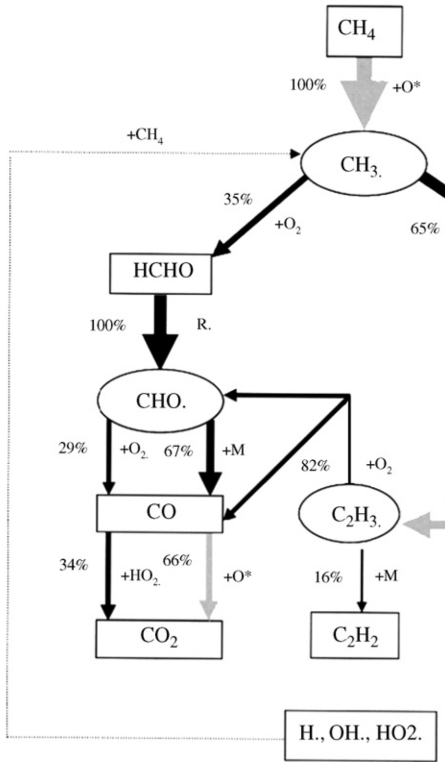

Fig. 5. Proposed mechanism for oxidative coupling of CH_4 over La_2O_3 at 1023 K. Black arrows are gas phase and grey arrows are surface reactions [33].

An example of the use of a ceramic membrane is $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) where good single pass yields (35%) have been reported at 900 °C [34]. Another example of a catalytic membrane reactor is the perovskite hollow fibre membranes [35]. In the membrane reactor air is fed to one side of the membrane and methane to the other side. A considerable improvement in the yield of ethylene has also been obtained by operating in a recycle mode with continuous removal of ethylene [14]. This approach needs absorbers or membranes that can remove ethylene selectively from dilute streams. Zeolites and microporous carbons have been proposed and used, but these materials must operate at lower temperatures than required for oxidative coupling. High yields of ethylene have been obtained by adsorbing the olefin in a 5 A molecular sieve at 30 °C and desorbing it by heating the sieve to 400 °C. In a variation of the recycle process a catalyst (Ga/HZSM-5) is used for converting the ethylene to aromatics at 500 °C [36]. The combination of oxidative coupling and dehydroaromatization has also been proposed and studied recently [37]. An increase in the benzene productivity is observed due to an increase in the production of ethylene and ethylene is an intermediate in the aromatization as discussed above.

The use of CO_2 instead of O_2 has also been studied lately [38]. Several different metal oxides have been tested as catalysts, but the yields are low.

A state of the art review of oxidative coupling has recently been presented [29]. The review contains all aspects of oxidative coupling from fundamentals to reaction and process engineering.

2.5. Partial oxidation of methane to methanol and formaldehyde

The direct selective oxidation of methane into methanol is a very attractive route and if a process could be established it would mean a breakthrough for the utilization of methane into useful chemicals:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH \qquad (4)$$

A large amount of research has been devoted to the direct partial oxidation of methane. For the methane to methanol technology several paths seem to exist:

1. A high temperature route based on homogeneous radical gas-phase reactions.
2. A low temperature catalytic route involving heterogeneous catalysis.
3. Homogeneous catalysis in solution.
4. Catalysis based on enzymes.

For the gas-phase radical chain reactions carried out at high pressure it seems to be no positive effect of the presence of a solid catalyst. In fact, reactor inertness is crucial for obtaining high selectivity of methanol and even the feed gas should be isolated from contacting with the metal wall. Quartz and Pyrex glass-lined reactors have been shown to give the best results. Typical experimental results from several studies [39] for the gas-phase partial oxidation of methane is shown in Fig. 6. The figure clearly demonstrates the key factor for the direct conversion of methane to methanol, the improvement of the selectivity without reducing the conversion per pass.

Pressure has a pronounced effect on the selectivity from partial oxidation of methane. At conditions where oxygen is completely depleted, it has been shown that by increasing the pressure the formation of CO decreases and the selectivity of methanol

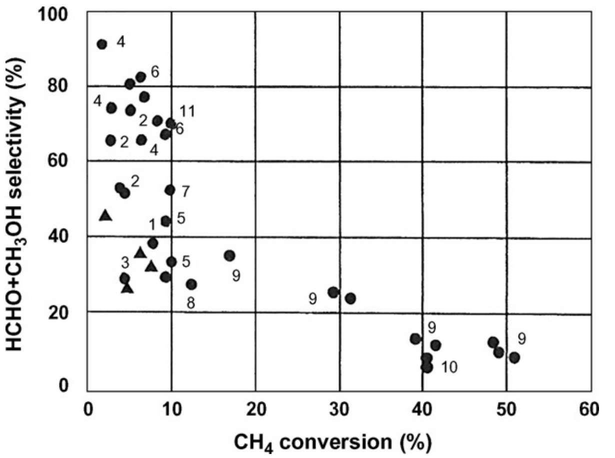

Fig. 6. Gas-phase partial oxidation of CH_4 from several studies. From Tabata et al. [39].

increases. Zhang et al. [40] claim that a pressure of 5.0 MPa would be suitable for methane oxidation at least in the temperature range 430–470 °C. Most results indicate a selectivity of 30–40% at a conversion 5–10% under the best conditions, i.e. temperatures of 723–773 K and pressures of 30–60 bar. The experimental and theoretical evidence so far supports the view that the possibilities of producing high yields of methanol are limited in the gas-phase system [41]. However, process schemes involving gas-phase partial oxidation and recycling of unconverted methane has been proposed as a possible GTL route [42]. It exits also reports that claim an even better performance although it has been difficult to reproducible.

At lower pressure, i.e. 1 atm, the catalyst is very important for the yields obtained by direct partial oxidation of methane. Although pressure has a pronounced effect on the formation of methanol, oxidation under high pressure is controlled by gas-phase reactions as described above. Some experimental results are shown in Table 3. Most results are obtained at temperatures above 773 K and HCHO is the main oxidation product. By carrying out the reaction at 600 °C in excess of water vapour on highly dispersed MoO_3/SiO_2, high selectivities to $CH_3OH + HCHO$ at conversions of CH_4 in the range of 25% have been reported [43]. The improved selectivity as a result of water addition, was ascribed to the formation of silicomolybdic acid (SMA: $H_4SiMo_{12}O_{40}$) over the silica surface.

It has been reported that up to 16% yields of oxygenates (methanol + formaldehyde) has been obtained by adding NO (1 vol.%) to the feed using a low surface area V_2O_5/SiO_2 catalyst at 923 K. The effect can probably be explained by a heterogeneous–homogeneous mechanism [45].

Isolated molydate species supported on silica are reported to have the highest specific activity and selectivity for the direct oxidation of methane to formaldehyde and a detailed mechanism of methane oxidation to formaldehyde has been presented [46,47].

Experimental studies on the direct partial oxidation of methane to methanol over a solid catalyst have so far not been successful. Otsuka and Wang [44] claim that the reason why CH_3OH cannot be obtained at the high temperatures needed for activation of CH_4 is that CH_3OH would immediately be decomposed or oxidized into HCHO and CO_x. Catalysts that are able to activate CH_4 at lower temperatures are therefore most important for the direct synthesis of CH_3OH. This is a very challenging problem due to the strength of the C–H bond in CH_4.

Table 3
Typical catalysts tested for the partial oxidation of methane [44].

Catalysts	Temperature (°C)	Conversion of CH_4 (%)	Selectivity of CH_3OH (%)	Selectivity of HCHO (%)
SiO_2	620	4.8	0	24
Mo/SiO_2	650	5.2	0	32
V_2O_5/SiO_2	650	13.5	0	25.3
$MoSnP/SiO_2$	500	7.2	0	64.8

Activation of methane at low temperatures has been studied using homogeneous catalysis. Shilov showed already in the 1970s that methane could be converted to methanol by Pt(II) and Pt(IV) complexes [48,49]. The catalytic system oxidizes selectively methane and not the more reactive product methanol. Organometalic approaches to methane conversion became a subject mainly after the work of Periana et al. [49] who proposed a process involving concentrated H_2SO_4 and a Hg(II) complex as a catalysts:

$$CH_4 + 2H_2SO_4 \rightleftarrows CH_3OSO_3 + SO_2 + 2H_2O \tag{5}$$

According to Periana et al. methyl bisulfate can readily be hydrolyzed to methanol:

$$CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4 \tag{6}$$

A bipyrimidyl platinum (II) complex has also been used as catalyst instead of the mercury complex [50]. By using the Pt complex a methane conversion of 90% and a selectivity of the methyl bisulfate of 81% were obtained at 493 K and 35 bar. As shown above it is expected that the bisulfate can be hydrolyzed to methanol. A complete cycle would require the costly regeneration of concentrated H_2SO_4 as indicated in the proposed catalytic cycle in Fig. 7. In more recent contributions [51,52], the key challenges and approaches for the development of the next generation of organometallic, alkane functionalization catalysts based on CH activation are presented and discussed. The question whether a process consisting of several steps such as shown in Fig. 7 can be developed and even operated in an economical way remains to be answered. However, it illustrates a system where the rate constant for breaking the C–H bond in CH_4 on Pt is much higher than the C–H bond in the product (methyl bisulfate).

It is known that methane monooxygenase catalyzes the selective oxidation of CH_4 to CH_3OH with oxygen at ambient conditions [53]. The enzyme activates O_2 at iron centers with the

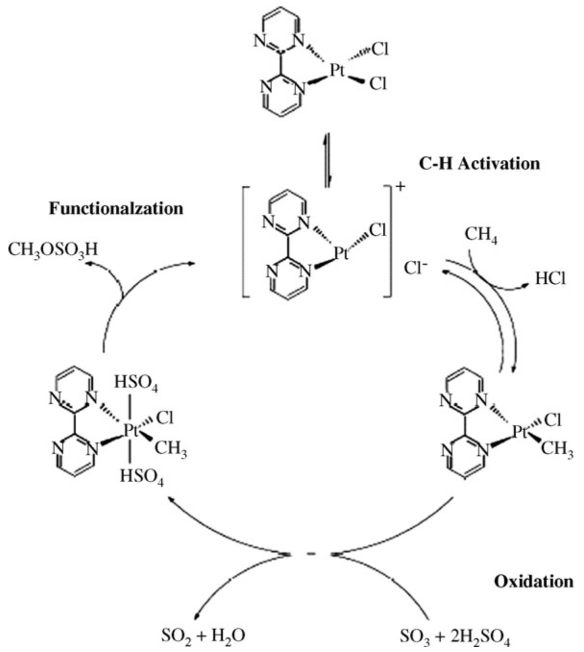

Fig. 7. Reaction mechanism for the oxidation of methane to methyl bisulfate using a bipyrimidyl Pt(II) complex in concentrated sulfuric acid [50].

aid of a reductant. In fact, there are some examples of research aiming at mimicing these systems using heterogeneous catalysts. Otsuka and Wang [44] have shown that $FePO_4$ is an interesting model catalyst when H_2 is added to the CH_4 and O_2 feed. CH_3OH and HCHO selectivities of 23 and 24%, respectively have been obtained at very low conversions (0.6%). However, the use of biological catalysts for practical purposes (large scale) is still very limited.

Methane can be converted to proteins and processes for production of bioproteins from natural gas have even been operated commercially.

2.6. Different processes (plasma, halogenation, photocatalysis and others)

One method for functionalizing methane is by chlorination. Methane can be converted to methanol or ethylene by oxychlorination with methyl chloride as an intermediate. The reaction to methyl chloride can take place in the gas phase or on a solid surface such as La-based catalysts [53,54]. The approach then involves acid-catalyzed hydration or oligomerization of methyl chloride as shown below:

$$CH_4 + HCl + \frac{1}{2}O_2 \rightarrow CH_3Cl + H_2O \qquad (8)$$

$$CH_3Cl + H_2O \rightarrow CH_3OH + HCl \qquad (9)$$

$$2CH_3Cl \rightarrow C_2H_4 + 2HCl \qquad (10)$$

Bromine has also been proposed as an alternative to chlorine [55–57].

A number of processes have been proposed from the Benson process at high temperatures [58] and the Olah [59] approach where methane was monohalogenated over either supported solid super acids or supported Pt at 180–250 °C.

This type of process does not seem very attractive due to the problems with halogenated hydrocarbons and the corrosive nature of the reactants. Oxidative chlorination is used commercially in the production of vinylchloride, but in the case of large scale methane conversion alternative approaches exist. The conversion via synthesis gas uses oxidants with lower toxicity and costs than the conversion via halides. Processes based on synthesis gas are also well established.

A number of different plasma technologies have been used by many both for the coupling of methane to ethylene and for the partial oxidation to methanol. It seems that the energy consumption is higher and the productivity for plasma processes is still lower than for other processes. There is, however, much research work devoted to the use of plasma technology for methane conversion.

It has been demonstrated that methane, dissolved in water, at temperatures >373 K and in the presence of a semiconductor photocatalyst and electron-transfer agent, can be converted to methanol and hydrogen using light [60]. The productivity, however, is still low. It is claimed that the conversion of methane is limited by the quantity of methane that can be dissolved in water. The concentration of methane in water can be increased by using methane hydrates and in fact this is has also been studied experimentally [60].

It has also been shown that acetic acid and methanol can be produced by a homogeneous reaction of CH_4 and CO_2 using $K_2S_2O_8$/trifluoroacetic acid (TFA) as catalyst/solvent [61]. A selectivity of about 75% to liquid products at a conversion of 25% is reported. TFA is expensive and difficult to handle and an alternative solvent must be found. The direct oxidative condensation of methanol to acetic acid using Pd(II)/H_2SO_4 has also been proposed and yields above 10% have been reported [62].

Methane is also an excellent feedstock for producing carbon (and hydrogen). Carbon black is produced commercially from methane and new materials with exiting properties like carbon nanofibers and nanotubes, can be produced [63].

3. Concluding remarks

The main obstacle for converting methane directly to more valuable products by heterogeneous catalysis is the low selectivity at high conversions; the products are more reactive than methane.

It has been a large focus on oxidative coupling of methane to C_2 hydrocarbons during the last 15–20 years. The obtained yields are still low due to the formation of CO_x. New ideas and new developments seem to be necessary for a renewed interest. Membranes and plasma technology are among the focus areas today.

The direct partial oxidation of methane to methanol over a solid catalyst has so far not been successful. However, relatively high yields of formaldehyde may be obtained and research work is being carried out on this route. For the activation of methane at low temperatures using homogeneous catalysis so far no practical applications have been developed in spite of a large research effort.

The direct catalytic conversion of methane remains a great challenge for the catalysis community. Several large research programs have recently been launched, an example being the Dow Award Methane Challenge Grant [64].

Methane conversion will also in the near future be based on synthesis gas. Since a large part of the capital cost of GTL plants is associated with the production of synthesis gas, there is presently a large focus on technology for production of synthesis gas from natural gas. Partial oxidation of methane [65,66] is an example of a topic of great interest. The conversion of biomass and coal to fuels will also involve synthesis gas as the primary product.

References

[1] S. Fosse Håkonsen, A. Holmen, Oxidative dehydrogenation of light alkanes, in: G. Ertl, H. Knötzinger, F. Schüth, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 7, 2008, p. 3384, Chapter 14.11.2.
[2] J. Rostrup-Nielsen, Catal. Today 18 (1993) 305.
[3] D. Schanke, E. Rytter, F.O. Jaer, Stud. Surf. Sci. Catal. 147 (2004) 43.
[4] T.H. Fleisch, R.A. Sills, M.D. Briscoe, J. Nat. Gas Chem. 11 (1–2) (2002) 1.
[5] Anon., Oryx GTL plant official opened, Focus on Catalysis, no 9 (2006) 4.
[6] A. Holmen, O. Olsvik, O.A. Rokstad, Fuel Process. Technol. 42 (1995) 249.
[7] A. Holmen, O.A. Rokstad, Å. Solbakken, Ind. Eng. Chem. Proc. Des. Dev. 15 (1976) 439.
[8] S.A. Miller, Acetylene. Its properties, Manufacture and Uses, vol. 1, Ernest Benn Ltd., London, 1965.
[9] K.R. Hall, Catal. Today 106 (1–4) (2005) 243.
[10] K.A. Bullin, J.G. Cantrell, High temperature hydrocarbon cracking. United States Patent 7,250,449, July 31, 2007 PCT/US02/33414.
[11] D. Trimm, I.O.Y. Liu, N. Cant, J. Mol. Catal. A: Chem. 288 (2008) 63.
[12] Q. Broutin, C. Busson, J. Weill, J. Billaud, Thermal coupling of methane, in: L.F. Albright, B.L. Crynes, S. Nowak (Eds.), Novel Production Methods for Ethylene, Light Hydrocarbons and Aromatics, Marcel Dekker, New York, 1992.
[13] Y. Xu, X. Bao, L. Lin, J. Catal. 216 (2003) 386.
[14] J.H. Lunsford, Catal. Today 63 (2000) 165.
[15] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, Y. Xu, Catal. Lett. 21 (1993) 35.
[16] L. Wang, R. Ohnishi, M. Ichikawa, J. Catal. 190 (2000) 276.
[17] H. Zheng, D. Ma, X. Bao, J.Z. Hu, J.H. Kwak, Y. Wang, C.H.F. Peden, J. Am. Chem. Soc. 130 (2008) 3722.
[18] H. Wang, L. Su, J. Zhuang, D. Tan, Y. Xu, Z. Bao, J. Phys. Chem. B 107 (2003) 12964.
[19] Z. Liu, M.A. Nutt, E. Iglesia, Catal. Lett. 81 (3–4) (2002) 271.
[20] W. Ding, G. Meitzner, E. Iglesia, J. Catal. 206 (2002) 14.
[21] S. Kikuchi, R. Kojima, H. Ma, J. Bai, M. Ichikawa, J. Catal. 242 (2006) 349.
[22] J.-P. Tessonnier, B. Louis, M.-J. Ledoux, C. Pham-Huu, Catal. Commun. 8 (2007) 1787.
[23] M. Ichikawa, Recent progress on the methane-to-benzene catalytic technology and its industrial application, in: Plenary Lecture, 8th Natural Gas Conversion Symposium, Natal, Brazil, May 27–31, 2007.
[24] L. Li, R. Borry, E. Iglesia, Chem. Eng. Sci. 56 (6) (2006) 1869.
[25] A.K. Kinage, R. Ohnishi, M. Ichikaawa, Catal. Lett. 88 (3–4) (2003) 199.
[26] T. Koerts, M.J.A.G. Deelen, R.A. van Santen, J. Catal. 138 (1992) 101.
[27] M. Belgued, P. Pareja, A. Amariglio, H. Amariglio, Nature 352 (1991) 789.

[28] G.E. Keller, M. Bhasin, J. Catal. 73 (1982) 9.
[29] E.V. Kondrakov, M. Baerns, Oxidative coupling of methane, in: G. Ertl, H. Knötzinger, F. Schüth, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 6, 2008, p. 3010, Chapter 14.11.2.
[30] J. Labinger, Fuel Process. Technol. 42 (1995) 325.
[31] Y.S. Su, J.Y. Ying, W.H. Green, J. Catal. 218 (2003) 321.
[32] J. Sun, J.W. Thybaut, G. Marin, Catal. Today 137 (1) (2008) 90.
[33] Y. Simon, F. Baronnet, G.M. Come, P.M. Marquaire, Stud. Surf. Sci. Catal. 147 (2004) 571.
[34] F.T. Akin, Y.S. Lin, Catal. Lett. 78 (2002) 239.
[35] Y. Tan, Z. Pang, Z. Gu, S. Liu, J. Membr. Sci. 302 (1–2) (1997) 109.
[36] S. Pak, C.E. Schmith, M.P. Rosynek, J.H. Lunsford, J. Catal. 165 (1997) 73.
[37] J.S. Espindola, N.R. Marcilio, O.W. Perez-Lopez, Stud. Surf. Sci. Catal. 167 (2007) 31.
[38] I. Wang, Z.H. Zhu, Energy Fuels 18 (2004) 1126.
[39] K. Tabata, Y. Teng, T. Takemoto, E. Suzuki, M.A. Banares, M.A. Pena, J.L.G. Fierro, Catal. Rev. Sci. Eng. 44 (2002) 1.
[40] Q. Zhang, D. He, J. Li, B. Xu, Y. Liang, Q. Zhu, Appl. Catal. A: Gen. 224 (2001) 201.
[41] R. Lødeng, O.A. Lindvåg, P. Søraker, P.T. Roterud, O.T. Onsager, Ind. Eng. Chem. Res. 34 (1995) 1044.
[42] N.A. Pawlak, V.I. Vedeneev, Method and Apparatus for Producing Methanol with Hydrocarbon re cycling, Patent WO 2007/075178 (05.07.2007).
[43] T. Sugimo, A. Kido, N. Kido, N. Azuma, A. Ueno, Y. Udagawa, J. Catal. 190 (2000) 118.
[44] K. Otsuka, Y. Wang, Appl. Catal. A: Gen. 222 (2001) 145.
[45] J.A. Barbero, M.C. Alvarez, M.A. Banares, M.A. Pena, J.L.G. Fierro, Chem. Commun. (2002) 1184.
[46] N. Ohler, A.T. Bell, J. Phys. Chem. B 110 (2006) 2700.
[47] S. Chempath, A.T. Bell, J. Catal. 247 (2007) 119.
[48] N.F. Goldshleger, V.V. Eskova, A.E. Shilov, A.A. Skteinman, Zh. Fiz. Khim 46 (1972) 785.
[49] R.A. Periana, D.J. Taube, E.R. Evitt, G. Loffler, P.R. Wentreck, G. Voss, T. Masuda, Science 259 (1993) 340.
[50] R.A. Periana, D.J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, Science 280 (1998) 560.
[51] R.A. Periana, G. Bhalla, W.J. Tenn, K.J.H. Young, X.Y. Liu, O. Mironov, C.J. Jones, V.R. Ziatdinov, J. Mol. Catal. A: Chem. 220 (2004) 7.
[52] R.G. Bergman, Nature 446 (2007) 391.
[53] J.A. Labinger, J. Mol. Catal. A: Chem. 220 (2004) 27.
[54] S.G. Podkolzin, E.E. Stangeland, M.E. Jones, E. Peringer, J. Lercher, J. Am. Chem. Soc. 129 (2007) 2569.
[55] V. Degirmenci, D. Uner, A. Yilmaz, Catal. Today 106 (1–4) (2005) 252.
[56] Z. Liu, L. Huang, W.S. Li, F. Yang, A.T. Au, X.P. Zhou, J. Mol. Catal. A: Chem. 273 (2007) 14.
[57] S. Svelle, S. Aravinthan, M. Bjørgen, K.-P. Lillerud, S. Kolboe, I.M. Dahl, U. Olsbye, J. Catal. 241 (2006) 243.
[58] M. Weissman, S.W. Benson, Int. J. Chem. Kinet. 16 (1984) 307.
[59] G.A. Olah, J. Am. Chem. Soc. 107 (1985) 7097.
[60] C.E. Taylor, Catal. Today 84 (2003) 9.
[61] M. Golombok, T. Nijbacker, M. Raimondi, Ind. Eng. Chem. Res. 43 (19) (2004) 6001.
[62] R.A. Periana, O. Mironov, D. Taube, G. Bhalla, C.J. Jones, Top. Catal. 32 (3–4) (2005) 169.
[63] I. Kvande, D. Chen, Z. Yu, M. Rønning, A. Holmen, J. Catal. 256 (2008) 204.
[64] Anon., Chem. Eng. News, 86(4) (2008) 14.
[65] B.C. Enger, R. Lødeng, A. Holmen, Appl. Catal. A: Gen. 346 (1–2) (2008) 1.
[66] A. Donazzi, A. Beretta, G. Groppi, P. Forzatti, J. Catal. 255 (2008) 241.