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Direct methane conversion routes to chemicals and fuels

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ABSTRACT

This paper addresses the options developed over the past two decades for the conversion of methane into valuable chemicals and fuels while avoiding the high energy requirements of the steam reforming process for producing H_2/CO mixtures. Several aspects of the approaches undertaken accordingly are briefly examined here. Each option has its own set of limitations. Nonetheless, the cost-effective separation of useful products is a common denominator across the board in these processes, with the other most important issue being the separation of oxygen from air, requiring C–H bond activation by oxygen. The widespread use of methane for producing fuels and chemicals appears to be within reach, but current economic uncertainties limit both the amount of research activity and the implementation of emerging technologies, although the extensive use of methane for the production of fuels and chemicals is expected to become a reality very soon.

1. Introduction

Methane is the main component of natural gas (NG), landfill gas and a by-product from oil refining and chemical processing. It has an enormous potential value as a source of clean fossil energy or as a raw material provided it can be brought to the point of use economically. NG reservoirs are large and widespread throughout the world, mainly in the Middle East and Russia, although other areas also have their fair share. The estimated reserves at the end of 2006 amounted approximately to 6300 trillion cubic feet [1], but the technology for the conversion of these reserves into chemicals and liquid fuels remains as yet elusive due to the extremely high stability of the C–H bonds in the CH_4 molecule. The mastery of methane chemistry would provide chemicals and liquid fuels, presenting an alternative to petroleum in these applications and enabling the use of a plentiful, though often remote, natural gas that is currently uneconomical to transport to target markets. In addition, it could also reduce the severe greenhouse effect of CH_4 [2] (21 times higher than the equivalent volume of CO_2) or the gas flaring associated with petroleum production, and it might even provide a way of upgrading landfill gas.

Many concepts have been developed for improving the industrial processes that convert methane into olefins, higher hydrocarbons and gasoline via indirect and direct conversion processes. However, these industrial technologies involve expensive separation steps and/or require high temperatures, usually above 600 °C, with the corresponding high energy consumption. On the one hand, direct methane conversion removes this requirement and consequently improves the economy of the process; on the other hand, since methane is a very stable molecule, its reactions have generally recorded high activation energy values, and once activated it is difficult to keep the reaction within pre-determined limits [3–5]. The unfavourable thermodynamics for methane self-interaction reactions has led us to conclude that without strong oxidants it would be difficult to convert methane into higher hydrocarbons at moderate temperatures using conventional catalytic approaches.

Currently, two viable large-scale approaches for converting methane to liquid hydrocarbons are being used: the methanol-to-gasoline (MTG) route and Fischer–Tropsch (FT) synthesis. Both processes begin with the production of synthesis gas (H_2/CO mixtures) from methane, which is a high-temperature, endothermic and costly operation [6]. Generally speaking, the steam reforming process involves two reactions, namely, the splitting of hydrocarbons with steam (Eq. (1)) and water gas shift (WGS) (Eq. (2)):

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^\circ_{298K} = +206.2\,\text{kJ/mol} \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^\circ_{298K} = -41.2\,\text{kJ/mol} \tag{2}$$

Direct methods for the conversion of methane to useful chemicals and fuels circumvent the extremely expensive intermediate syngas step [7]. Conceptually, direct methods should have a distinct economic advantage over indirect methods, but to date no direct processes have reached a commercial stage. Product yields are generally smaller [8] when operating in a single-pass mode, which makes separations difficult and costly.

Here, we offer an overview of recent developments relevant to the low- and high-temperature activation of methane, in either the

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presence or absence of oxygen, with the aim being to explore their implications for the future. The widespread use of methane for the production of fuels and chemicals appears to be near, but current economic uncertainties limit both the amount of research activity and the implementation of emerging technologies, although the extensive use of methane for the production of fuels and chemicals is expected to become a reality very soon.

2. Oxidative processes for methane conversion

2.1. Oxidative coupling of methane to higher hydrocarbons

The oxidative coupling of methane (OCM) involves the reaction of CH_4 and O_2 over a catalyst at high temperatures to form C_2H_6 as a primary product and C_2H_4 as a secondary product. Unfortunately, both the CH_4 and the C_2H_4 may be converted to CO_2, and the single-pass combined yield of C_2H_4 and C_2H_6 (C_2 products) is limited to about 25%. In the OCM process at around 800 °C, the following selective (Eqs. (3)–(5)) and non-selective (Eq. (6)) reactions occur simultaneously:

$$2CH_4 + 1/2O_2 \rightarrow C_2H_6 + H_2O \quad (\Delta H^\circ = -174.2\,\mathrm{kJ/mol}) \tag{3}$$

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \quad (\Delta H^\circ = -103.9\,\mathrm{kJ/mol}) \tag{4}$$

$$C_2H_6 \rightarrow C_2H_4 + H_2 \quad (\Delta H^\circ = +114.6\,\mathrm{kJ/mol}) \tag{5}$$

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O + \text{large amount of heat} \tag{6}$$

Since the pioneering work of Keller and Bhasin [9], a large body of work has been developed over the past twenty years as a potentially interesting process for upgrading natural gas. Many metal oxide catalysts have therefore been tested for this reaction. The catalysts can be grouped as: (i) oxides of groups 4 and 5 metals; (ii) oxides of group 3 metals; (iii) oxides of group 2 metals; (iv) oxides of group 1 metals; (v) lanthanide-based oxides; and (vi) transition metal oxides. The work already done in OCM reaction with the (i)–(vi) categories of catalysts up to 1993 has been reviewed and discussed in some detail [8,10].

Unfortunately, both CH_4 and C_2H_4 can be converted to CO_2, and the single-pass combined yield of C_2H_4 and C_2H_6 (C_2+ products) appears to be limited. In fact, an upper theoretical limit has been reported of about 30% yield to C_2 at 1 bar and O_2/CH_4 molar ratio of 0.5 [11,12]. Over the better catalysts, which include SrO/La_2O_3 and $Mn/Na_2WO_4/SiO_2$, a C_2 selectivity of about 80% can be achieved at a CH_4 conversion of 20% [13]. About half of the C_2 is C_2H_4 and half is C_2H_6, although the C_2H_4/C_2H_6 ratio can be enhanced by using a second catalyst. Still better performances have been recently reported for the Mn/Na_2WO_4 catalyst, with a C_2+ yield being achieved when using a CH_4/O_2 ratio of 5 and steam as diluent in the feed stream [14]. This catalyst records good stability for periods on stream up to 100 h (66–61% selectivity to C_2+ and C_2+ yield of 24.2–25.4%). The high C_2 selectivity is almost always achieved under oxygen limiting conditions; thus, the specific activity of the catalyst is not a factor. As the overall reaction is exothermic, a zone within the catalyst bed may be 150–300 °C hotter than the external temperature. Heat management, therefore, is a serious engineering problem. This is complicated by the fact that the metals normally used for the construction of reactors catalyze the total combustion of methane.

The reaction network is interesting from a fundamental perspective because it is an example of a heterogeneous–homogeneous system [15]. Methyl radicals formed at the surface of the catalyst enter the gas phase where they combine to form ethane. At atmospheric pressure, this coupling occurs mainly in the void space between catalyst particles. In addition to coupling, the gas phase radicals may enter the chain reactions that result in the formation of CO and subsequently CO_2. A simplified reaction scheme is presented in Fig. 1. Isotopic labelling experiments have shown that at small conversion levels most of the CO_2 is derived from CH_4, but at commercially significant conversion levels C_2H_4 would be the dominant source of CO_2. Additional experiments have shown that this occurs mainly via a heterogeneous reaction. One of the challenges in catalyst development is to modify a material so that the secondary reaction of C_2H_4 will be inhibited while the activation of CH_4 will still occur. There is no inherent reason for these two reactions to take place on the same types of sites.

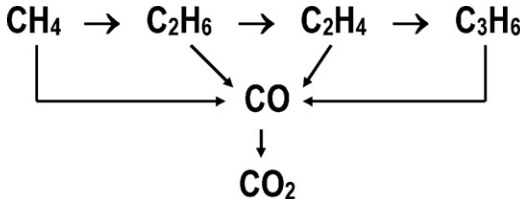

Fig. 1. Simplified reaction mechanism for the oxidative coupling of metane.

Both porous ceramic and dense ionic membranes and mixed-conducting ones have been applied for the OCM reaction [16]. Porous membranes such as alumina, zirconia, or Vycor glass have high stability for the reactions but low oxygen selectivity. By contrast, the oxygen selectivity for dense ionic or mixed-conducting oxide membranes is theoretically infinite and, therefore, air can be used as an oxygen source without contaminating the products with nitrogen and nitrogen oxides. A novel kind of hollow-fibre ceramic membranes, consisting of a dense, thin separating layer integrated with a porous substrate of the same material, record much higher oxygen permeation rates than the disc-shaped membranes [17], and hence appear particularly suited to commercializing mixed-conducting membrane reactors for OCM. Although the membrane concept is particularly suited to increasing CH_4 conversion, the major problem to be solved is the increase in the permeation rate.

In spite of the work existing on OCM, this technology has not yet been commercialized because there are important hurdles to be overcome in this process: (i) since C_2 hydrocarbons are much more reactive than methane, high selectivity in the process can be obtained only at low methane conversion; (ii) as the reaction is conducted at high temperatures (ca. 800 °C), a catalyst with high thermal and hydrothermal stability is required; (iii) using a low O_2/CH_4 molar ratio in the feed, the selectivity to C_2 hydrocarbons is high, but CH_4 conversion is rather low; and (iv) due to the low concentration of ethylene in the exit stream the cost of its separation is high, thereby rendering its separation uneconomical.

2.2. Partial oxidation of methane to oxygenates

The direct conversion of methane into C_1 oxygenates (CH_3OH and HCHO) involves partial oxidation under specific reaction conditions. This reaction operates at 350–500 °C under fuel-rich mixtures with the oxidant to minimize the extent of combustion reactions. Under these conditions, the gas-phase oxidation reactions of methane operate at high temperatures, which are detrimental to the control of selectivity to C_1 oxygenates.

$$CH_4 + 1/2O_2 \rightarrow CH_3OH(HCHO) \tag{7}$$

Accordingly, considerable efforts have been made to develop active and selective catalysts for the partial oxidation of methane. High selectivities to methanol have already been obtained by working under non-catalytic reaction conditions [18]. The Huels process uses cold-flame burners operating at 60 bar, with a selectivity of 71% to methanol and 14% to formaldehyde, and a recycle ratio of 200 to 1 [19]. The adiabatic temperature rise under these condi-

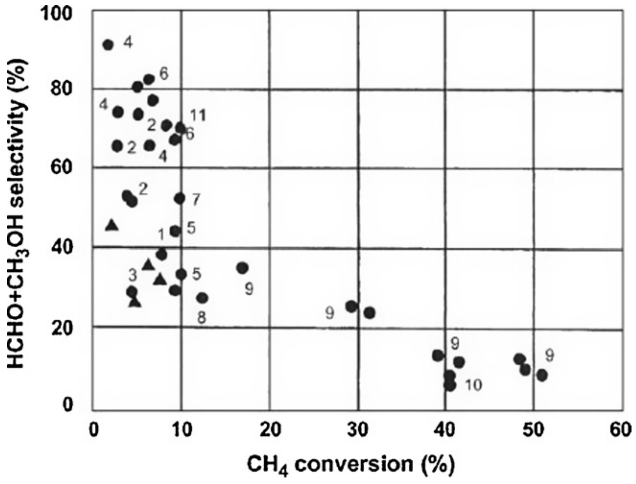

Fig. 2. Gas-phase partial oxidation of methane from several studies. Taken from reference [21].

tions is approximately 25 °C. A proper design of the flame reaction zone and close control of burning conditions allow obtaining high selectivities, even at conversions up to 3%.

Thermodynamic and kinetic analyses reveal that the rate-limiting step of the partial oxidation of methane is the first H-abstraction to form methyl radicals. Thus, initiators and sensitizers have been incorporated into the reaction mixture with a view to decreasing the energy barrier of this H-abstraction. Methanol yields as high as 7–8% are obtained in the absence of catalysts operating at 350–500 °C and 50 bar. As reactor inertness is essential for obtaining good selectivity to methanol, the feed gas should be isolated from the metal wall by using quartz and Pyrex glass-lined reactors [20]. A typical experimental conversion-selectivity plot for the gas-phase partial oxidation of methane is shown in Fig. 2 [21]. This plot ably demonstrates that any improvement in the direct conversion of methane to methanol must come from the enhancement of selectivity without reducing the conversion per pass.

Considerable efforts have been devoted to developing active and selective catalysts, but neither the product yield of C$_1$-oxygenates nor the complete mechanism of the reactions has been clarified. The selective O-insertion into CH$_3$, or other fragments resulting from the first H- abstraction of the CH$_4$ molecule, is usually conducted on redox oxides of the MoO$_3$ and V$_2$O$_5$ type [21,22]. In these systems, the key to maximizing catalytic performances is to maintain isolated metal oxide structures on a silica substrate in a slightly reduced state [23,24]. The presence of these partially reduced oxides allows the reduction–oxidation cycles of catalytic surfaces to proceed more rapidly and smoothly. Additionally, gas-phase radical initiators – i.e., nitrogen oxides – strongly enhance catalyst performance.

The performance of V$_2$O$_5$/SiO$_2$ catalyst is significantly altered by adding small amounts of NO in the gas feed [25]. Fig. 3 shows the effects of the CH$_4$/O$_2$ ratio and reaction temperature on the conversion of methane and on the yield values to C$_1$-oxygenates using a low specific area V$_2$O$_5$/SiO$_2$ catalyst combined with the addition of the NO radical initiator to the feed stream. The conversion of methane increases with temperature at all oxygen partial pressures (Fig. 3A). Similarly, the yield to C$_1$-oxygenates increases with the oxygen partial pressure at lower temperatures; however, it decreases at higher temperatures (Fig. 3B). The combined effect of both temperature and oxygen partial pressure affords a yield that reaches a maximum value at high temperatures (650 °C) and low partial pressure of oxygen (CH$_4$/O$_2$ = 1.8 M). The yield to C$_1$-oxygenates reaches 16% at atmospheric pressure, which is the highest value reported. The strong effect of NO appears to be due to the chain propagation of the radical reactions in the close vicinity of the catalyst bed. These trends are predicted by the reaction models [21,26]. The profiles in Fig. 3B clearly underline the relevance of both oxygen partial pressure and reaction temperature for a given NO concentration in the feed stream. The reactions induced by radicals are strongly affected by the reaction conditions. In particular, the methyl-methylperoxo ($CH_3^\bullet/CH_3O_2^\bullet$) radical equilibrium depends on the concentration of oxygen and on temperature and is shifted to O-containing radicals as temperature decreases.

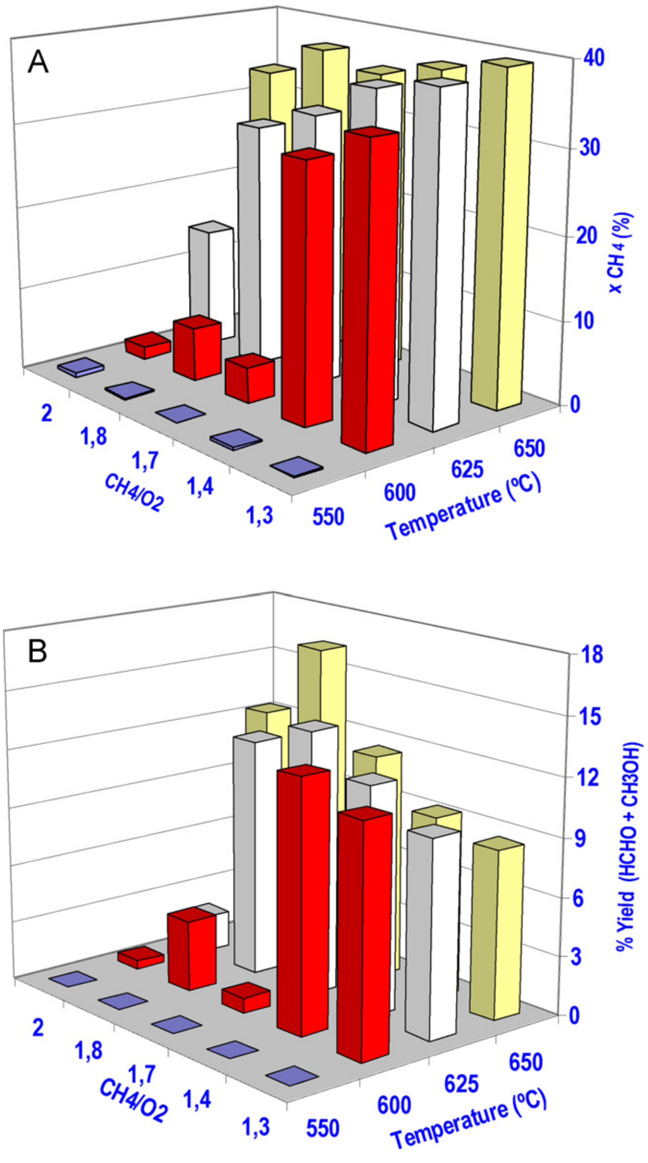

Fig. 3. Effect of temperature and of CH$_4$/O$_2$ ratio on the CH$_4$ conversion (A) and on the yield to C$_1$-oxygenates (B). (Reaction conditions: catalyst weight 0.30 g, total flow 122 mL/min, 22.9–34.4% CH4, 1% NO in N$_2$). Taken from reference [25].

2.3. Homogeneous liquid-phase oxidation

Low-temperature homogeneous activations of C–H bonds do not involve radicals and may lead to more selective reactions than those promoted by heterogeneous catalysts operating at high temperatures, such as OCM. The key problem lies in finding a catalyst system with suitable reactivity and selectivity while tolerating oxidizing and protic conditions. In the early 1970s, Shilov showed that methane could be converted to methanol by Pt(II) and Pt(IV) complexes [27] because these complexes do not oxidize CH$_3$OH

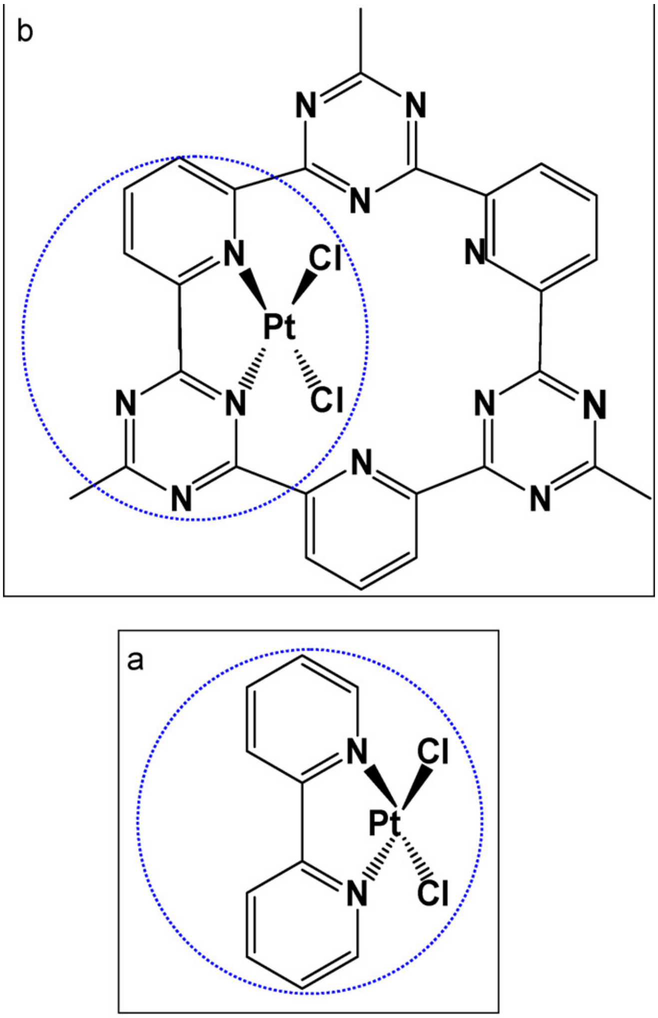

Fig. 4. (a), bipyrimidyl Pt(II) complex used in the oxidation of methane to of methyl bisulfate in concentrated sulphuric acid. (b), covalent triazine-based framework (CTF) with numerous accessible bipyridyl structure units which are suitable to coordinate Pt(II) complex.

to CO_x. Since that breakthrough, Periana et al. [28,29] have developed several oxidation catalysts based on Pt(II), Pd(II), and Hg(II) salts that have been proven to functionalize C–H bonds, leading to good yields of partially oxidized products (Eq. (8)). For example, [(2,2′-bipyrimidine)$PtCl_2$] catalyzes (Fig. 4a) the selective oxidation of CH_4 in fuming sulphuric acid to give methyl bisulphate in a 72% one-pass yield at 81% selectivity based on methane. Methyl bisulphate is then hydrolyzed to methanol (Eq. (9)):

$$CH_4 + 2H_2SO_4 \rightarrow CH_3OSO_3 + SO_2 + 2H_2O \quad (8)$$

$$CH_3OSO_3 + H_2O \rightarrow CH_3OH + H_2SO_4 \quad (9)$$

The major drawbacks of H_2SO_4 as a solvent system include not only the difficulty of separating the methanol product from the sulphuric acid but also the need for expensive corrosion-resistant materials and periodic regeneration of spent H_2SO_4. Pd(II) salts also catalyze the conversion of methane to methanol products in sulphuric acid solvent. However, presumably because of the reduction in Pd(II) to Pd(0) species and the slow reoxidation of Pd(0), this system is not as effective as ligated Pt(II) complexes. A complete cycle would require the costly regeneration of concentrated H_2SO_4, as indicated in the proposed catalytic cycle reported by Periana et al. [29]. In more recent contributions [30], 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.

Table 1

Comparison of catalytic activity of the molecular Periana' system and the heterogeneous Pt-CFT and $K_2[PtCl_4]$-CFT catalysts in methane oxidation.

Catalyst[*]	Catalyst weight (mg)	[CH_3OH] (mol/L)	TON[**]
Periana catalyst	65	1.65	158
Periana catalyst	26	1.49	355
$K_2[PtCl_4]$-CTF		1.54	201
Pt-CTF	48 CTF + 92 $K_2[PtCl_4]$	1.80	246

[*] Reaction conditions: 15 mL H_2SO_4 (30% SO_3), 40 bar CH_4 pressure (25 °C), 2.5 h at 215 °C.

[**] Turnover number.

A new class of solid catalyst has recently been reported for the direct low-temperature oxidation of methane to methanol [31]. This solid catalyst is a covalent triazine-based framework (CTF) with numerous accessible bipyridyl structure units, which should allow the coordination of platinum, and resemble the sites for platinum coordination in the molecular Periana catalyst Fig. 4b. The performance of these new catalysts is compared in Table 1 with the activity of the Periana catalyst. The achieved methanol concentrations in the final reaction mixtures and the turnover numbers (TON) proved to be rather similar for the two types of catalyst. Activity is maintained throughout several cycles, and selectivity for methanol formation above 75% could be reached.

Efforts are being focused on more direct methods for generating acetic acid, such as the oxidative carbonylation of methane, but no new processes have yet been commercialized. Several new catalyst systems have been reported for the selective conversion of methane to functionalized methyl products such as methanol, esters, sulfonic acid, and acetic acid. In the reported cases of methane conversions to acetic acid, the methyl group of the acetic acid is derived from methane, whereas the carboxylic group is derived from various carbon sources, such as CO, CO_2, or carboxylic acid reactants. [32–34].

Methane undergoes liquid-phase sulfonation with 30 wt% SO_3 in sulphuric acid to form methanesulfonic acid (MSA) using metal peroxides [35] or peroxide salts [36] as free-radical initiators. The CH_3 radicals generated with peroxides can then react with SO_3 to form the $CH_3SO_3\cdot$radical, which can abstract hydrogen from methane to form MSA. Similarly, $K_2S_2O_8$ salt has been used as a free-radical initiator to sulfonate methane with SO_3 in fuming sulphuric acid [36]. Working at a pressure of 6.9 MPa, methane conversion to MSA in the 3–6% range can be achieved.

2.4. Biological oxidation

In nature, methane monooxygenase enzymes (MMO) transform CH_4 to CH_3OH in water under physiological conditions. Complexes mimicking the structural organisation and spectral features of MMO are known, but real functional chemical models capable of oxidizing CH_4 have yet to be created. In contrast to organometallic CH_4 activation, MMO proceeds via a different mechanism by creating a very strong oxidizing di-iron species able to attack a C–H bond in CH_4. An essential feature of MMO is an active site containing two iron centres. Metallophthalocyanines (MPc), and more specifically iron phthalocyanines (FePc), are good catalysts for clean oxidation processes. More specifically, FePc supported in μ-oxo dimeric form (Fe–O–Fe fragment) has better catalytic properties in CH_4 conversion in the presence of hydrogen peroxide as oxidant than its monomer counterpart (FePc). The heterolytic cleavage of the O–O bond in $Fe^{IV}NFe^{III}OOH$ complex and the formation of very

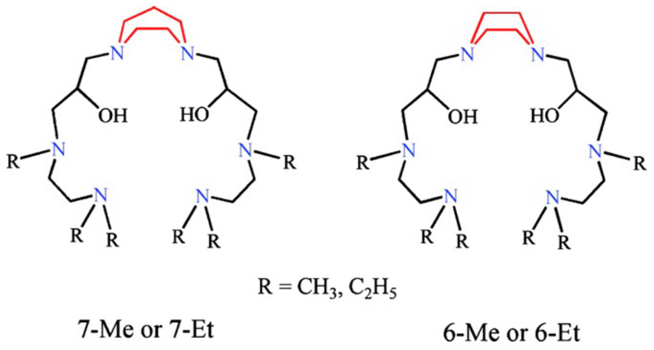

Fig. 5. Ligands used to construct the $[Cu^ICu^ICu^I(L)]^{1+}$ complexes. Adapted from reference [32].

strong oxidizing $Fe^{IV}NFe^{V}{=}O$ species are favoured in the presence of acid by the protonation of peroxide oxygen [37].

A new oxidation mechanism based on the use of metal clusters to harness the “singlet oxene”, the most reactive form of the oxygen atom, has recently been proposed [38]. In this proposal, the key to oxygen insertion is a complex containing three copper atoms, in which the atomic charges vary. By synthesizing a series of ligands to complex three copper atoms, mimicking the likely structure of the active site in pMMO, facile O-atom insertion into C–C and C–H bonds has been demonstrated in a number of simple organic substrates under ambient conditions of temperature and pressure. The ligands were designed to form the proper spatial and electronic geometry to harness a “singlet oxene” (Fig. 5). Consistent with the design strategy, upon activation with dioxygen the trinuclear $Cu^ICu^ICu^I$ cluster can mediate facile O-atom transfer to organic substrates similar to the chemistry catalyzed by pMMO.

3. Non-oxidative conversion of methane

In the absence of an oxidant, the activation of the C–H bonds of the highly stable CH_4 molecule requires high temperatures. Under such conditions, radical reactions in the gas phase prevail. However, as the strength of the C–H bond in the resulting C-containing products is weaker than methane, the products will be more reactive than methane. This means that the challenge in methane conversion is related to selectivity rather than to reactivity. In order to circumvent theses hurdles, several different approaches based on catalysis and reaction engineering have been proposed and tested. Some of these approaches are briefly described below.

3.1. Methane cracking

The thermal cracking of methane in an O-free environment produces hydrogen and elemental carbon. This reaction is a moderately endothermic process; the energy required per mole of H_2 produced (+37.8 kJ/mol H_2) is much lower than that required by steam reforming (+63.3 kJ/mol H_2) [39]. In addition to H_2, the process also yields carbon.

$$CH_4 \rightarrow 2H_2 + C \quad (\Delta H^\circ = +75.6\,\text{kJ/molCH}_4) \tag{10}$$

Thermodynamic calculations indicate that the thermal decomposition of methane at high temperatures may also give ethylene, acetylene and benzene as the main products, provided that the reaction can be stopped before carbon is formed [40]. Excessive carbon formation can be avoided using short reaction times and low partial pressures of methane. In addition, rapid quenching of the reaction mixture is also very important, whereby high yields of acetylene (ca. 90%) are obtainable at extreme temperatures (>1800 °C) and short reaction times ($<10^{-2}$ s).

The reaction mechanism consists of complex radical dehydrogenation reactions in the gas phase forming ethane, ethylene and acetylene and, finally, carbon and hydrogen. The chemistry of the process is well established and the challenge lies in the engineering of the pyrolysis reaction. Many processes for acetylene production have been developed and even operated commercially with some success. The differences between all these processes are due mainly to the way heat is supplied and removed from the reactor. This process has been used for decades in the production of carbon black, with a small part of hydrogen being used as fuel for the process (Thermal Black Process) [41]. Metal and carbon catalysts are often used to decrease the decomposition temperature. When using metal catalysts, H_2 production according to this simple approach involves two steps: catalytic decomposition (Eq. (10)) and the regeneration of deactivated catalyst in the presence of an oxidant such as air, O_2, CO_2, or H_2O. The interest in this approach for producing CO-free hydrogen involves the purity of the hydrogen (<10 ppm CO) required to feed the proton exchange membrane fuel cells.

3.2. Oxidative cracking and autothermal cracking

The thermal decomposition of methane occurs at very high temperatures (>1100 °C). Transition metal catalysts are often used to reduce this temperature; however, they are rapidly deactivated by carbon deposits on the metal phases. By contrast, metal-free carbon substrates have certain advantages over metal catalysts due to their availability, durability and low cost. Carbon-based catalysts are sulphur- and temperature-resistant and do not require the separation of a C-product from a carbon catalyst. The data available on the catalytic activity of a variety of carbon materials basically include activated carbons (AC) and carbon blacks (CB) [42–45]. Amorphous AC and CB carbons are much more active in the methane decomposition reaction than other well-ordered carbon materials such as graphite and nanotubes. This finding points to the direct correlation between the surface concentration of unsaturated, high-energy surface sites and catalytic activity. The driving force for the reaction is that defective carbon atoms tend to react with CH_4 molecules in order to satisfy their valence requirements.

The heat required to drive methane decomposition can be supplied in different ways. One process uses two vessels: a reactor and a heater, with catalyst particles circulating between the vessels in a fluidized state. Catalyst particles are heated by hot combustion gases (burning part of the methane or off-gas from an H_2 separation unit) and carry enough heat to the reactor to decompose CH_4. Another option consists in feeding a relatively small amount of oxygen into the reactor along with the CH_4 feedstock to generate the heat required for the endothermic methane decomposition reaction. Thus, the process involves the combination of endothermic (CH_4 decomposition) and exothermic (CH_4 combustion) reactions in the same unit. This process is called autothermal pyrolysis (ATP). It is evident that the ATP process uses much less oxygen and consequently produces fewer CO_2 emissions than conventional partial oxidation. The total enthalpy flow within the reactor is a function of temperature and O_2/CH_4 ratio. It appears that the enthalpy flow for the practical range of temperatures (600–900 °C) is close to zero, and corresponds to an ATP regime, at an O_2/CH_4 ratio close to 0.2.

In addition, the ATP process requires an oxygen production unit, which adds to the cost of hydrogen production. One promising approach considers the use of ceramic oxygen-permeable membranes. Dense ceramic membranes of perovskite-types oxides, e.g., Sr–Fe–Co and Ba–Sr–Co–Fe mixed oxides are good oxygen permeable systems [46]. Oxygen permeation rates of 10 mL/cm^2 min and higher are obtained.

3.3. Combination of methane conversion processes

The conventional route for producing ethylene on a commercial scale is the high-temperature non-catalytic steam cracking of hydrocarbons. Typical feedstocks used for this purpose include C_2–C_4 paraffins or even higher molecular weight hydrocarbons. Recently, methane has also been proposed as a hydrocarbon source for the industrial production of ethylene.

In a recent patent, Mamedov et al. [47] disclosed a novel concept in which methane is first converted to acetylene via high-temperature pyrolysis and then the acetylene rich stream is quenched and mixed with another hydrocarbon such as ethane. The acetylene and the ethane react in the absence of a catalyst, and hydrogen is transferred from ethane to acetylene to yield reasonably high levels of ethylene. This last step is considered as in situ hydrogenation. Accordingly, both pyrolysis and hydrogenation can be performed in a single process unit, or integrated reactor. This is illustrated by one example of application: under a temperature of 858 °C and residence time of 0.44 s, a stream consisting of 8.8% C_2H_2, 17.2% C_2H_6, 37.2% H_2 and N_2 balance fed into in situ hydrogenation yielded 12.75% C_2H_4, 2.13% C_2H_2, 3.47% C_2H_6, 41.4% H_2, 2.19% CH_4, less than 1% propylene, butenes and benzene, and N_2 balance. The ethane added during the hydrogenation step is understood to act as a template-like reagent to initiate and promote the desired reactions to form ethylene. Indeed, this process does not suffer from temperature runaway or from catalyst deactivation, and thus simplifies downstream processing units by reducing the operating and capital costs of an ethylene plant. This approach is allegedly less capital intensive than the conventional Methanol-to-Olefins process. In addition, because no catalysts are needed for acetylene synthesis or for in situ hydrogenation, the scale-up of this technology is more straightforward.

Another combined process for the production of aromatic hydrocarbons and syngas mixture from methane has recently been patented [48]. In this three-step process, a methane feed reacts first on an aromatization catalyst to yield an effluent stream comprising aromatic hydrocarbons, hydrogen and unreacted methane. This reaction is endothermic, and so inter-stage heating is required to return the feed to the required reaction temperature. The fuel required accordingly is obtained by removing and combusting a side stream from the dehydrocyclation effluent, after separating the aromatic components. The major components of the effluent stream are hydrogen, benzene, naphthalene, ethylene and residual methane. In a second step, benzene and naphthalene are recovered from the stream by solvent extraction followed by fractionation. Finally, in the last step, hydrogen and unconverted methane are reformed to yield a H_2/CO (syngas) mixture according to conventional steam methane reforming technology with nickel-based catalysts.

3.4. Methane aromatization

Methane can also be dehydrogenated (MDA) on catalysts in the absence of gas-phase oxygen to produce highly value-added chemicals such as benzene, naphthalene and hydrogen [49,4]. Although the reaction takes place at temperatures lower than those applied in thermal pyrolysis, the yield is limited by thermodynamics; that is, the CH_4 conversion at equilibrium under 1 bar and 700 °C is about 12.2% and almost double at 800 °C [8].

$$6CH_4 \rightarrow 9H_2 + C_6H_6 \quad (\Delta H^{\circ}_{298K} = +88.7\,\text{kJ/mol}CH_4) \qquad (11)$$

Wang et al. [50] showed that the bifunctional Mo/HZSM-5 catalyst is highly active and selective in this reaction. Since this finding, many other bifunctional catalysts consisting of narrow pore zeolites and a metal oxide MO_x (M = Mo, W, V, Cr) phase have been reported.

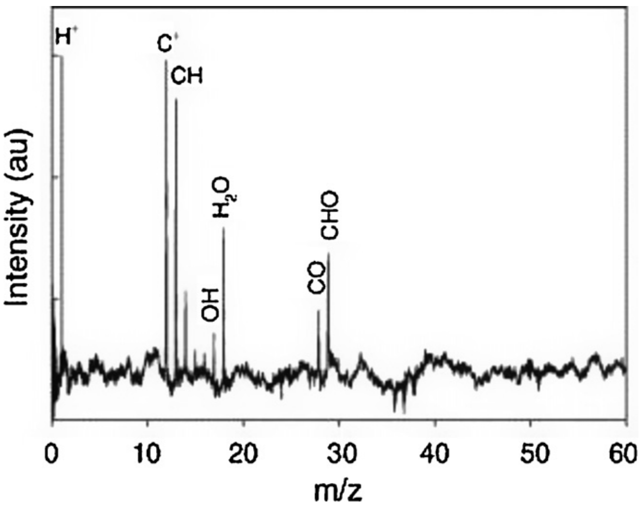

Fig. 6. MS signal observed in the induction period of CH_4 dehydroaromatization at 600 °C over 3%Mo/HZSM-5 catalyst. Taken from reference [51].

For a 3% Mo/ZSM-5 catalyst, it has been shown that MoO_3 is first converted into Mo_2C with the simultaneous formation of O-containing species such as H_2O, and CO (or CO_2), along with fragments of CH_4 dissociation. These fragments include signals of H^+, CH_x^+ (x = 0–3), with H_2O^+ and CHO^+ ions also being detected (Fig. 6) [51]. This suggests that the CH_x fragments from CH_4 decomposition react with surface oxygen on the catalyst to form a CHO radical, which then further dissociates into CO and H-atoms CH_4 dissociates first into CH_x (x = 0–3) radicals and H-atoms over Mo_2C, and then the direct oligomerization and aromatization of CH_x species in forming naphthalene occurs at the Brønsted acidic sites of HZSM-5 (Fig. 7) [51]. Ma et al. [52] precluded ethylene as an intermediate of the methane aromatization reaction because ethylene in the gaseous phase is not responsible for the formation of aromatic compounds. In addition, small molecules such as C_2H_4 and C_2H_6 do not appear in the gas-phase at contact times of ca. 10^{-3} s due to hydrogen deficiency. Therefore, both the activation of the C–H bond of methane and the formation of the initial C–C bond take place on the reduced Mo carbide species, which is formed from the reduction of MoO_x species by CH_4 at the early stage of the reaction, while the subsequent oligomerization, cyclization, and aromatization of the C_2 hydrocarbon fragments are catalyzed by the Brønsted acid sites of the HZSM-5 zeolite [53,54]. It has recently been proven by means of the 95Mo MAS-NMR spectra of carburized Mo/ZSM-5 catalysts that the MDA reaction occurs on isolated Mo_2C (or oxycarbide) species placed inside the channels of the ZSM-5 zeolite, which are indeed in the close vicinity of the Brønsted acid sites.

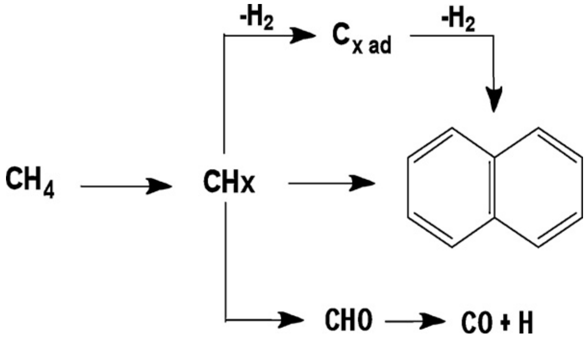

Fig. 7. Mechanism of CH_4 dehydrogenation under low spatial velocity (10^{-3} s) over 3%Mo/HZSM-5 catalyst. Taken from reference [51].

The catalysts are easily deactivated during on-stream operation. The activated methane molecules could re-adsorb and become anchored to the active Mo species to form coke. Further dehydrogenation and oligomerization of monocyclic aromatic products could also lead to the deposition of aromatic-type carbon species on the Brønsted acid sites. The carbon deposits associated with the Mo species are reactive and reversible; nevertheless, the coke formed on the Brønsted acid sites is inert and irreversible. The latter species is responsible for the deactivation of the Mo/HZSM-5 catalyst [39]. In the course of the reaction, carbon is accumulated on the catalyst surface and activity progressively drops. Graphitic carbon and additionally encapsulated carbon, originated mainly from the successive dehydrogenation and polymerization of CH_x radicals or naphthalene graphitization on the surface, were observed with the HRTEM. It has also been shown that deactivation is to some extent reduced by adding CO/CO_2 to the feed stream [54].

The thermodynamic constraints of the MDA reaction can be overcome by using hydrogen-selective transport membranes. Thus, recent theoretical work has reported promising results [55]. In addition, a substantial 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 in conjunction with Mo/HZSM-5 catalyst [56], even though the synthesis and operation of membranes are not straightforward.

4. Other methods

4.1. Methane halogenation and oxyhalogenation

Methane can be functionalized through chlorination or oxychlorination reactions. Methane conversion via halogenation was first proposed by Olah et al. [57] and Weissmann and Benson [58] in the mid 1980s. This method involves extracting hydrogen from methane and producing methyl halide (CH_3–X with X = Cl, Br) under relatively mild conditions. Therefore, the condensation of this methyl halide into higher hydrocarbons or oxygenates is an alternative route for commercial methane conversion into fuels and chemicals. Supported acid catalysts, such as $TaOF_3/Al_2O_3$, $ZrOF_3/Al_2O_3$, SbF_5/graphite and Nafion/TaF_5, are effective in chlorination reactions. The approach consequently involves the acid-catalyzed hydration or oligomerization of methyl chloride. Bromine has also been proposed as an alternative to chlorine [59,60]. A number of processes operating either at low [61] or high temperatures [58] have been proposed, although these processes do not seem attractive due to the problems associated with halogenated hydrocarbons and the corrosive nature of the reactants.

A more interesting approach involves the selective conversion of methane to monochloromethane by reacting methane with hydrochloric acid and oxygen to yield CH_3Cl in a first step. This intermediate is then hydrolyzed with water to yield methanol, and methanol can finally be dehydrated to obtain olefins [62]. Oxidative chlorination is used commercially in the production of CH_3Cl using copper-chloride catalysts according to Eq. (12):

$$CH_4 + HCl + 1/2O_2 \rightarrow CH_3Cl + H_2O \tag{12}$$

Similarly, lanthanum-based catalysts have proven to be active for the chlorination of methane, and the recycling of the hydrochloric acid might be applied [63]. A one-reactor concept has recently been proposed for the conversion of methane to hydrocarbons via bromomethane [64,65]. In the activation of methane with a halogen atom, other than in gas phase reactions, heterogeneous systems require acid centres to polarize the halogen molecule in order to break the symmetry of the CH_4 molecule and split the C–H bond by an electrophilic insertion reaction (Eq. (13)):

$$CH_4 + Br_2 \rightarrow [H - CH_3Br^+ + Br^-] \rightarrow CH_3 - Br + HBr \tag{13}$$

Sulphated zirconia (SZ) is a good candidate for the bromination of methane because it has high catalytic activity in the isomerization of small hydrocarbon molecules at low temperatures, which requires strong acid sites. It has recently been shown that monobromomethane (CH_3Br) can be obtained selectively at relatively high methane conversions (69%) with a proven strong acidity with relatively high acidity (sulphated 25 mol% ZrO_2/SBA-15) [66].

4.2. Microplasma activation

A direct and selective synthesis of C_1-oxygenates and dimethylether (DME) via methane partial oxidation at room temperature using a non-thermal discharge microreactor has been reported only very recently [67,68]. A flammable CH_4 and O_2 mixture is activated in this microplasma reactor by high energy electrons produced by dielectric barrier discharge (DBD), which initiates oxidative destruction of highly stable C–H bonds of CH_4 independently of reaction temperature.

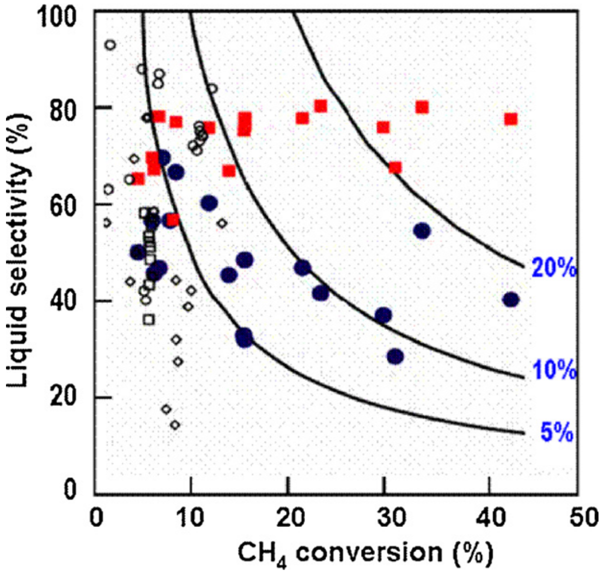

Fig. 8. Liquid selectivity (●: S_{liq} and ■: S_{total}) vs. methane conversion. Reaction conditions: O_2/CH_4, 0.5 and 1.0; reaction time, 130-530 ms. Three curves represent constant yield lines. Hollow symbols express sited literature; (□) Bjorklund and Carr [69]; (○) Feng et al. [70], (◊) Yarlagadda et al. [71].

Fig. 8 shows the selectivity to liquid components (C_{1oxy} and C_{1oxy} + DME) as a function of CH_4 conversion obtained by a wide range of operating conditions. The results are compared with other literature references that used thermochemical methods [69–71]. In this non-conventional method, thermal energy is added to initiate methane oxidation, while a small amount of oxygen, typically 10% at the most, is introduced so that heat generated by methane oxidation does not create high temperature hot spots. Although CH_4 conversion increases by increasing either O_2 content or reaction temperature, the selectivity to useful oxygenates hardly drops. Unlike a conventional technology, liquid product selectivity decreases slightly with CH_4 conversion, implying that liquid product separation worked effectively in this microplasma reactor. Although a one-pass liquid yield of over 15% is obtainable with this microplasma reactor, liquid selectivity was below 60%. In addition to oxygenates, this microplasma produces a relatively large amount of syngas with 40% selectivity and H_2/CO = 1. Assuming one-step catalytic DME synthesis to be a post-discharge reaction, an overall liquid yield of 30% with 80% selectivity is feasible. A further increase in oxygenate selectivity is an important issue. In addition, the effective integration of microplasma technology and existing catalytic processes is an attractive option for an economically and technologically viable material conversion process.

5. Conclusions

This report summarizes very different approaches to tackling the reasonably direct conversion of methane to chemicals and fuels by avoiding the two-step energy intensive steam reforming process. Considering that the C–H bond energy in the CH_4 molecule is very high, the use of a co-reactant is required for its activation. Although oxidative routes based on the use of dioxygen, if successful, would be of enormous industrial significance, it appears that a suitable active and selective catalyst has yet to be designed. Conversions involving selective chlorination are more attractive as far as activity and selectivity are concerned, but the problems associated with the use of highly corrosive environments remain. Methane coupling to unsaturated hydrocarbons may be useful, provided that more active and selective catalysts can be discovered, but a plentiful source of such unsaturated feed is of course required to exploit this approach.

OCM catalysis has reached maturity, as many catalytic systems have been tested for their performance and no further enhancements are envisaged. Selectivities of up to 85% for C_2 hydrocarbons have been obtained for methane conversions of around 10 to 15%. The general trend observed is that increasing the methane conversion, which is usually achieved by decreasing the CH_4/O_2 ratio in the feed, leads to a drop in selectivity. The highest C_2 yields fall to around 22% under single-pass reactor operation. High temperatures (>700 °C) and basic metal-oxide type catalysts are key ingredients for the generation of methyl radicals while avoiding deep oxidation to CO_x, which occurs through methoxy species preferentially formed at low temperatures. Apart from this general trend, sustained research efforts for the development of better oxides are essential to make the OCM reaction commercially feasible. Supported rare earth oxide catalysts promoted by alkaline-earth oxide (particularly SrO) are highly active, selective and thermally/hydrothermally stable for the coupling reaction, and hence show great promise for use in the OCM reaction.

Recent patents involving plasma-assisted methane conversion processes appear quite promising for simultaneously obtaining acetylene and liquid fuels. Notable projections emerge when looking at the combined processes, in which an endothermic reaction is coupled with another endothermic one. Proper management of the heat may result in overall autothermal operation, thus providing economic incentives for process development.

In short, many recent attempts have shown promise, but the challenge of designing suitably selective and active catalysts remains.

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