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Challenges for the utilization of methane as a chemical feedstock

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Abstract:

The abundance of methane has led to a strong interest to use methane as a feedstock in the chemical industry. One of the main challenges is the initial activation of the methane molecule. This has resulted in the development of several different approaches to utilize methane, some more developed than others. In this work the current status of the different approaches is discussed and the main issues for industrial utilization described. A special focus of this work is the status of catalyst development.
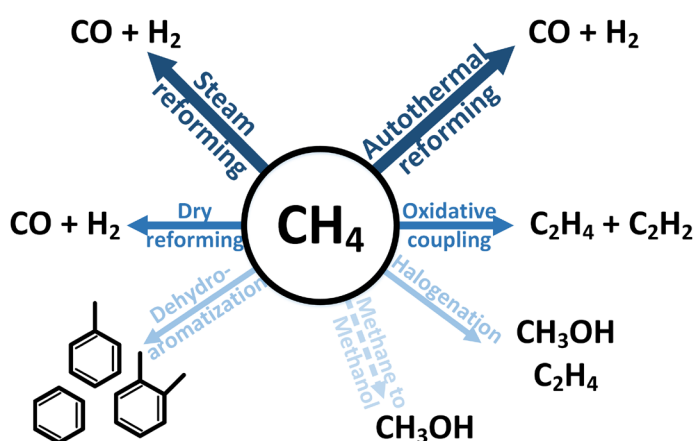
Keywords: Methane activation, heterogeneous catalysis, methane upgrading

Biographies:

Dr. Robert Franz received his MSc degree in Chemical and Process Engineering from Karlsruhe Institute of Technology (Germany) in 2016, and his PhD in Chemical Engineering on the topic of catalytic methane valorization from Delft University of Technology (The Netherlands) in 2021. Since 2021 he is working as a research engineer for BASF SE.


Dr. Evgeny Uslamin graduated from Novosibirsk State University (Russia) in 2014 and received his PhD degree in Inorganic Chemistry and Catalysis from Eindhoven University of Technology (The Netherlands) in 2019. Since 2019 he is a research associate in the Inorganic Systems Engineering group at Delft University of Technology. In 2021, he has got a part-time position at the University of Tyumen, where he guides the establishment of a new TsyfroCatLab.

Prof. Dr. Evgeny Pidko received Ph.D. from Eindhoven University of Technology in 2008, where in 2011-2017, he was an Assistant Professor of Catalysis for Sustainability. In 2016 he became a part-time professor of theoretical chemistry at ITMO University, St. Petersburg. In 2017, he joined Delft University of Technology as an associate professor and head the Inorganic Systems Engineering group; and in 2020 he was appointed Full Professor. Since 2021, he is advising the establishment of the TsyfroCatLab at the University of Tyumen. His research program successfully combines experiments and theory to understand catalytic reaction mechanisms and use these fundamental insights to guide the development of new, more sustainable and efficient chemical technologies.

1 Introduction

Methane (CH_4) is both the simplest and one of the most abundant hydrocarbons available. Methane is the main component of the natural gas present in concentrations of 70–90%.[1] At the end of 2018 the total proven reserves of natural gas amounted to 196.9 trillion m^3,[2] which is sufficient to fulfill human demands for the next 50 years if gas consumption remains on 2018 levels. Furthermore, methane is the main component of biogas, making up more than 50% in almost all cases.[3] Despite this abundance, the usage of methane in the chemical industry is still limited. More than 90% of methane used worldwide is burned to generate electricity, heat (for cooking) or similar.[1] Methane is not only burned to generate energy. Significant quantities of methane are burned or flared in the extraction of oil. Methane is a common by-product in oil extraction (so-called associated gas). The common options available to operators of oil extraction operations are to burn the gas, re-inject it into the ground or release it into the atmosphere. On a molar basis the contribution of methane to the greenhouse effect is 25 times greater than that of CO_2.[4] Flaring the associated gas is therefore preferred over releasing methane into the atmosphere. As a result, in 2017 a total of 140 bcm of methane (corresponding to 270 Mt of CO_2) were flared but an even larger amount of methane was released into the atmosphere (*Figure 1*).[5]
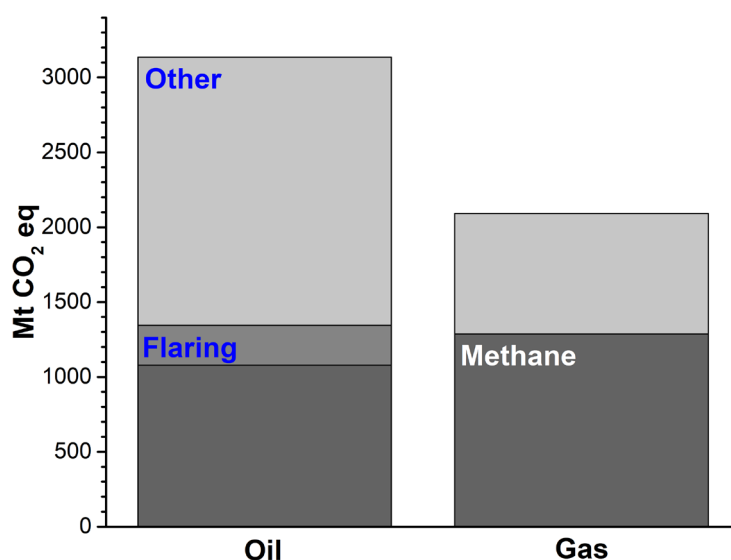
Methane is sparingly used as a feedstock in the chemical industry due to various issues related to methane activation. In a methane molecule, the carbon atom is surrounded by four hydrogen atoms, forming a regular tetrahedron (bond angle of 109.471 °). The carbon atom is thus symmetrically protected by four identical bonds. Also, the C-H bonds are highly stable and only weakly polarized. The first challenge of methane usage in the chemical industry is to activate the C-H bond. The second challenge is to maintain a high selectivity, since the downstream products are commonly more reactive than methane.

The primary example of methane usage in the chemical industry is methane reforming to syngas (CO and H_2). The great heat requirements of this reaction only allow for profitable operation on a large scale. To convert smaller amounts of methane, at remote locations for example, other processes would be necessary. Therefore, significant research efforts have been undertaken to develop new methane conversion routes. In the following we will give an overview of the different reactions, their status on the path to industrial implementation and the biggest challenges on this road.
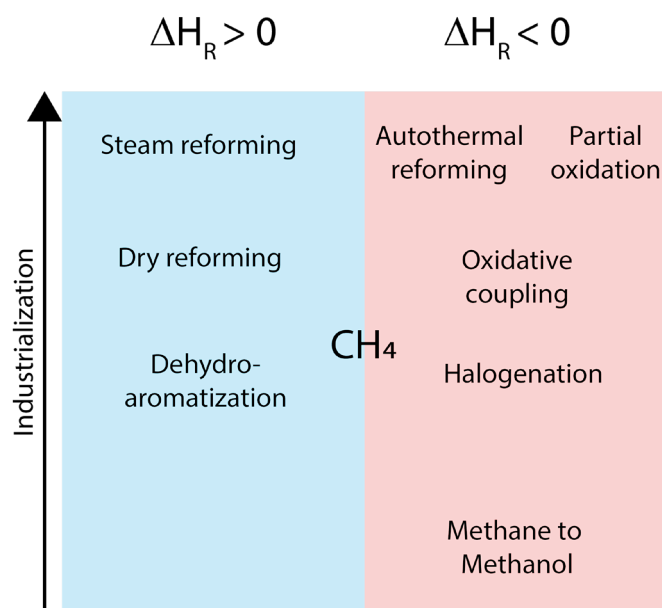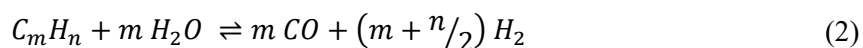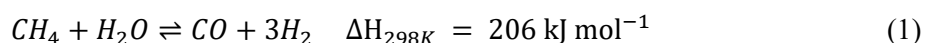
$\Delta H_R > 0$ $\Delta H_R < 0$

Steam reforming   Autothermal reforming   Partial oxidation

Dry reforming   Oxidative coupling

CH₄   Halogenation

Dehydro-aromatization

Methane to Methanol

Industrialization

Figure 2 presents an overview of the different reactions for methane valorization. The reactions are subdivided into endo- and exothermic reactions to highlight the two main challenges typically encountered in methane conversion, namely, coke formation for endothermic reactions and the stabilization of the intermediate products for the exothermic reactions. The endothermic reactions will be discussed first, starting with the most advanced process – steam reforming (SR). Likewise, for the exothermic reactions, the processes with the most industrial applicability, autothermal reforming (ATR) and partial oxidation (POX), will be discussed first followed by a brief overview of the less developed processes.

2 Methane steam reforming

2.1 Overview

Steam reforming is the most well-known example of hydrocarbon reforming reactions. This process should not be confused with catalytic reforming. The latter refers to the conversion of paraffinic hydrocarbons to isoalkanes and aromatics (i.e. hydrocarbons with high octane numbers). Steam reforming is the reaction of methane or other hydrocarbons with steam to produce a mixture of CO and H_2 that is commonly referred to as syngas:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H_{298K} = 206 \text{ kJ mol}^{-1} \tag{1}$$

$$C_mH_n + m\,H_2O \rightleftharpoons m\,CO + \left(m + {}^n/_2\right) H_2 \tag{2}$$

This reaction has been used in industry since the 1930s.[6] It is the key process in the supply of both synthesis gas and hydrogen for the chemical industry. In view of its enormous economic and technological importance, methane steam reforming has been a subject of intense research both in industry and in academia for almost a century.[6-8] The high flexibility of the process makes it particularly attractive for the chemical industry. It can be adapted to a wide range of hydrocarbons, for example from methane to naphta.[9-11] The reaction is catalyzed and a large variety of different, typically Ni-based catalysts are commercially available, optimized for the possible hydrocarbons.[6] The desired H_2/CO ratio in the product stream can be well tailored depending on the intended downstream process, e.g. hydroformylation or methanol synthesis. For steam reforming of methane, typical H_2/CO values are in the range of 2.8–4.7.[11]

The process conditions are set according to the compromise between thermodynamics and operational cost considerations typical of industry. The temperature of the reformer is set at 700–900 °C, while the pressure is normally kept at 20 bar or higher.[6] This high temperature is necessary due to the strongly endothermic nature of the reaction.[1] Operation at low pressures would be thermodynamically preferable, since the total amount of molecules increases with conversion. However, typical downstream applications, such as NH_3-synthesis or the Fischer-Tropsch process, require the supply of hydrogen and synthesis gas at elevated pressures. Operation at elevated pressures is thus economically preferable to operation at low pressures with an additional compression of the increased gas volumes.[6] Due to the associated very high capital and operational expenses, steam reforming is typically not feasible for the valorization of smaller or highly remote gas reserves[12] and it is usually combined with immediate consumption of the syngas in another reaction on-site. Even in this context, the costs of syngas production are considerable. For an industrial-scale Gas to Liquids (GtL) plant, it represents the lion's share of the capital expenditure.[13]
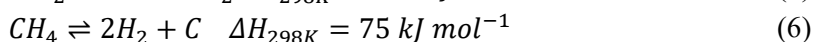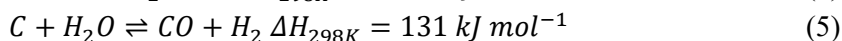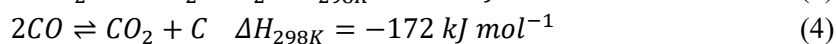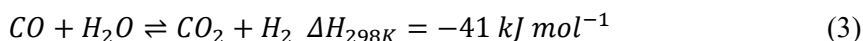
2.2 Principles of catalyst design in steam reforming

The thermodynamics of steam reforming requires temperatures that can approach 1000 °C. Above 1000 °C the formation of radicals from methane cracking becomes more and more relevant. However, only at around 1500 °C is the conversion achievable through this gas-phase reaction pathway sufficiently high.[14] Thus, heterogeneous catalysts are necessary to keep the reaction temperature sufficiently low for a profitable operation. The goal for a company operating such an energy-intensive bulk process is to limit the downtime of a steam reforming plant to the scheduled maintenance intervals. Thus, an industrial catalyst must allow for stable operation in the timescale of years rather than months or weeks.[15] Regeneration procedures would reduce the profitable operation period of an already quite expensive process. If catalyst stability over a period of years is the main goal, a good overview of potential problems is necessary. According to literature, a catalyst can deactivate due to one or several of the reasons shown in *Table 1*.

Table 1: Mechanisms of catalyst deactivation[16]

Mechanism	Type	Brief description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites which block sites for catalytic reaction
Fouling, coking	Mechanical, chemical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation, sintering	Thermal, chemical	Thermally induced loss of catalytic surface area, support area, and active phase-support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor-solid and solid-solid reactions	Chemical	Reaction of vapor, support, or promoter with catalytic phase to produce inactive phase
Attrition/ crushing	Mechanical	Loss of catalytic material due to abrasion; loss of internal surface area due to mechanical-induced crushing of the catalyst particle

In steam reforming of hydrocarbons, the main challenges in designing a stable catalyst are sulfur poisoning, catalyst coking and sintering.[6] As already mentioned previously, the typical steam reforming catalysts employ nickel as an active metal.[17] This is due to the low cost of Ni compared to other catalytically active metals such as Rh. Therefore, in the following descriptions, we will assume Ni-based catalysts. In a reformer, the main reaction is typically accompanied by the following side reactions:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H_{298K} = -41 \; kJ \; mol^{-1} \qquad (3)$$
$$2CO \rightleftharpoons CO_2 + C \quad \Delta H_{298K} = -172 \; kJ \; mol^{-1} \qquad (4)$$
$$C + H_2O \rightleftharpoons CO + H_2 \quad \Delta H_{298K} = 131 \; kJ \; mol^{-1} \qquad (5)$$
$$CH_4 \rightleftharpoons 2H_2 + C \quad \Delta H_{298K} = 75 \; kJ \; mol^{-1} \qquad (6)$$

The principles of coke formation have been reviewed extensively in literature.[15, 18] Depending on the feedstock used, the operating conditions in the reactor and the characteristics of the catalyst, different species of coke can be generated. For the conditions typical of steam reforming, carbon filaments and pyrolytic carbon are the most common carbon species.[18] Carbon filaments are whisker-like structures that can be compared to carbon nanotubes.[19, 20] Their geometry does not allow them to block the catalyst surface. However, a continued growth of carbon fibers can lead to breakage of catalyst particles and blockage of the entire reactor in severe cases.[18, 21] Pyrolytic carbon on the other hand grows on the catalyst surface and thus deactivates the active sites. However, an excessive growth of pyrolytic carbon will also increase the pressure drop over the reactor.[18]

These carbon structures do not appear randomly over the Ni surface. Coke formation can be traced to two distinct structural configurations of the Ni surface: defects in the Ni surface and large surfaces in general. In a first step, coke nuclei must be formed and then stabilized on a Ni surface for coke growth to proceed. Nucleation preferentially takes place on Ni defect sites, with step sites being the prime example.[11, 22] Step sites are more reactive than close-packed Ni surfaces, since they allow for methane to interact with more Ni atoms simultaneously. This increased activation of methane also means that a reaction like methane decomposition will take place more easily on at a step site. This fresh coke nucleus must be stabilized in order to grow and such a stabilization is best achieved on large Ni surfaces than small ones.[11, 22-24] Thus, the bigger and more defect-rich a Ni surface, the easier carbon formation is initiated.

Carbon deposits are not the sole cause for the blockage and deactivation of the active sites on the catalyst surface. The deactivation of catalytic sites due to strong adsorption of reactants, products or impurities is so common that it even has its own name: catalyst poisoning.[18] Group VIII metals are quite susceptible to reactions with sulfur and natural hydrocarbon sources are typically contaminated with H_2S.[25] Under steam-reforming conditions, a group VIII metal will react with H_2S to form hydrogen and chemisorbed sulfur, making this the main route of catalyst poisoning:

$$M + H_2S \rightarrow M - S + H_2 \qquad (7)$$

Nickel is more sensitive to the formation of sulfide than the other group VIII metals.[11] The regeneration of a deactivated catalyst poisoned by sulfur is possible but labor and energy intensive.[25] Therefore, the best and most commonly practiced solution for this problem is to carefully desulfurize the feed upstream of the reactor.[15, 26] Interestingly, the deactivating effect of the sulfur can be used to combat the formation of carbon deposits on the excessively reactive sites at the catalyst surface and increase the lifetime of the catalyst. This is the concept of the so-called SPARG process, where well-controlled low concentrations of co-fed H_2S are used to selectively deactivate the excessively reactive Ni sites on which the most coke is formed. The result is a significantly enhanced catalyst lifetime.[24]

Sintering is the last significant deactivation mechanism and is the reduction in surface area caused by particle growth at elevated temperature. Sintering of both the support and the active phase has been extensively

reviewed in literature.[15, 18, 27] Possible mechanisms include solid-state diffusion, surface diffusion and phase changes.[26] Two important thresholds for the onset of sintering are the Hüttig temperature and the Tamman temperature. The prior signifies the mobility of atoms near defects. The Tamman temperature on the other hand is seen as the point at which the bulk atoms become mobile. Empirical correlations for both were given by *Moulijn et al.* as:[28]

$$T_{Hüttig} = 0.3\, T_{melt} \quad \text{(T in K)} \tag{8}$$
$$T_{Tamman} = 0.5\, T_{melt} \quad \text{(T in K)} \tag{9}$$

Metallic bulk nickel melts at 1455 °C. Thus, the nickel particles on the surface are highly susceptible to sintering in the temperature range of 700–900 °C typical of steam reforming ($T_{Hüttig}$ = 518 °C, T_{Tamman} = 863 °C).[16] Sintering can be accelerated by the presence of impurities in the feed. The feeding of Cl_2 for example leads to the formation of $NiCl_2$, which sinters at lower temperatures ($T_{Hüttig}$ = 384 °C, T_{Tamman} = 641 °C). Traces of CO in the feed during heating or cooling of the reactor are similarly dangerous as $Ni(CO)_4$ has a boiling point of 43 °C.[18, 29, 30] This is not a problem for steam reforming process itself, since $Ni(CO)_4$ is no longer stable at typical operating temperatures.

Catalyst supports typically consist of metal oxides, such as MgO, Al_2O_3 or $MgAl_2O_4$.[6] The higher melting points of metal oxides compared to reduced metals means that the agglomeration of nickel particles is the main sintering problem. However, supports can easily sinter because of a thermally induced phase-change. The prime example for this behavior is Al_2O_3 with its plethora of metastable phases shown in *Figure 3*.
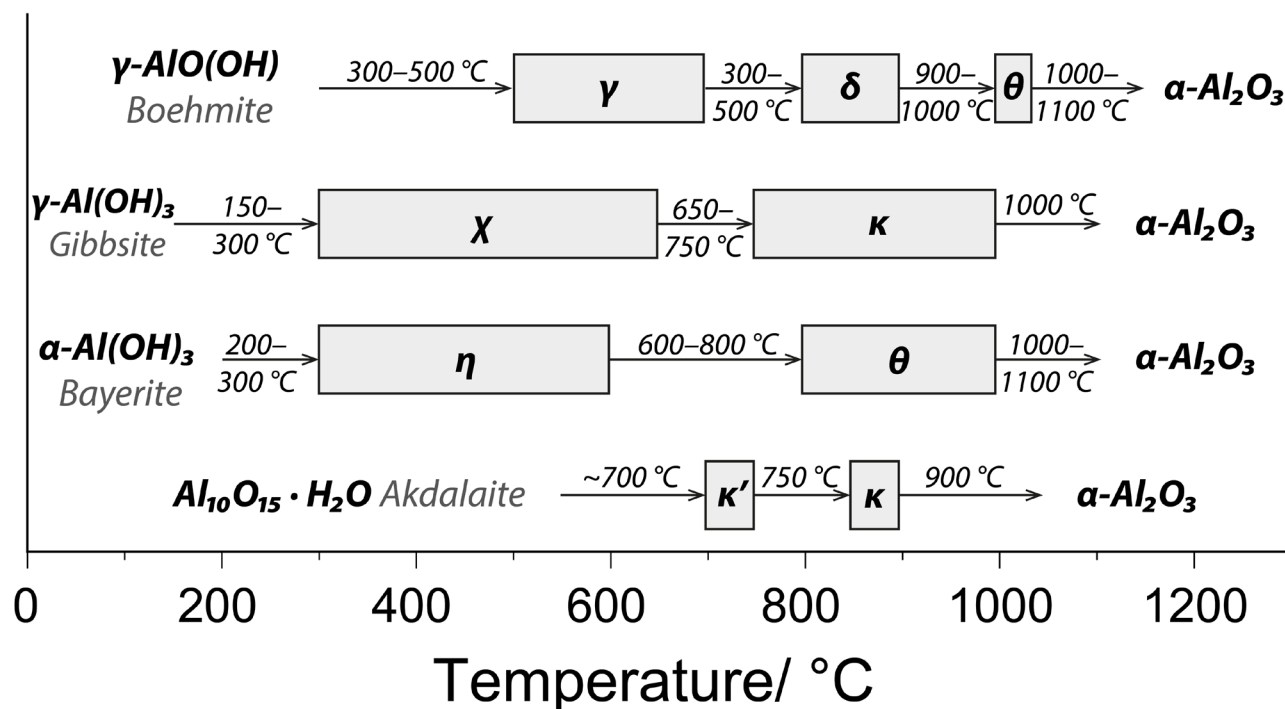
Figure 3: *Phase changes upon calcination of the common aluminum hydroxides leading to the formation of α-Al₂O₃ (corundum). Shown are stable phases and phase transitions as a function of temperature, created after refs. 31, 32.*

The packing density of Al_2O_3 increases, when the temperature is increased and phase change occurs. The most stable modification (α-Al_2O_3) exists in hexagonal close-packed configuration.[33] Thus, a structural change in the support at elevated temperature can decrease the total surface area and the available number of active

sites drastically. Besides phase changes, the sintering of the support is also governed by diffusion processes, just as the sintering of the active metal.[16] Similarly, the presence of other elements can accelerate or inhibit the sintering of the support. Using Al_2O_3 as an example again, the following statements can be found in literature: alkali metals and steam enhance sintering, whereas metals such as Ca or Ni form spinel phases with Al_2O_3, reducing sintering.[16] Alternatively, a treatment with sulfuric acid can also improve the stability of Al_2O_3.[27]

To sum up, the main challenge in catalyst design for steam reforming is the engineering of the nickel particles. These must be dispersed to provide a high Ni surface area. At the same time the highly reactive nickel ensembles that generate the most coke must be deactivated to guarantee stable operation. The minimum requirements for the support are relatively simple by comparison. The typical support is a metal oxide that can be pretreated to increase the sintering resistance even further. Additionally, support materials such as MgO or Al_2O_3 tend to stabilize Ni particles and thus contribute to the catalyst stability.

3 Dry reforming of methane

Dry reforming of methane (DRM) is a reaction closely related to steam reforming and is under extensive investigation at the moment. Methane or other hydrocarbons are reacted with carbon dioxide instead of steam:

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \quad \Delta H_{298K} = 247 \; kJ \; mol^{-1} \tag{10}$$
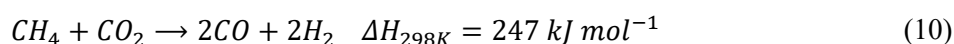
DRM has several advantages over the steam reforming of methane. Firstly, it allows for the direct chemical utilization of CO_2, which is the most abundant greenhouse gas. Secondly, the resulting product gas has a significantly lower H_2/CO ratio than in steam reforming, which can be very beneficial for specific downstream chemical conversion processes.[34] The biggest downside of dry reforming is the noticeably more pronounced endothermic nature of the reaction compared to SR or ATR. At the same time the usage of CO_2 means an increase in the overall carbon levels and thus an elevated risk of coke formation.

The combination of elevated coke levels and high purity requirement for CO_2 has delayed the industrial implementation of DRM.[35, 36] Especially the former of the two challenges has stimulated considerable research activity. The basics of catalyst design are similar for dry and steam reforming of methane. Countless different approaches have been and are being investigated to obtain a catalyst that is sufficiently resistant to coke formation in DRM. Nevertheless, the closest existing applications in industry is so-called tri-reforming of methane, in which both CO_2 and H_2O are fed together with methane.[6, 34]

4 Non-oxidative methane upgrading

Methane can also be converted to higher hydrocarbons without the necessity to add additional gases. The best example for this is the so-called methane dehydroaromatization (MDA):

$$6CH_4 \longrightarrow C_6H_6 + 9H_2 \quad \Delta H_{298K} = 83 \; kJ \; mol^{-1} \tag{11}$$
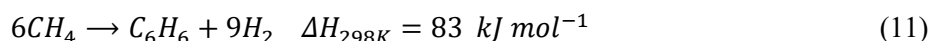
Due to the endothermic nature of this reaction, it is also carried out at elevated temperatures, with typical values being 650–800 °C.[37] In contrast to the reforming reactions described earlier, the conversion values at thermodynamic equilibrium in this temperature range are rather low. At 800 °C, the equilibrium conversion of methane is only around 25%.[37] Furthermore, the issue of coke management is even more pressing due to the absence of an oxidant such as H_2O or CO_2 in the feed. At thermodynamic equilibrium the benzene yield is effectively zero with the selectivity to coke being almost 100%.[38] In real-life tests, such results typically do not set in because of the kinetic control over the reaction pathways provided by the catalyst. Nevertheless, the

selectivity towards useable aromatics, such as BTX over other products such as naphtalene or coke still requires further optimization.

Significant effort has been invested into the catalyst design and mechanistic understanding in order to optimize the product yields. The most commonly investigated catalyst type is a zeolite with added extraframework metals (e.g. refs. [39, 40]). Among different modified zeolites, Mo-containing Mo/ZSM-5 and Mo/MCM-22 were found to provide the best results in the non-oxidative methane conversion to aromatics.[38, 41] The production of aromatics proceeds via a complex reaction network.[42] The overall mechanism is still unclear but a two-step mechanism with ethane and ethylene as intermediates is generally accepted.[37, 43] In this mechanism methane is first activated over the Mo species to form C2 intermediates which then react over the Brønsted acid sites (BAS) of the zeolite. Furthermore, it has been suggested that MDA proceeds via a carbon pool mechanism, similar to the mechanism proposed for methanol to hydrocarbons process (MTH).[44] *Figure 4* shows the schematics of the MDA reaction mechanism. The pore structure of the zeolite is key to provide shape selectivity with regard to the product distribution.[37, 41]
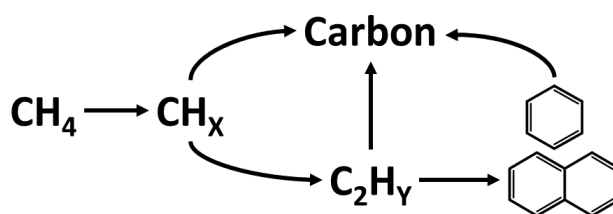

Figure 4: *Simplified reaction mechanism for MDA, modified with permission from ref 45. Copyright 1999 Elsevier.*

Deactivation of MDA catalysts is typically a result of the accumulation of polyaromatic coke inside the zeolite pores, which blocks the access to the confided carbidic Mo species and, simultaneously, enhances their sintering and the formation of bulk Mo-carbide.[46] Therefore, any industrial process must periodically regenerate the catalyst. The most straightforward regeneration procedure would be the removal of coke via oxidation with air. Indeed, cycled operation of methane and oxygen can significantly increase catalyst lifetime.[47] The oxidation periods should be limited to short pulses of oxidant, to optimize the results.[48] The challenge of a reactor that allows such operation on a larger scale has yet to be addressed, however. Although different reactor concepts have been investigated in literature (e.g. in refs. [49-52]), no breakthroughs in terms of industrial implementation have been reported so far. Despite a lot of research on this topic, cost-effective MDA on an industrial scale is still elusive.

In 2014, a new approach to nonoxidative methane upgrading was developed in the group of Bao.[53] Through a combination of ball-milling and high temperature treatment, an Fe/SiO$_2$ catalyst was synthesized with isolated Fe sites in the SiO$_2$ lattice. Conversion of methane at 950 °C and higher was reported to exclusively yield ethylene, benzene and naphthalene. It has been proposed, that the isolated Fe sites generate methyl radicals which then react to longer hydrocarbons in homogeneous gas-phase reactions.[41] Coke formation, i.e. C-C coupling on the catalyst surface would require clusters of Fe sites according to the proposed theory.

This already shows two of the biggest problems in this reaction concept: the very high temperatures necessary and the synthesis of a catalyst with sufficient Fe dispersion. *Sakbodin et al.* combined this catalyst with an H$_2$-permeable membrane to improve yields.[54] While they achieved the same products, the conversion was significantly lower than reported previously by *Guo et al.* (23% at 1050 °C and 3.2 L g^{-1} h^{-1} vs. 42% at 1030 °C and 14.5 L g^{-1} h^{-1}).[53] Additionally, no TGA data was provided to guarantee the absence of coking. This is relevant, as in a later publication, the same group reported a 10% selectivity to coke for this system at 1000 °C, both in powdered form and when coated to the reactor wall.[55] Thus, this approach is still at the stage

where catalyst synthesis optimization is necessary before any final statement can be made on the industrial feasibility of the process.

5 Partial oxidation and catalytic partial oxidation

In contrast to the previously described reactions, partial oxidation of methane (POX) is an exothermic reaction that proceeds according to the following equation:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \quad \Delta H_{298K} = -36 \; kJ \; mol^{-1} \tag{12}$$
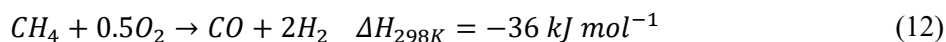
This reaction can proceed uncatalyzed at 1150–1500 °C and 25–80 bar.[56] The high temperatures are the result of the exothermic nature of the reaction and are also necessary to overcome the high barriers for uncatalyzed gas-phase reactions. Operation with air as the oxidant is theoretically possible, but the use of pure oxygen is more attractive as it reduces the required downstream gas separation. Despite the use of pure oxygen, POX can be economically attractive in certain scenarios. POX units can be used for virtually all hydrocarbon feedstocks and are thus employed in refineries to generate hydrogen from residual oil.[56, 57] The selectivity issues typical of partial oxidation reactions can be controlled in two manners. Firstly, working with sub-stoichiometric amounts of oxygen automatically reduces the chance of CO_2 production. Secondly, the formation of H_2 and CO over CO_2 is thermodynamically advantageous at the temperatures of over 1000 °C typical for POX.[58]

Research is also ongoing to develop a catalytic version of this process, which could operate at lower reaction temperatures (so-called catalytic partial oxidation or CPOX) decreasing the operation and capital costs of the overall process.[26] The catalytically active metals for CPOX are, in principle, the same as for steam reforming but the even higher temperatures of CPOX appear to make noble metals such as Rh more attractive than Ni.[56] The reaction proceeds in different steps over the catalyst with the oxygen rapidly being consumed in the upstream part of the catalyst followed by steam reforming and WGS in the downstream section of the bed.[56, 59]

6 Autothermal reforming of methane

There is a process that is closely related to catalytic partial oxidation but is already being used commercially, namely the so-called autothermal reforming (ATR). Essentially, ATR consists of a combination of POX and steam reforming being carried out in the same reactor. Thus, the feed contains significant amounts of steam besides methane and oxygen. The advantage of such a process is that it yields syngas with a H_2/ CO ratio of around 2, which is very favorable for Fisher-Tropsch and methanol syntheses.[56] Operating conditions can range between 900–1150 °C and 1–80 bar.[56] Two possible modes of operation have been established. Firstly, the reactant mixture can be fed directly to a catalyst bed. Alternatively, the mixing section at the inlet of the reactor doubles as a burner, discharging into an empty portion of the reactor. The catalyst is then placed further downstream in the reactor as illustrated in *Figure 5*.[57] The second option has proven to be more versatile and is thus commonly used in industry, for example in the SynCOR[TM] process of Haldor Topsøe.[60]
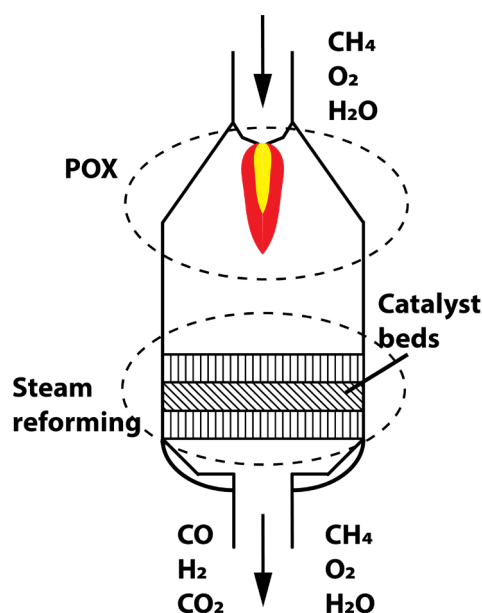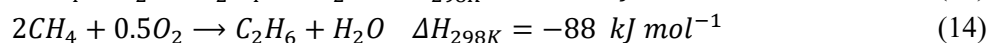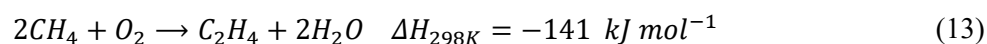
Figure 5: A schematic of an ATR reactor, modified with permission from ref 60. Copyright 2012 Haldor Topsøe A/S.

The main advantages of ATR are the absence of elements such as heat exchangers (allowing for more a compact design) and the cold reactor walls (internal methane combustion provides the necessary heat for steam reforming). The latter allows for higher operating pressures than pure steam reforming. Therefore, ATR is typically employed in "secondary" reformers downstream of the primary steam reformer. Alternatively, ATR is also being investigated as a hydrogen source for fuel cells.[61, 62]

7 Oxidative coupling of methane

Oxidative coupling of methane (OCM) refers to the conversion of methane with oxygen to C_2 hydrocarbons at temperatures in the range of 500–1000 °C:

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \quad \Delta H_{298K} = -141 \ kJ \ mol^{-1} \tag{13}$$
$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O \quad \Delta H_{298K} = -88 \ kJ \ mol^{-1} \tag{14}$$

The first reports on this reaction were published in the early 1980s.[63, 64] Despite extensive research on potential catalytic systems since then, no industrially feasible process has been developed yet.[65] In the context of product gas separation and purification, a single-pass yield of 30% is typically seen as the critical value for an industrially competitive process.[66] This value has proven challenging due to the nature of the reaction mechanism. The reaction proceeds via a heterogeneous-homogeneous mechanism.[1, 67] In a first step, methane is activated on the catalyst surface and a C-H bond cleaved, yielding a ˙CH₃ radical. This radical can then participate in a number of reactions. The recombination of two ˙CH₃ radicals yields ethane, which can then be dehydrogenated to form ethylene. *Figure 6* shows a simplified reaction scheme that illustrates the selectivity problem. The methyl radicals are highly reactive and carbon oxides can be formed at any point during the reaction. Thus, the higher the conversion of methane becomes, the lower the selectivity towards C_2.
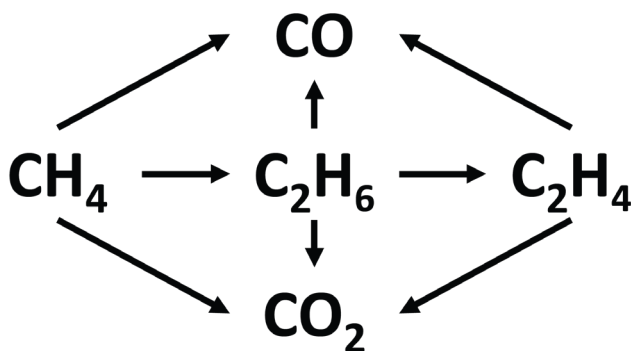
Figure 6: Simplified schematic of the OCM process, modified with permission from ref 67. Copyright 2008 John Wiley & Sons, Inc.

The catalysts investigated in literature can typically be classified into four different categories[67]. These are reducible metal oxides[68, 69], non-reducible metal oxides[70], halogen-containing oxide materials[71] and solid electrolytes.[72] Recently, a fifth category has been added. The California-based company Siluria Technologies has reported to have developed a novel nanowire catalyst.[1] Apart from this description, further information on the catalytic system is difficult to obtain. The patent on nanowire catalyst synthesis is valid for both common reducible and non-reducible metal oxides typically used as OCM catalysts.[73] It has been claimed that the nanowire catalyst can operate at lower temperatures than conventional bulk catalysts.[74] Coupled with a short contact time over a nanowire catalyst, this could explain a superior performance of such a system. In 2018 Saudi Aramco licensed Siluria's technology to implement on a larger scale.[75] Therefore, it can be assumed, that the yield and product separation challenges are close to being solved.

8 Methane halogenation

The assumed approach by Siluria of short contact times highlights the difficulty of maintaining a decent selectivity in the single-step upgrading of methane to directly useable chemicals. Methane halogenation and methane oxyhalogenation are two related reactions with which intermediates can be produced without requiring the high temperatures of methane reforming:

$$CH_4 + X_2 \longrightarrow CH_3X + HX \tag{15}$$
$$2CH_4 + 2X_2 + O_2 \longrightarrow 2CH_3X + H_2O \tag{16}$$
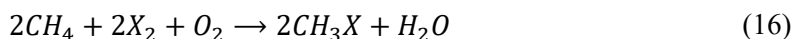
The thus halogenated methane can then be upgraded to useable products more easily than pure methane via e.g.:

$$CH_3X + H_2O \longrightarrow CH_3OH + HX \tag{17}$$
$$2CH_3X \longrightarrow C_2H_4 + 2HX \tag{18}$$

In all of these reactions X_2 stands for the two halogens typically used: Cl_2 or Br_2. F_2 is too reactive and toxic to be used for such a reaction, while the thermodynamics of CH_3I formation are too unfavorable.[1] The upgrading of methyl halides over zeolites was discovered around the same time as the methane to olefins (MTO) reaction[76] and has been studied since then.[77-79] While this approach has significant theoretical advantages, Cl_2 and Br_2 are highly toxic and corrosive. Therefore, such a process is only feasible in a closed-loop process, such as the one displayed in *Figure 7*.
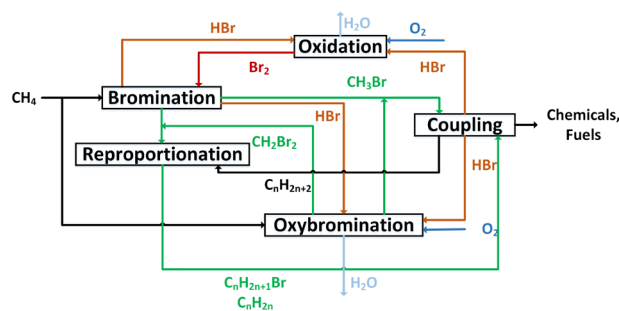
Figure 7: *Example of closed-loop methane upgrading with bromine, adapted from ref 80 with permission. Copyright 2017 John Wiley and Sons, Inc.*

Besides the inherent risks of working with halogens, this approach faces a second challenge. Any industrial process would be a multistep process with corresponding separation and purification steps, increasing the costs.[1] On the other hand, the entire halogen cycle can run at temperatures below 500 °C and at atmospheric pressure compared to the harsher conditions necessary for methane steam or dry reforming.[81] Halogenation and oxyhalogenation have been evaluated for methane upgrading before.[82] At the time of publishing (1996), the actual hydrocarbon synthesis via methyl halides was considered competitive compared to partial methane oxidation coupled with Fischer-Tropsch (FT) synthesis. However, the costs of separation and purification in the halide approach were considered prohibitive. In the 25 years since this comparison was carried out, the available Gas to Liquids (GtL) technologies have undoubtedly been improved. Unless the separation costs in the halogenation process are drastically reduced or external parameters shift significantly (e.g. the price of emissions), an industrial implementation of the halogenation approach appears unlikely.

9 Methane to methanol

The direct selective low-temperature conversion of methane to methanol and other oxygenates is a "dream reaction" investigated for more than a century. The theoretical advantages of such an approach are undeniable. In an ideal scenario, even small reserves of methane could be exploited and converted to methanol with air as an oxidant. The reaction product would then be a liquid at room temperature and thus easy to separate, transport and implement in a wide range of down-stream chemical conversion processes. The extensive research undertaken on the conversion of methanol to hydrocarbons (MTH) further emphasizes the fact that methanol is an industrially attractive chemical intermediate.

$$CH_4 + 0.5\,O_2 \longrightarrow CH_3OH \quad \Delta H_{298K} = -164\ kJ\ mol^{-1} \qquad (19)$$

The oxidative upgrading of methane has been investigated in three different regimes so far: at temperatures above 300 °C and temperatures below 300 °C using either heterogeneous or homogeneous catalysts. Similar to the oxidative coupling of methane, the desired product is less stable than either CH_4 or CO_2. Thus, the main challenge is that higher degrees of methane conversion typically result in poor selectivity to methanol.

The oxidative upgrading of methane at temperatures above 300 °C can proceed both non-catalytically and using catalysts. Typically, the reaction is carried out with a considerable excess of methane to improve the selectivity. For the non-catalytic reaction, ambient pressure operation favors the formation of formaldehyde, while methanol is generated at elevated pressures.[83] The reaction proceeds via a radical mechanism.[83-85] The yields achievable in this manner can be relatively high, such as Y_{MeOH} = 10% reported by *Feng et al.* at 330 °C and 50 bar.[85] The main problem with this approach is the rather long residence time necessary for such results.[86]

The residence time can be reduced considerably by the use of heterogeneous catalysts, which are typically MoO_3/SiO_2 or V_2O_5/SiO_2 or derivatives thereof.[87-91] Despite research on these systems the yields reported so

far are too low for any industrial consideration.[86] Additionally, the Mo-based systems have been reported to experience significant stability issues due to Mo-volatilization.[92]

At the same time, the naturally occurring enzyme methane monooxygenase (MMO) is capable of oxidizing methane to methanol. Two known variations of MMO have been extensively studied in literature. Soluble MMO (sMMO) is known to contain a dinuclear Fe cluster.[93-95] Particulate MMO (pMMO) on the other hand contains Cu but the exact nature of the active site is still a topic of discussion.[93, 96] This provided the inspiration for the attempt to convert methane to methanol over well-defined metal clusters in zeolites and Metal-Organic Frameworks (MOFs) resembling the structures of the enzymatic reactive ensembles. For zeolites the focus has been on Cu (e.g. refs. [97-102]) and Fe (e.g. refs. [103-107]), but Ni[108] and Co[109-111] have also shown to be active. Catalytically active Metal-Organic Frameworks have also been reported but focused exclusively on Fe and Cu as active metals so far.[112-115]

These studies focused on the elucidation of the active site nature. For a better overview of the different proposed active sites, we refer to recent excellent reviews.[92, 116] Different reaction modes have been tested such as batch reactions[102, 117-119] or continuous operation.[101, 120, 121] Regardless of the testing conditions, the yields of methane are several orders of magnitude from any industrial applicability. The research projects on zeolite catalysts were carried out to gain insight into the nature of the active site, meaning yield was not a priority. Nevertheless, these tiny methanol yields at the edges of detectability nicely emphasize the previously mentioned issue of conversion vs. selectivity in partial oxidation reactions. The pronounced difference in stability between methanol and methane compounds the problem for this reaction.

The increased interest in the direct conversion of methane to methanol in recent years has led to growing awareness of this issue of product stability.[92, 122] Using nature (and thus MMO) as an inspiration again, it is obvious that the activity and selectivity of MMO are only achievable through the combination of two factors: a well-designed active site and a gating mechanism that prevents methanol from reaching the active site to be oxidized further.[123]

A gating mechanism is challenging to achieve in a synthetic catalyst. The existing work on homogeneous catalysis provides insight into how the yield can be increased nevertheless. A plethora of different homogeneous systems has been reported so far. The most promising results so far are based on the work of *Shilov* and *Shul'pin*.[124] Typically, complexes of transition metals such as Pt^{II}, Pd^{II} or $Au^{I/III}$ in highly acidic media are capable of oxidizing methane to methanol derivatives.[12, 92] The most famous example is the so-called Periana system (*Figure 8*). It consists of a bypridimine-$PtCl_2$ complex that can oxidize methane using oleum both as a solvent and as an oxidant.[125] At reaction conditions of greater than 200 °C and 30 bar, single-pass yields of greater than 70% were reported.

a)

$CH_4 + 2\ H_2SO_4 \xrightarrow{\text{34 bar, 220 °C}} CH_3OSO_3H + 2\ H_2O + SO_2$

b)

Cu-ZSM-5
Cu-MOR
Cu-SSZ-13
Cu-SAPO-34

$2\ CH_4 + O_2 \xrightarrow{\text{1 bar, 200 °C}} 2\ CH_3OH$
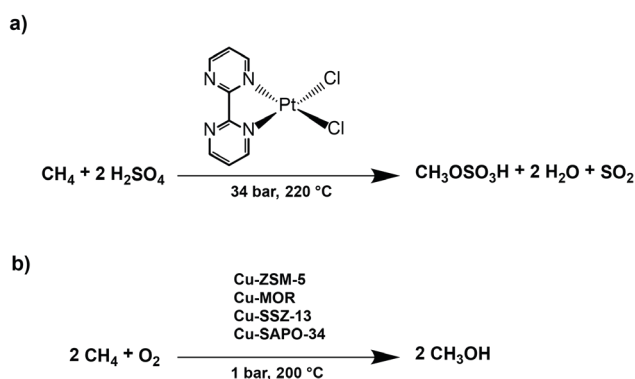
Figure 8: *Examples of methane oxidation strategies with a protective group for methanol using the (a)Periana catalyst or (b) via a step-wise procedure using Cu-exchanged zeolites.*

The key is that methanol is present as methyl bisulfate and thus protected against further oxidation.[126] This concept of a "scavenger molecule" that reacts with methanol and prevents overoxidation has been labelled as essential to make this reaction industrially relevant.[122] Besides sulfuric acid-based systems, fluorine-based acids such as trifluoroacetic acid are also known to be a good reaction medium.[127, 128] The group of *van Bokhoven* has published excellent reviews giving an extensive overview of the different systems, in which methanol is protected by such a "scavenger molecule".[92, 129] Coordination of the Periana catalyst to solid supports has been reported in literature.[130, 131] Beyond such conversion of homogeneous to heterogeneous catalysts there is little information available on heterogeneous systems that increase the yield by employing "scavenger molecules". While the use of protective groups leads to higher yields of methanol derivatives, numerous challenges still exist on the path to industrial application. These range from corrosion due the strong acids used over catalyst stability in the presence of water or methanol to product purification.[92] Industrial implementation of methane to methanol is consequently still far away. However, the growing admission amongst researchers that yield is essential can be a basis for optimism.

10 Conclusion and outlook

As could be seen in the previous sections, there is a wide variety of options available in theory to utilize methane as a chemical feedstock. However, most of these options are still in various stages of development. The growing importance of sustainability greatly increases the importance of implementing large-scale processes that allow for the further utilization of methane. Catalyst development for the different processes faces two main challenges. If the reaction is endothermic the catalyst must be highly resistant to coke formation and if the reaction is exothermic the typical problem is the overoxidation of the target product.

Especially the latter issue is critical since the improvement of a heterogeneous catalyst powder by itself cannot solve the problem. The nanowire catalyst developed by Siluria appears to provide a breakthrough by allowing for a reactor design in which the minimized contact time with the catalyst reduces overoxidation. For methane to methanol the best prevention of overoxidation reported so far was achieved by employing so-called scavenger molecules or protective groups. Thus, the entire approach in methane to methanol research ought to be redeveloped away from the formula of only "O_2 + CH_4 + catalyst" and the research focus away from a pure consideration of the active site.

Out of the box thinking for especially these reactions is critical for both process optimization and sustainability. This would not only increase the usability of methane in the chemical industry. The direct conversion of methane to useable chemicals would also eliminate the necessity of intermediates like synthesis gas, removing an entire reaction (including separation and purification steps) from the chemical supply chain. The thus reduced energy demand by itself would represent a major step towards a more sustainable chemicals production.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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