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Chapter

Advances in Selective Oxidation of Methane

Saeed Alshihri and Hamid Almegren

Abstract

Selective oxidation of methane is one of the most challenging reactions in catalysis. Methane is a very stable molecule and requires high energy to be activated. Different approaches of single step methane conversion have been suggested to overcome this challenge. However, the current commercial process of methane conversion to methanol is via the indirect way, in which methane is first converted to synthesis gas in highly intensive energy step, and synthesis gas is then converted into methanol. The first step is responsible for 60% of the capital cost of the plant. There are enormous researches that have been conducted in a direct way and some good results have been achieved. This chapter will summarize the recent advances in the direct selective oxidation of methane to methanol.

Keywords: direct methane conversion, natural gas, oxygenates, catalysis, methanol

1. Introduction

The global consumption of energy and hydrocarbon-related commodities will continue to increase as the world population increases. The three sources of energy oil, gas, and coal are still dominating over 80% of the global energy matrix. However, natural gas is considered as the bridge fuel between the fossil fuel of today and the renewable fuel of tomorrow. It is cheap, more abundant than oil, and has lower CO_2 emissions compared with oil and coal. These factors place natural gas, and by extension methane, as a principal candidate for replacing petroleum as a chemical feedstock and addressing various environmental issues. Natural gas is a flammable substance obtained from oil or gas fields and coal mines. At present, the confirmed natural gas reserves have a total volume of 187 trillion metric, of which 24.8% is found in the Middle East, 30.4% in Europe and Eurasia, 8.4% in the Asia Pacific region, 7.5% in Africa, 6.8% in North America and 4.1% in Middle and South America [1–5]. Natural gas is typically used as a fuel for power generation and for domestic heating. In 1971, global primary energy consumption was based on 48% oil, 29% coal and 18% natural gas. However, in 2015, the consumption of 13.1 billion tonnes (oil equivalent) of fuel was based on 33% oil, 30% coal and 24% natural gas [1], reflecting a shift from oil to natural gas. This transition from oil to natural gas consumption is expected to gradually increase until 2035 [1–3].

Natural gas resources are located in remote areas, and its utilisation is affected by high transportation costs. Therefore, conversion of natural gas to high value chemicals is the most promising solution. Methane and ethane are the main components of natural gas; they are stable and have no functional group, magnetic

moment or polar distribution to facilitate chemical attacks. The C-H bonds of these light hydrocarbons are strong and require high reaction conditions to be activated.

One of the most challenging processes in the chemical industry is the conversion of natural gas or methane to methanol, which is an important intermediate source of energy in our daily lives. Methanol can be used as a convenient energy storage material, a fuel, and a feedstock to synthesise hydrocarbons which mankind get from fossil fuel nowadays [2, 3] One of the importances of methanol comes from its direct use as a fuel or blending with gasoline to improve the octane number although it has half the volumetric energy density (15.6 MJ/L) relative to gasoline (34.2 MJ/L) and diesel (38.6 MJ/L) [4–6]. There had been 15,000 methanol-powered cars during the 1990s granted by the Environmental Protection Agency (EPA), but the use was discontinued due to an increased natural gas price [7]. Methanol is also a key feedstock for chemical manufacturing. The most major derivatives from methanol are formaldehyde, acetic acid, methyl tertiary butyl ether (MTBE) and dimethyl ether (DME). In recent years, methanol to hydrocarbons (MTH) research has been growing rapidly including methanol-to-gasoline (MTG) and methanol-to olefins (MTO) technology [8–10].

In industries, an indirect route for the conversion of natural gas to methanol is used. In this reaction, methane is first converted to synthesis gas by steam reforming, and the synthesis gas is then converted to methanol. However, the production of syngas is an energy-intensive process, which is operated between 800 and 1000°C, and more than 25% of the feed (natural gas) has to be burned to provide the heat of reaction. The direct conversion of methane to methanol in a single step without going through the reforming step is a desired alternative to the current technology [2, 4, 5]. In spite of the fact that there are no actual plants yet for the process of direct methane to methanol (DMTM), previous experimental and theoretical works have demonstrated the feasibility of this route [2, 4, 5]. Here, this chapter will mainly focus on the recent efforts on the direct conversion of methane to oxygenates.

2. Conventional catalytic approach to convert methane to oxygenates

2.1 Gas phase reaction based on homogeneous radical mechanism

This reaction is a free radical conducted under high temperature and pressure. The thermodynamic and kinetics studies identified the partial oxidation of methane as the rate limiting step due to the formation of methyl radical [7, 11]. Many studies with different oxidants have been conducted in this route. Babero et al. studied the partial oxidation of methane at 500 C temperature using nitrogen oxide as an oxidant [12]. Another study compared between oxygen and nitrogen oxide for the partial oxidation of methane in the gas phase [13]. The effect of adding small quantities of hydrocarbons such as ethane was investigated to promote the activation of methane and increase the selectivity of methanol [14]. Pressure is one of the most important factors which has a pronounced effect on the selectivity of methane oxidation. Dozens of studies have been performed in attempts to promote the selectivity toward oxygenates using high pressures and temperatures [8, 9, 15]. The results of these studies show that a conversion of 5–10% and a methanol yield of 30–40% can be achieved at a temperature of 723–773 K and pressures of 30–60 bar in the gas phase reaction. There are several works that investigated the reactor design and modifications. Zhang et al. designed a new tubular reactor based on quartz-line and stainless-steel line. The reaction was conducted at a temperature of 430–470°C and 5.0 Mpa pressure, and a high yield of methanol was obtained [9].

The methane conversion to methanol was also conducted in the absence of catalysts at high reaction conditions. Methanol yields as high as 7–8% are obtained in the absence of catalysts operating at 350–500°C and 50 bar [10, 11, 16]. 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 [17]. A typical experimental conversion-selectivity plot for the gas-phase partial oxidation of methane is shown in **Figure 1** [18]. 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. 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 [8].

The suggested mechanism for the direct conversion of methane to methanol via homogeneous gas phase reactions is shown in **Figure 2** [19].

2.2 A low temperature catalytic route involving homogeneous and heterogeneous catalysis

At moderate conditions, catalysts play an important role in the partial oxidation conversion of methane to methanol in terms of controlling the selectivity of the desired yield. Several catalysts have been investigated at 1 atm and mild temperatures.

In homogeneous systems, in the early 1970s, it was shown that methane could be converted to methanol by Pt(II) and Pt(IV) complexes because these complexes do not oxidise CH_3OH to CO_x [20]. Since that breakthrough, several oxidation catalysts based on Pt(II), Pd(II) and Hg(II) salts have been proven to functionalize C-H bonds [21, 22], leading to good yields of partially oxidised products (Eq. (1)). For example, [(2,2′-bipyrimidine)$PtCl_2$] catalyses 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 hydrolysed to methanol (Eq. (2)).
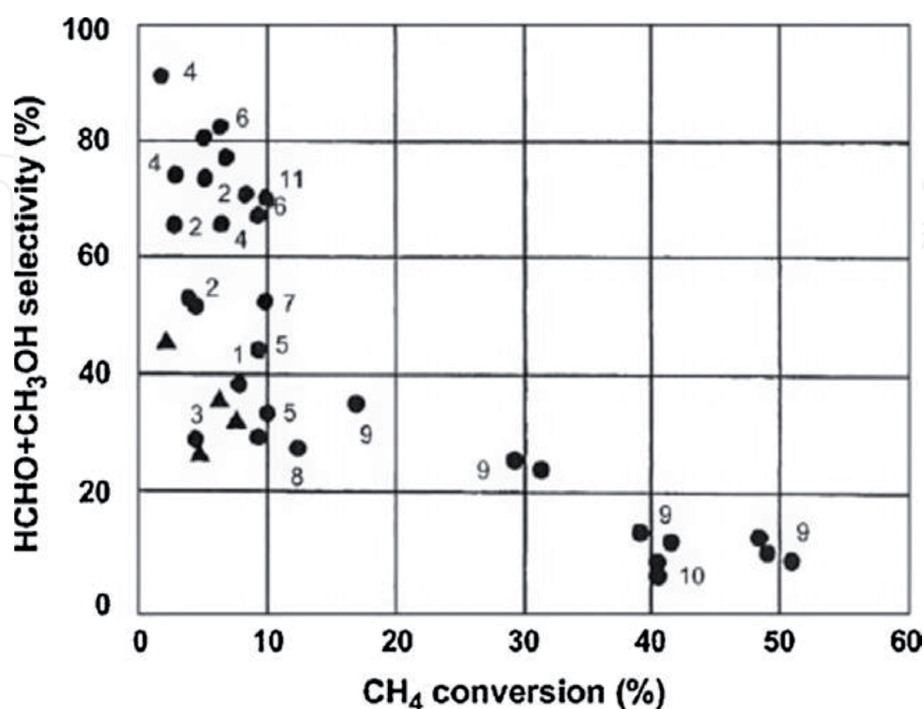

Figure 1.
Homogeneous gas-phase partial oxidation of methane from several studies: (1) Lott and Sliepcevich;
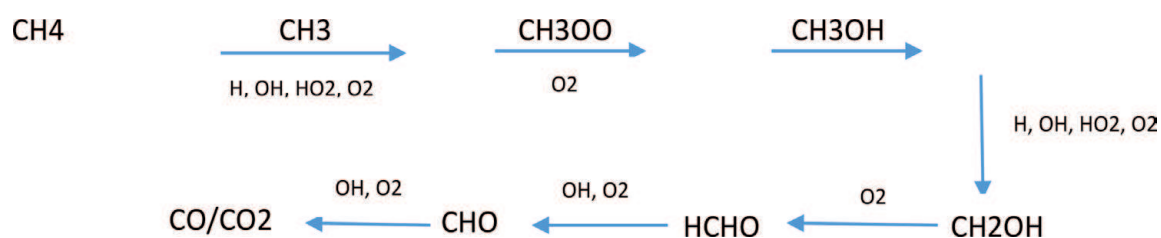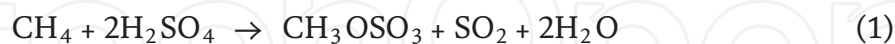*(3) Tripathy; (4) Brockhaus; (6) Hunter; (8) Rytz and Baiker [18].*

CH4 → CH3 (H, OH, HO2, O2) → CH3OO (O2) → CH3OH → (H, OH, HO2, O2) ↓ CH2OH → (O2) HCHO → (OH, O2) CHO → (OH, O2) CO/CO2

Figure 2.
Schematic diagram of the methane conversion via homogeneous gas phase reaction.

$$CH_4 + 2H_2SO_4 \rightarrow CH_3OSO_3 + SO_2 + 2H_2O \qquad (1)$$

$$CH_3OSO_3 + H_2O \rightarrow CH_3OH + H_2SO_4 \qquad (2)$$

The major drawbacks of the liquid phase include not only the difficulty of separating the methanol product from the solvent but also solvents such as sulphuric acid need expensive corrosion-resistant materials and periodic regeneration of the consumed H_2SO_4. A new class of solid catalyst based on immobilised complexes has recently been reported for the direct low-temperature oxidation of methane to methanol [23]. This solid catalyst has a covalent triazine-based framework (CTF) with numerous accessible bipyridyl structure units, which should allow the coordination of platinum (**Figure 3a** and **b**) [23]. The performance of these new catalysts showed that the activity is maintained throughout several cycles, and selectivity for methanol formation above 75% could be reached.

In nature, methane monooxygenase enzymes (MMO) transform CH_4 to CH_3OH in water under ambient conditions [11]. A number of metal complexes have been proposed to mimic the chemistry of these enzymes [11, 24, 25], but the systems which generate active oxygen species capable of converting CH_4 to CH_3OH are yet to be created. In contrast to organometallic CH_4 activation, MMO proceeds via a different mechanism by creating a very strong oxidising 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 [11]. 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 an oxidant than its monomer counterpart (FePc). The heterolytic cleavage of the O-O bond in the $Fe^{IV}NFe^{III}OOH$ complex and the formation of very strong oxidising $Fe^{IV}NFe^V = O$ species are favoured in the presence of acid by the protonation of peroxide oxygen [11, 24, 25]. 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 [11, 26]. In this proposal, the key to oxygen insertion is a complex containing three copper atoms, in which the atomic charges vary. By synthesising 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' [11, 25, 26]. It has been shown that the activity for methanol synthesis is 5 mol (CH_3OH) kg (catalyst)$^{-1}$ h^{-1} for sMMO as a complete enzyme with NADH present and this result represents the bench-market by which MMO catalysts should be judged. However, when NADH cofactor is removed, H_2O_2 can be used as the terminal oxidant with the enzyme but the catalytic activity decreases to 0.076 mol (CH_3OH) h^{-1} kg (MMOH)$^{-1}$ [27].
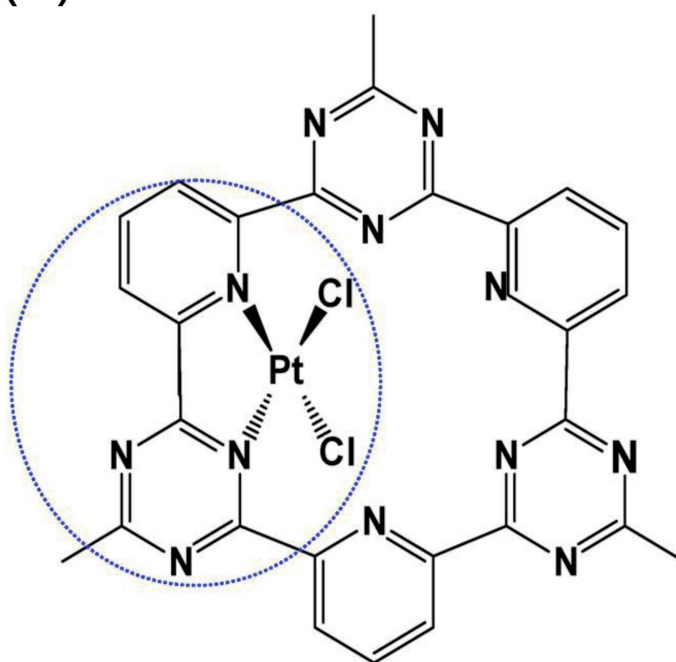
Figure 3.
(a) Bipyrimidyl Pt(II) complex used in the oxidation of methane to methyl bisulphate in concentrated sulphuric acid. (b) Covalent triazine-based framework (CTF) with numerous accessible bipyridyl structure units which are suitable to coordinate the Pt(II) complex.

In heterogeneous catalytic systems, many attempts have been conducted for the oxidation of methane. In most cases, SiO_2 was used as a support with different metals, and O_2 as oxidant. It was claimed that [28, 29] with a similar condition, HCHO might be produced with one-pass yield from 0 to 4%. However, high one pass HCHO yields were reported in some publications, but the results were not confirmed by other groups. It is stated that the results by different researchers have always been quite different, and some of them were even contradictory to one other [25, 30]. For instance, in one published work, a high selectivity (90%) to oxygenates (CH_3OH + HCHO) was obtained at CH_4 conversion of 20–25% at 873 K in an excess amount of water vapour over MoO_3/SiO_2 catalysts prepared by a sol-gel method [31]. Another work conducted the experiments under similar reactions with MoO_3/SiO_2 catalyst prepared by a similar method, but the yield of oxygenates was not greater than 4% [25]. Another example of contradiction showed that by using N_2O as an oxidant, CH_3OH could be achieved with a noticeable selectivity in the presence of H_2O over MoO_3/SiO_2 [32]. Results published by other groups used

similar catalytic systems, but the results showed no detectable formation of CH_3OH [33, 34]. Metal-containing zeolites such as Co, Cu, and Fe have been studied at low temperature in batch mode [35, 36]. The direct conversion of methane to methanol over this metal-containing zeolite consists of three steps: (1) formation of active species by calcinations in air, (2) reaction of the active species with methane at low temperature and (3) extraction of methanol, using a polar protic solvent [37]. However, these catalytic systems are not yet a continuous process as an extraction procedure for methanol is required [36, 37]. A series of catalysts based on MoO_3 and WO_3 were studied, and the WO_3-based catalysts were less effective for the production of methanol. The Ga_2O_3/MoO_3 catalyst showed the maximum methanol yield [38].

In a series of seminal publications, Hutchings and co-workers demonstrated that Fe-ZSM-5- and Fe-Cu-ZSM-5-based zeolites and Au-Pd supported on titania could activate methane at temperatures under 100°C using aqueous hydrogen peroxide as the terminal oxidant [39, 40]. The initial product of reaction was shown to be methyl hydroperoxide which subsequently reacted to yield methanol and formic acid. **Figure 4** shows the time on line activity over Au-Pd/TiO_2.

The turnover frequencies based on Fe were high with albeit very low conversions. More recently, Al-Shihri et al. [41] showed that the reaction pathway of oxidation in aqueous hydrogen peroxide over ZSM-5 catalysts followed the reaction sequence $CH_4 \rightarrow CH_3OOH \rightarrow HCHO \rightarrow$ formic acid. Although at the reaction conditions used the formaldehyde was oxidised rapidly to formic acid, it was also converted to low molecular weight polyoxomethylene polymer. Similar findings were achieved in preliminary results using Au-Pd catalysts. However, the use of aqueous hydrogen peroxide to oxidise methane is unlikely to prove economic unless its parallel catalysed decomposition into oxygen and H_2O can be supressed. Thus, the development of a viable liquid phase process based on the use of aqueous hydrogen peroxide as the terminal oxidant would be challenging.

An attractive alternative approach is to couple in situ direct generation of hydrogen peroxide from hydrogen and oxygen with methane oxidation in a tandem process. Au-Pd catalysts have proved to be highly active for the direct hydrogen peroxide synthesis reaction and capable of enhancing the tandem catalytic oxidation of alcohols, especially using nanostructured oxide supports [42, 43]. However, while the production rate of hydrogen peroxide is high, the achievable
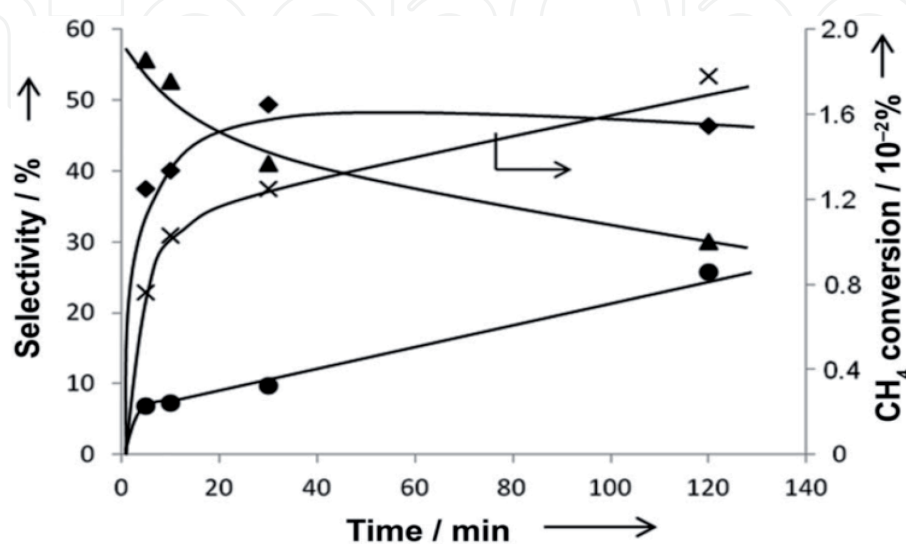

Figure 4.
Time on line activity reaction temperature: 50°C, [H_2O_2]: 5000 μmol, solvent: H_2O, 10 mL. Catalyst: 1.0 × 10⁻5 mol of metal, 28 mg 2.5 wt% Au-2.5 wt% Pd/TiO.

concentration in the liquid phase remains low due to the catalysed decomposition of the formed hydrogen peroxide. This means that a tandem process in the liquid phase is more likely to find application in the selective oxidation of high value chemicals. For direct selective oxidation of light hydrocarbons to oxygenated compounds, a gas phase continuous process based on the use of heterogeneous catalysts would be more attractive. In a tandem oxidation process, the oxidant would be oxygen, air or N_2O mixed with hydrogen to generate surface hydroperoxy in situ by the surface reaction of hydrogen-oxygen.

In a preliminary study, Al-Shihri et al. demonstrated that Au-Pd catalysts were able to catalyse the gas phase direct selective oxidation of methane at moderate conditions using the tandem synthesis of hydrogen peroxide from hydrogen-oxygen mixtures. The products of reaction were trapped and found to be methylhydroperoxide, polyoxomethylene, and a small amount of formic acid. Based on analogy with the liquid phase reaction sequence described above [41], the production of polyoxomethylene would be expected to involve initially the formation of formaldehyde as a reaction intermediate, although none was detected. This aspect is currently being investigated prior to publication of these exciting new results. The production of methyl hydroperoxide, formaldehyde and polyoxomethylene from methane is highly desirable. Polyoxomethylenes are valuable polymeric materials and also potential hydrogen storage materials; methyl hydroperoxide can be utilised to form methanol or react to form other compounds. In our preliminary study, the most promising Au-Pd catalysts were based on the use of nanostructured oxide supports. However, the catalysts were prepared by simple impregnation and were far from optimum in terms of metal particle dispersion and degree of Au-Pd alloy formation. These factors are important in the activity, selectivity, and maximising the selectivity in the use of the hydrogen, that is, avoiding direct combustion to water.

Shan et al. showed that mononuclear rhodium species supported by zeolite or titanium dioxide in aqueous solution can convert methane to methanol and acetic acid with high selectivity, using oxygen and carbon monoxide under mild conditions [44]. In a recent study, the direct conversion of methane to methanol was investigated using experimental and computational study. The results of this study showed that low Ni loadings on a $CeO_2(111)$ support can perform a direct catalytic cycle for the generation of methanol at low temperature using oxygen and water as reactants, with a higher selectivity than ever reported for ceria-based catalysts [45].

Gold-based catalysts have also shown interesting performance for the activation of C-H bond in alkane selective oxidation with dioxygen. A particular focus has been put on the synthesis of cyclohexanone and cyclohexanol. Zhao and co-workers [46] first applied gold catalysis in the activation of cyclohexane: Au/ZSM-5 and Au/MCM-41 favoured selectivity around 90% and conversions of 10–15% at 150°C, even though a loss in both activity and selectivity after their reuse is a drawback for industrial application. Two recent studies on the selective cyclohexane oxidation were performed by tailoring a supported gold on different materials, namely amorphous silica doped with titania and alumina prepared by a modified direct anionic exchange method [47].

In the direct gas phase oxidation of methane to methanol, no noble metal except Pd was investigated, and there was no promising results obtained when Pd was used and that might be due to the excessive interaction between Pd and the supports [25, 48]. Therefore, in order to overcome the extent of interaction between Pd and the support, and to increase selectivity toward methanol, bimetallic systems seem to be a more promising solution. Great success has been achieved in a variety of catalytic processes by combining two metallic elements in bimetallic catalysts, such as the platinum-iridium (Pt-Ir) system for petroleum reforming, platinum-tin (Pt-Sn) for alkane dehydrogenation, the nickel-gold (Ni-Au) system for steam reforming of alkanes, and the palladium-gold (Pd-Au) for selective oxidations [49].

2.3 Challenges in technologies for the conventional methods

The industrial production of methanol is executed via indirect way, in which methane is first converted to synthesise gas in highly intensive energy step. The synthesis gas is then converted to methanol. The intensive energy synthesis gas step occurs in operational plant at pressure range between 200 and 600 psi and temperature range between 700 and 1000°C [50]. This step is responsible for 60% of the capital cost of the plant. Therefore, the direct conversion of methane to methanol is highly desirable. Several approaches have been investigated and reported; however, no breakthrough has been achieved yet.

The homogeneous gas phase partial oxidation has the potential to replace the industrial method. In a technical evaluation study of this method, it was shown that a methanol selectivity of over 70% at 15% methane conversion can be achieved. However, the low conversion of methane per pass and relatively low methanol selectivity is still observed in most of the academic reports [51, 52]. The problem is due to kinetic and thermodynamic reasons [53]. This way requires a pressure of around 10 atm and temperature (1000°C) to activate methane and convert it to methanol with reasonable selectivity. The C-H bond in methane (440 kJ/mol) is stronger than the same bond in methanol (389 kJ/mol). That means at high temperatures, the methanol is more reactive than methane, which might lead to the decomposition of methanol to low grade product [52, 54–56]. In addition, the gas phase homogeneous is a free radical reaction, which means that it is difficult to control the process on the large scale [51, 54, 57].

The catalysts play an important role in activating methane at low reaction conditions and produce methanol with low byproducts [58, 59]. Two advantages of this method are the reduction of energy consumption used for methane conversion to methanol, and the low concentration of CO_2 produced in this process [58, 59]. The important factor in this process is to find catalysts that could activate methane at moderate conditions and convert it selectively to methanol. Although intensive work has been reported, no catalytic system has achieved the target conversion and selectivity.

A low temperature homogeneous catalyst in solutions is another way to convert methane to methanol at low temperatures. However, two challenges of this method is first the introduction of the catalysts with reasonable reactivity and selectivity that also tolerates oxidising and protic conditions [11]. The second challenge is the use of acid as a solvent such as sulphuric acid, which is applied in many studies. The main disadvantage of using sulphuric acid as solvent is the difficulty in separating the methanol from the solvent. Moreover, the acid might corrode and poison the catalysts through the reaction [11].

In nature, methane monooxygenases (MMOs) demonstrate high activity for methanol synthesis with a production rate of 5 mol (CH_3OH) kg (catalyst)-1 h^{-1} at ambient conditions. However, this method is still not practical yet due to the difficulty in purifying these proteins and the further oxidation reaction of methanol to formaldehyde.

3. Unconventional approach to convert methane to oxygenates

3.1 Conversion of methane to methanol via plasma technologies

Plasma can be used in many applications including oxidation of methane to methanol [60]. In plasma, the oxidation of methane to methanol can be conducted under atmospheric gas pressure. Plasma is often referred to as the fourth state of

matter, and it includes several components: positive ions, negative ions, electrons and neutral species. Plasma technology can be classified into thermal plasma and non-thermal plasma [61]. Thermal plasma can be described as a gas consisting of electrons, highly excited atoms, ions, radicals, photons and neutral particles, while electrons that have much higher energy than other surrounding particles populate non-thermal plasma. Okazaki et al. [62] reported that the conversion of methane to methanol was achieved using non-equilibrium plasma chemical reactions under atmospheric pressure by ultra-short pulsed barrier discharge in an extremely thin glass tube reactor. Various designs for plasma reactors for the oxidation of methane have been proposed to enhance the selectivity toward methanol. For example, in thermal plasma reactors, the dielectric barrier discharge (DBD) reactor was used for the synthesis of methanol from methane. This reactor was able to reduce the required temperature and pressure needed [63]. Another reactor is a new non-thermal discharge micro-reactor, which is used for a single-step, non-catalytic, direct and selective synthesis of methanol via methane partial oxidation at room temperature [64]. The non-thermal plasma can be developed by integrating the reactor with catalyst to improve the activity and selectivity of methane oxidation. In a recent study, the Cu-doped Ni was loaded on CeO_2, which led to enhance the selectivity of methanol until 36% [65]. In another study, multicomponent catalysts were combined with plasma in two different approaches, in-plasma catalysis (IPC) and post-plasma catalysis (PPC), for achieving high levels in both methane conversion and aimed methanol selectivity through the synergetic effect of the $Fe_2O_3^-CuO/\gamma-Al_2O_3$ catalyst [66].

3.2 Methane oxidation to methanol using photocatalysts

The photocatalytic process is a photochemical reaction that is carried out with external energy provided by ultraviolet light radiation that has energy equal to or greater than the energy band gap of a semiconductor. Several of oxidation and reduction processes are involved in the photo-generated electron and hole. TiO_2 catalysts have been used as semiconductor photocatalysts for a wide range of environmental applications [67]. In addition, tungsten oxide (WO_3) is also a good photocatalyst due to its high chemical stability in aqueous solution under acidic conditions in the presence of an oxidising agent [68]. For example, one study demonstrated that the WO_3 photocatalyst produced hydroxyl radicals that react with a methane molecule to produce a methyl radical, which promote the formation of methanol [69]. Another study [70] investigated different experimental parameters for the methane conversion such as catalyst concentration, laser power, laser exposure time, effects of free radical generator (H_2O_2) and electron capture agent (Fe^{3+}), using visible laser light. Also, this study examined the comparison between WO_3 and TiO_2, and it was found that the WO_3 showed the highest methane conversion [70, 71]. A recent work has studied the introduction of some electron scavengers such as (Fe^{3+}, Cu^{2+}, and Ag_+) and H_2O_2 species to the WO_3 catalyst to enhance the selectivity of methanol. They found that WO_3/Fe^{3+} is the most active catalyst with a methanol selectivity of 58.5% [68]. Another photocatalyst for the methane oxidation to methanol is vanadium oxide supported by MCM-41. Nitric oxide (NO) was used as an oxidant for the oxidation of methane under UV irradiation at 295 [72]. **Figure 5** shows an example of methane conversion to methanol via photocatalysis.

3.3 Conversion of methane to methanol using supercritical water

The supercritical water oxidation (SCWO) is a reaction that occurs in water at elevated temperatures and pressures above the thermodynamic critical point of the
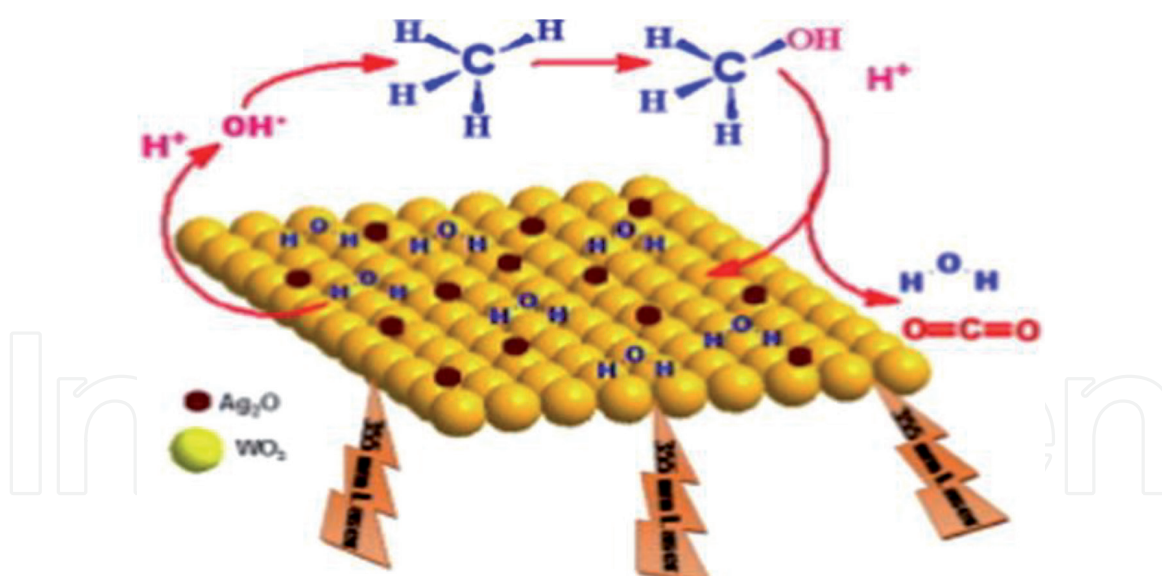
Figure 5.
Graphical representation of reaction of conversion of methane to methanol via photocatalysts [73].

mixture. Under the supercritical fluid conditions, the properties of water such as viscosity and dielectric constant can be adjusted between high gas-like diffusion rates and high liquid-like collision rates by varying pressure and temperature [60]. The catalytic oxidation of methane was examined over Cr_2O_3 under supercritical water conditions, and it was found that this catalytic system under supercritical conditions enhances the conversion rate of ethane and promotes the selectivity of methanol [74]. Another study investigated the isothermal conditions with a laminar reactor in SCWO for the direct partial oxidation of methane to methanol. They achieved a methanol selectivity of 35% at a conversion of 3% at temperatures of 400–410°C [75]. Savage PE et al., [76] have examined two types of reactors, glass-lined reactors and stainless steel reactors. A parametric study has been conducted using both reactors, and the glass lined reactor showed higher conversion of methane to methanol.

3.4 Conversion of methane to methanol using membrane technology

Membrane technology has been used for methane conversion to methanol using membrane reactor at moderate conditions. The advantage of using a membrane reactor is the fact that it can perform two functions at once, reaction and separation. The membrane can be classified based on the type of materials and porosity. The membrane can be made either by polymeric or organic materials with different porosity [60]. The organic membrane has advantages over the polymer in terms of the tolerance to chemical and temperature effects. Moreover, the organic membrane is mainly composed of metallic or ceramic materials and has greater physiochemical stability. Two research works studied the methane oxidation to produce methanol using Methylosinus trichosporium OB3b with a high concentration of Cu^{2+} and they found that the optimization of the conversion rate was positively affected by several parameters including the temperature, pH and concentrations of sodium formate, phosphate buffer and cyclopropanol [77, 78]. In another study, the methane oxidation was carried out using a membrane reactor where the methane and oxygen were introduced by two separate dense silicone tubes. A high methanol production of 1.12 g/L and 60% methane conversion were reported [79].

3.5 Challenges of unconventional ways to convert methane to methanol

The unconventional technologies such as plasma, photocatalysts, supercritical and biological are long-term processes, and still away from practical. The methane oxidation under plasma conditions is considered as a clean method as there are no harmful emissions produced such as CO_2 and CO [80]. The plasma reactor is simple, benign and cheap. However, the productivity of methanol is low due to the limitation of methane solubility in the reaction medium at ambient conditions.

Photocatalysis technology is an attractive way to convert methane to methanol, as the basic requirement for this method is the use of three abundant reactants of light, water and methane. Despite the two decades of work on photocatalysis, the selectivity of methanol is still low [68, 70].

Supercritical water oxidation is an efficient process to treat a variety of hazardous and non-hazardous wastes. However, there are some factors that limit the application of this technology in methane oxidation such as the complication of the reactor design, the high temperature used and the high corrosion rate when using halogens such as chlorine for some waste treatment [60, 81].

The use of membrane technology for methane conversion to methanol is feasible due to the advantage of the effective separation of methane and methanol. However, some challenges still exist for large scale application: first, the relatively high energy requirement for large scale plant, second, the low tolerance of polymer-based membrane to high temperatures and chemicals, third, the high conversion of methane will produce different organic compounds, and that might cause swelling or breakage of the membrane [60, 81].

4. Summary

In this chapter, we discussed the utilisation of methane as the main component of natural gas that can be converted to methanol. We discussed various processes that can activate methane and convert it in a single step to methanol, including their feasibility, recent progress and challenges associated with the conventional and unconventional methods. We showed that these processes have advantages and disadvantages. However, most of them suffer from the low yield of methanol. The unconventional methods are long-term processes and still far away from practical. The low temperature route using heterogeneous catalysts has a great potential and can be alternative to the current industrial process as some catalytic systems were shown to activate methane at moderate reaction conditions using different oxidants. Nevertheless, the selectivity toward methanol is still low. Therefore, more effort is needed to design and synthesise robust and cheap catalysts that could convert methane directly and selectively to methanol using air as an oxidant in a continuous flow reaction system.

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