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RECENT PROGRESS ON THE DIRECT CONVERSION OF METHANE TO METHANOL

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ABSTRACT

Methanol is a valuable industrial chemical that serves as a clean fuel and a precursor to many highdemand chemicals like acetic acid, methyl tertiary butyl ether, dimethyl ether, formaldehyde, methyl halides, and methylamine, among others. Methane on the other hand is an abundant gas that constitutes about 85-96 %wt of natural gas compositions obtained from the cracking of petroleum or as a byproduct of coalification or biomass fermentation process. It is reportedly the second most abundant greenhouse gas emitted into the atmosphere after CO2 and also has 25 times as much greenhouse effect as CO₂. Therefore, the conversion of methane to methanol is a transformative approach to creating fuels and important chemical feedstocks and intermediates and also a sustainable way to reduce the emission of greenhouse gases and mitigate global warming. Currently, methanol is manufactured industrially at a commercial scale from methane via the indirect energy-intensive syngas/FTS route which is expensive and environmentally unfriendly and proceeds at high temperatures and pressures. Therefore, direct conversion of methane to methanol is desirable to replace the indirect syngas/FTS with the possible advantages of reduced energy consumption, simplified process routes, and potentially higher selectivity and yield. This mini-review explores the recent advancement in the different direct-methane-tomethanol conversion methods, challenges, and opportunities.

1. INTRODUCTION

Methane (CH₄) is the simplest member of aliphatic saturated hydrocarbons called alkanes. It constitutes about 85-96 %wt of natural gas compositions obtained from the cracking of petroleum or as a byproduct of coalification or biomass fermentation process [1,2]. According to the International Energy Agency (IEA, 20A23), approximately 140 billion cubic meters of natural gas are flared during the upstream petroleum refining and hydrocarbon production processes annually, leading to emissions of nearly 400 million tons of CO₂ into the atmosphere [3].



Fig. 1. Global methane emissions from the energy, 2000-2022, and Direct CO₂ combustion emissions from flaring and flaring intensity in the Net Zero Scenario, 2010-2030 [3]

CH₄ is one of the abundant, cheap, yet important feedstocks for the industrial production of many valuable chemical intermediates, petrochemicals, and fuels. The abundance, inexpensiveness, and high calorific potential of CH₄ make it a valuable fuel source for residential heating and cooking, as well as for generating electricity in gas turbines [4]. Despite all the advantages offered by CH₄,

it has 25 times as much greenhouse effect as CO_2 due to its high ability to absorb and release infrared radiation (IR) causing a thermal layer in the atmosphere [4,5].

The presence of CH₄ in the atmosphere is harmful to the environment because when it descends into the atmosphere, it quickly interacts with chloride radicals in the stratosphere and the hydroxyl radicals in the troposphere causing alterations in its composition and distribution [5]. Therefore, the conversion of CH₄ to methanol (CH₃OH) is not only a transformative approach to creating fuels and important chemical feedstocks and intermediates but also a sustainable way to reduce the emission of greenhouse gases and mitigate climate change.

Methanol (CH₃OH) - the simplest alcohol - is a versatile chemical with widespread applications in fuel production, chemical synthesis, and as a solvent. It is considered a promising clean-burning fuel with a high-octane number. Methanol has also proven to be one of the most valuable building blocks for obtaining more complex chemical structures, such as acetic acid, methyl tertiary butyl ether, dimethyl ether, and methylamine among others [6]. Methanol production is the second most convenient energy carrier for hydrogen storage and conservation after ammonia production [6]. Recent studies indicate the potential of methanol as a cost-effective and environmentally friendly fuel source for a variety of energy applications. For instance, according to a study conducted by Dalena and his colleagues in 2018, methanol can produce hydrogen for powering fuel cells with high energy efficiency rates. [6] Additionally, it can be converted to acetic acid via the Cativa process and Dimethyl Ether (DME) which is a clean-burning fuel alternative to diesel fuel for transportation and industrial applications. Another potential application of CH₃OH is its use in direct methanol fuel cells (DMFCs), which convert methanol into electricity without the need for an external fuel source, making them suitable for portable and stationary energy applications [6].

In the industry, large-scale production of methanol occurs via a conventional method involving a multi-step indirect process via Fischer-Tropsch Synthesis [6, 7]. The first step in this method is usually the reforming of methane to syngas (a mixture of CO and H₂) using Ni catalysts as shown in equations 1. Steam can be added to the syngas to produce more H₂ for effective hydrogenation reaction via water gas shift (WGS) reaction as shown in equation 2. This process is highly endothermic and often takes place under high temperatures and pressure. One commonly used reforming strategy is steam methane reforming (SMR). However, autothermal reforming (ATR) and dry methane reforming (DMR) have also been used [8].

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO \qquad \Delta H^o{}_r = 206 \text{ kJmol}^{-1}$$
(1)
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^o{}_r = -41 \text{ kJmol}^{-1}$$
(2)

The second step in the FTS indirect methane-to-methanol conversion is the exothermic catalytic hydrogenation of syngas to methanol at $5-10^6$ Pa and 220–300 °C using Cu–Zn/Alumina-based catalysts as shown in equation 3 [9].

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$
 $\Delta H^o_r = -49.5 \text{ kJmol}^{-1}$ (3)

Although researchers have debated whether the methane-to-methanol conversion occurs via CO hydrogenation or the CO_2 hydrogenation route. However, a comparison of the enthalpy of the reaction of both routes at 298K by the recent isotopic studies has shown that indirect FTS methane-to-methanol conversion occurs predominantly through CO_2 hydrogenation a route [10].

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H^{\circ}_{298K} = -90.77 \text{ kJmol}^{-1}$$
(4)
$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H^{\circ}_{298K} = 41.19 \text{ kJmol}^{-1}$$
(5)

As a result of the highly endothermic process involved in the first step of the FTS indirect methaneto-methanol conversion, it is energy-intensive, expensive, environmentally unfriendly, requires high temperatures and pressures, and often suffers from low selectivity and yield [11]. For instance, the synthesis of methanol from methane via the FTS route has been reported to take place at a temperature range of 700–1100 °C and 3–25 bar pressure while the temperature and pressure ranges for the direct conversion of methane to methanol occur at 380–470 °C and 1–5 MPa respectively [11].

In recent years, considerable research efforts have focused on directly or innovatively converting methane to methanol via electrochemical, partial oxidation, plasma irradiation, solar, and biological methods [11]. This approach aims to create new catalysts and optimize reaction conditions and reactor designs to effectively convert methane to methanol under relatively mild conditions via heterogeneous catalytic partial oxidation and homogenous non-catalytic gas-phase partial oxidation [12]. The possible advantages offered by the direct conversion technique over the indirect oxidation method include reduced energy consumption, simplified process routes, and potentially higher selectivity and yield. However, achieving commercialization of this method has

been unsuccessful to date due to the lack of identification of an effective catalyst under such mild conditions [12,13].



Fig. 2. Direct and indirect routes for converting methane to methanol [11]

The process of converting methane directly to methanol involves two main steps: the activation of the strong C-H bond in methane to produce methoxy (CH_3O^*) intermediates, followed by the oxidation of methoxy to methanol. Scientists have conducted extensive research on various catalysts, reaction conditions, and reactor designs to optimize these steps and improve the overall process efficiency. However, the main challenges in direct methane conversion to methanol include overcoming the high thermodynamic stability of methane, controlling selectivity towards methanol, and managing catalyst deactivation. Moreover, developing catalysts that perform well under mild reaction conditions remains a crucial focus area [12,13].

Despite these challenges, advancements in catalyst design, reaction engineering, and fundamental understanding of reaction mechanisms have shown promise in advancing the direct conversion of methane to methanol. This approach holds the potential for transforming methane, a potent greenhouse gas and underutilized resource, into a valuable chemical feedstock with broad industrial applications.

In this context, this term paper provides an overview of the recent progress, challenges, and prospects in the direct conversion of methane to methanol. By exploring key catalysts, reaction mechanisms, and process optimization strategies, the review paper contributes to the advancement of sustainable methane utilization and the transition toward a more carbon-efficient chemical industry.

2. METHODS USED IN THE DIRECT CONVERSION OF METHANE TO METHANOL

Methane is a thermodynamically stable molecule that is difficult to convert directly to other products like methane and syngas because of its high ionization energy, low polarity, low proton and electron affinity, and strong C-H bond that is approximately 440 kJmol⁻¹ [14,15]. However, the direct conversion of methane to methanol involves the kinetic or thermodynamic activation of C-H of the methane molecule via partial oxidation under mild or moderate conditions [11,13]. Due to the inertness of the C-H bond of the methane, its noncatalytic partial oxidation is not usually achieved under mild conditions. To make the process more feasible, researchers focus more on developing suitable catalysts that can lower the activation energy required to break the C-H bond and ultimately allow the reaction to proceed at lower temperatures and pressures. Researchers also optimize the reaction conditions towards selectively converting methane directly to methanol by considering the differences in the bond strengths between the C-H bond in methane (\sim 440 kJmol⁻¹) which is stronger than the one in methanol (~47 kJmol⁻¹) [13]. This weaker C-H bond in methanol restricts the selectivity of oxidation of methane-to-methanol to be partial, making the products obtained highly dependent on the amount of oxygen and methane available for reaction in the reactor (usually 1:2). Excess oxygen can completely oxidize methanol produced under the reaction conditions for methane activation to carbon dioxide or even oxidize methane directly to carbon monoxide or carbon dioxide as can be seen in table 1.

| S/N | Reaction | ΔH ^o 298K (kJmol–1) |
|-----|--|--------------------------------|
| 1 | $2CH_4 + O_2 \rightarrow 2CH_3OH$ | -126 |
| 2 | $2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$ | -519 |
| 3 | $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ | -901 |
| 4 | $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$ | -126 |

Table 1: Comparison of Gibb's free energy of oxidation of methane and methanol at 298 K

2.1. Conventional catalytic partial oxidation of methane to methanol

Direct conversion of methane to methanol is a desirable field that has the prospect of eliminating the energy-intensive indirect conversion via syngas and FTS. The direct conversion of methane to methanol would overshadow the conventional indirect method if it can at least selectively produce 80% of methanol and a yield of 5.5% for single-pass methane conversion [12]. The key reaction involved in this process – partial oxidation of methane – depends primarily on the system's

temperature, reactor type, methane/oxygen ratio of the feed gas, residence time, pressure, and additives.

$$CH_{4(g)} + 0.5O_{2(g)} \rightarrow CH_3OH_{(l)} \qquad \Delta H^{o}_{298K} = -126$$
 (6)

Mechanistic study of partial oxidation shows that methane C-H is first catalytically activated followed by bond-splitting via electrophilic attack to produce the anion intermediate CH_3^- . Oxidized products of methane are then obtained by oxidation of CH_3^- [16]. Partial oxidation often occurs at 200–500 °C and 30–200 bars via catalyst–mediated liquid or gaseous phase reaction. During the liquid phase of conventional partial oxidation, superacids are employed as catalysts [13]. Although non-catalytic conversion of methane is possible at 370–470 °C, the theoretical methane conversion and selectivity of methanol are only 30% and 5% respectively [13]. This is much lower compared to the methane conversion and methanol selectivity obtained through the indirect syngas/FTS route, which are 68% and 54% respectively [17,18]. Below are the most common conventional partial oxidation routes used to directly convert methane to methanol.

2.1.1 Low-temperature heterogeneous catalyst-mediated route

Heterogeneous catalysts have been reported to be only effective in catalyzing methane directly to methanol at a very narrow temperature [X-Y]. Common heterogeneous catalysts explored by researchers for the partial oxidation of methane to methanol are active metal-oxide species. Some researchers used modified and unmodified metal oxide catalysts such as MoO₃, MgO, FeO, and SnO₂ [19-27]. Zhang et al. (2008) achieved 7%–8% methanol yield with 60% methanol selectivity and 13% methane conversion by partially oxidizing methane directly using Mo–V–Cr–Bi–P oxide heterogeneous catalysts in customized quartz-lined fixed-bed tubular reactor operating at 380 500 °C and 5.0 MPa [24]. They also reported 60% and 11.2% methanol selectivity and methane of about 3–4.5% with selective production of methanol of 35% has also been reported [26,27]. An early-stage study conducted by Aoki et al. in 1994 revealed that methanol can be oxidized into oxygenates using a MoO₃/SiO₂ catalyst and water vapor as an oxidant during methane partial oxidation. They ascribed the reason to the high catalytic activity of the silicomolybdic acid (SMA)-like structure of the MoO₃/SiO₂ catalyst [28].

Considerable research efforts have been put into metal-zeolite heterogeneous catalysts as they show promise in the partial oxidation of methane to methanol at modest temperatures due to their ability to mimic the activities of methane monooxygenases (MMOs) enzymes [13]. For instance, it is possible to stabilize mono-, bi-, or tri-nuclear complexes of Cu or Fe in the micropore structure of zeolites like Zeolite Socony Mobil-5 (framework type MFI) or mordenite (MOR) by ion-exchange of zeolite and subsequent activation with an oxidant as shown in figure 3.



Fig. 3. Proposed mechanisms for oxidation of methane to methanol on Cu-zeolite complexes.

Michalkiewicz in 2004 reported 74% methanol selectivity using Fe-NaZSM-5 catalyst with a very low methane conversion rate of 0.06%. When they modified the catalyst to Fe-HZSM-5, they obtained higher methane conversion of up to 11.22% but the methanol selectively decreased greatly to 16.51% [29]. Krisnandi and colleagues studied four types of Co/ZSM-5 zeolites in 2015 at 423 K in a batch reactor (volume c.a. 200 cm³). 0.5 g of Co/ZSM-5 catalyst was used with a methane to N2 ratio of 0.5:2. According to the authors, all four zeolites studied showed good selectivity to methanol production. However, the hierarchical Co/ZSM-5 catalyst has the highest methane conversion rate of 42% yielding about 7.56% methanol [30]. A slight modification to this process by XU and colleagues by impregnating Co-ZSM-5 with Fe & Cu via chemical vapor

impregnation using H_2O_2 as an oxidant showed excellent selectivity of >90% towards methanol production and 0.5% conversion with 1.5% Fe and 1.5% Cu/ZSM-5 [31].



Fig. 4. Plots of conversion vs selectivity for methane oxidation reactions catalyzed by 1.5% Fe 1.5% Cu/ZSM-5 [31].



Fig. 5. Temporal analysis of methane conversion and reaction selectivity assessed for 10 h [31].

A similar study using FeZSM-5 zeolite catalyst and nitrous oxide oxidant showed oxidation of methane to methanol by a-oxygen predeposited from nitrous oxide with a trace amount of other oxygenates like dimethyl ether and acetaldehyde [32]. Among the metal-containing zeolites widely studied such as Zn, Co, Cu, Fe, and Ni using oxidants such as H₂O₂, N₂O, O₂, and H₂O, Cu-zeolite systems with H₂O, and O₂ have shown more promise for possible industrial applications [33,34]. So far, heterogeneous gas-phase catalytic partial oxidation of methane to methanol shows promise but lacks scalability at the moment at the industrial level due to the difficulty of obtaining a better yield and selectivity of methanol simultaneously with a high methane conversion rate.

2.1.2 High-temperature heterogeneous gas-phase catalyst-mediated route

Gas-phase partial oxidation of methane to methanol usually proceeds via free radical generation. In this reaction phase, partial oxidation of methane to methyl radical is considered the rate-limiting step. Therefore, controlling the pressure in the reactor is a crucial step to control the selectivity of methane oxidation using this process [13]. Another important factor is the nature of the wall of the reactor. The reactors that show excellent results so far are Pyrex and Quartz glass-lined reactors due to their inert properties [16]. Figure 6 shows the statistics of gas-phase partial oxidation of methane from several studies [35].



Fig. 6. Partial oxidation of CH₄ via gas-phase from several studies [35].

While most results show selectivity of 30–40% at a conversion of 5–10% within the temperature and pressure ranges of 723–773 K and 30–60 bar respectively, Zhang and his colleagues opined

that the temperatures between 430–470 °C at 5.0Mpa would be the most appropriate conditions for partial oxidation of methane to methanol at gas phase [24]. So far, no reasonable selectivity towards methanol formation has been obtained for gas-phase partial oxidation methane at high temperatures. According to Otsuka and Wang, the why it is difficult to obtain CH₃OH at high temperatures is that CH₃OH itself is more reactive than methane and tends to decompose or oxidize immediately to HCHO and CO_x [36]. This places a high demand to discover catalysts that can activate methane at low temperatures. However, if a concerted system can be developed in such a way that methanol is separated as it is formed, then gas-phase heterogeneous oxidation of methane to methanol may be possible. Unfortunately, methanol is liquid at room temperature and such removal may be impossible.

2.1.3 Low-temperature solution-based route using a homogeneous or heterogeneous catalysts

A couple of researchers have explored the direct conversion of methane to methanol using homogeneous catalysts at low temperatures. The likelihood of achieving a breakthrough via catalytic homogeneous methane to methanol conversion at low temperatures is higher than the use of heterogeneous catalysts at high temperatures because it does not involve methyl radicals. Even though the work of Shilov et al. in 1972 revealed that the conversion of methane to methanol over Pt(II) and Pt(IV) complexes explored is possible [37], the research in this area became dominant after the work of Periana et al. in 1993 who used concentrated H₂SO₄ and a Hg(II) complex as catalysts [38]. He suggested that methanol can be obtained by hydrolyzing methyl bisulfate produced from reacting HCl with methane.

$$CH4 + 2H_2SO_4 \rightarrow CH_3OSO_3 + SO_2 + 2H_2O(5)$$

$$\tag{7}$$

$$CH_3OSO_3 + H_2O \rightarrow CH_3OH + H_2SO_4$$
(8)

Labinger also showed that bipyrimidyl platinum (II) complex can hydrolyze alkanes, especially methanol to methanol at 120 °C instead of the mercury complexes [39].

$$RH + H_2O + PtCl_6^{2-} \rightarrow ROH + PtCl_4^{2-} + 2HCl$$

Even though this process shows the phenomenon where the rate constant for breaking the C-H bond in CH_4 on Pt is higher than that in the product (methyl bisulfate), the prospect of extending

this type of process to the industrial level is very slim because of the cost that may be associated with separation and regeneration of the spent concentrated sulfuric acid. The corrosive nature of concentrated H_2SO_4 also aggravates the economic unfavourability associated with this process.



Fig. 7. Reaction mechanism for the oxidation of methane to methyl bisulfate using a bipyrimidyl Pt(II) complex in concentrated sulfuric acid [39].

Investigation using heterogenous catalysts in ionic liquid liquids as solvents was also reported in the literature. For example, Li and colleagues reported direct methane conversion to methanal. They used AUNPs [Au/SiO2] catalyst, [Bmim]Cl ionic liquid as the solvents, trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) as the acidic reagents, and $K_2S_2O_8$ as the oxidant. Methane conversion of 24.9% was achieved yielding 17.8% of methanol with selectivity up to 71.5% [40].

2.1.4 Biocatalytic-based oxidation

Biocatalytic direct conversion of methane to methanol occurs under ambient temperature and physiological conditions [32]. This conversion process is based on the action of the Methane monooxygenase (MMOs) – enzymes used by Methanotrophs to oxidize methane to methanol and its conversion mechanism is similar to that of FeZSM-5. MMOs are of two types: The particulate MMO (pMMO) and the soluble MMO (sMMO). The most common type is the pMMO and it is

usually bound to the cell membrane of the methanotrophic bacteria. It cannot work properly unless it is in a Cu-saturated environment. Particulate MMO (pMMO) is the more common membranebound form [41] and requires a copper-saturated environment to function properly [42]. The sMMO occurs in bacterial cytoplasm at very low concentrations of Cu conditions [43]. During the methanotrophic process, methanol dehydrogenase enzyme (MDH) can further oxidize methanol via formaldehyde and formate to carbon dioxide [44]. Therefore, to maximize the production of methanol, it is important to inhibit the activities of MDH enzymes to suppress further oxidation as shown in Fig. 7.



Fig. 8. Inhibition pathway of MDH during methane oxidation to methanol in methanotrophic bacteria. The red-colored section is halted if 100% of the produced methanol is extracted from the cell [44].

The efficiency of the biocatalytic methane oxidation to methanol depends on the nature, concentration, and effectiveness of the inhibitors. Razumovsky and colleagues studied the dynamic of the biocatalyst based on cells of the bacteria *Methylosinus sporium B-2121*, both suspended in a medium and immobilized in the polyvinyl alcohol cryogel. According to the authors, the concentration of the methanol observed using an immobilized biocatalyst was ($62\pm 2 \text{ mg L}^{-1}$)

fivefold compared to the free cells [45]. Another study by Lunsford revealed that MMO enzymes activate O₂ at iron centers using NADH as the reductant [46].

The prospects of the oxidation of methane to methanol using biomimetic catalysts based on MMO are high. However, various factors hinder the development of industrially viable biotechnology for natural gas conversion to methanol. Some of the challenges are over-oxidation of methane beyond methanol, the toxicity of source methane impurities, product inhibition, gas-liquid mass transfer limitations, maintaining catalytic activity and methanotroph viability, and optimized biotechnological conditions [44].

2.2. Photocatalytic direct methane conversion to methanol

The photocatalytic conversion of methane to methanol is based on the photochemical reaction induced by UV radiation when it strikes the semiconductor surface to create an energy band gap consisting of electron (e)–Hole (h+) pairs. A couple of researchers have explored the photocatalytic direct conversion of methane to methanol. However, tungsten oxide (WO3) exhibits excellent photocatalytic activities toward the direct conversion of methane to methanol. This is accrued to its non-toxicity, moderate oxidizing power, and high chemical stability in aqueous solution under acidic conditions [47]. For instance, a comparison study conducted by Gondal and colleagues on the photocatalytic activities of NiO, TiO₂, and WO₃ revealed WO₃ to be an excellent photocatalyst compared to NiO and TiO₂ [48].



Fig. 9. Graphical representation of the mechanism of photocatalytic conversion of methane to methanol using WO₃/Ag₂O [48]

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It has been reported in the literature that the addition of electron scavengers such as Ag^{+,} Cu²⁺, Fe³⁺, and H₂O₂ species to the photocatalysts during photocatalytic direct methane conversion to methanol improves the production of methanol. To confirm the claim, Taylor and Noceti conducted a study on the addition of H₂O₂ to the WO₃ photocatalysts. They reported that the addition of H₂O₂ to the photocatalyst stabilizes the hydroxyl radicals and hence enhances the production of methanol [49]. This is contrary to the report by Gondal who noticed that adding H_2O_2 does not positively affect the formation of methanol during photocatalytic [48]. He noticed that the addition of Fe³⁺ maintained the production of methanol throughout the reaction process. Villa and coresearchers examined the effects of the addition of Ag^{+,} Cu²⁺, Fe³⁺, and H₂O₂ species to the aqueous suspension of the WO₃ photocatalyst. The results indicated that the addition of Fe³⁺ and Cu^{2+} improved the photocatalytic activities of the WO₃ photocatalyst but WO₃/Fe³⁺ (2 mM) demonstrated superior performance, yielding 55.5 μ mol h⁻¹ g⁻¹ of methanol and methanol selectivity of 58.5% [47]. The authors ascribed the excellent performance of these species to their ability to capture the photogenerated electrons, which improved the charge separation that favors the production of HO[•]_{ads}, and thus generated a higher amount of CH₃OH. Ag⁺ and H₂O₂ on the other hand decrease the yield of methanol. According to the authors, the detrimental behavior of Ag⁺ is due to the formation of dark-color metallic Ag during the irradiation process that reduces the photoactivity of the semiconductor. V-containing MCM-41 catalyst was also reported to have photo-catalytically directly converted methanol to methanol [50].

While the performances of various photocatalysts have been investigated and shown to be effective in the direct conversion of methane to methanol with reasonable selectivity, it has not been expanded to the industrial scale yet. The reason is due to the lack of suitable large-scale reactors for this process and the lack of extensive exploration of the photocatalysts.

2.3. Plasma technology method of methane conversion to methanol

The use of plasma for the direct conversion of methane to methanol has been studied extensively over the years by researchers. Plasma, which is produced from the ionization of gases is usually considered the fourth state of matter due to the presence of negative ions, positive ions, neutral species, and electrons. There are two major classes of plasma: thermal and non-thermal plasma. Thermal plasma is the ionization of gases using heat supplied from an external source to generate radicals, highly excited atoms, ions, photons, electrons, and neutral particles. Non-thermal or nonequilibrium plasma on the other hand is generated using alternative energy sources like electric fields without the need for extreme temperature conditions [51]. This generates low-supplied power plasma with electrons that have much higher energy than other surrounding particles. Therefore, plasma conversion of methane to methanol involves oxidative ionization or decomposition of methane using thermal or non-thermal methods. The most widely studied plasma method for the direct oxidative decomposition of methane to methanol is the non-thermal method due to the less heat involved. During thermal plasma methane-to-methanol conversion, dielectric barrier, discharge (DBD) reactors are usually used to overcome the difficulty of separations associated with catalyst-only batch reactors and to control temperature, pressure, gas composition, flow rate, and applied voltage, which can affect the selectivity of the methanol [52-54].

A study by Okazaki successfully used non-thermal plasma chemical reactions to convert methane to methanol under atmospheric pressure using ultra-short pulsed barrier discharge (DBD) in extremely thin glass tube reactors. Water vapor was used as an oxidant with exergy regeneration. They obtained a 1% methanol yield using 50% water vapor. According to them, the yield can increase when rare gases such as Kr or Ar are added to the source gas to dissociate the source gas molecules [55]. Nozaki et al. obtained a one-pass methane conversion of 40% with selectivity for useful oxygenates (including methanol) of 30-50% using non-catalytically converting oxidizing methane directly to methanol at room temperature using a single-step non-thermal discharge micro-reactor [56]. A modification of this method by Okumoto et al. using pulsed DBD plasma under room temperature and atmospheric pressure resulted in 64% methanol selectivity and 0.65 µmolJ⁻¹ maximum production at low specific input energy of 360 J/l [57]. A study by Wang et al. used feed consisting of CH4/O2, CH4/CO, CO/H2, and CH4/H2/O2 in 50W radio frequency (RF) Ar plasma systems non-catalytically converted 19.1% of methane to 1.12% yield of CH3OH by CH4/O2 [58]. Cu-doped Ni supported on the CeO2, was reported by Mahammadunnisa et al. in 2015 to have enhanced the selectivity of methanol up to 36% [59]. Another multicomponent catalyst comprising of Fe2O3–CuO/ γ –Al2O3 catalyst was introduced to the plasma technology via in-plasma catalysis (IPC) and post-plasma catalysis (PPC) and was confirmed to greatly enhance the selectivity of methanol [60].

Recent studies focus more on the influence of catalyst addition on non-thermal plasma technology [61-67]. Chawdhury et al. integrated γ -Al₂O₃ supported Cu catalyst with metal oxide promoters (ZnO, ZrO₂, and MgO) to the plasma zone to obtain an in-plasma catalytic reactor [60]. The results showed the best methanol selectivity of ~28% over the CuZrAl catalyst with approximately 11% CH₄ conversion.



Fig. 10. Schematic diagram of the integrated reactor set-up for plasma-based direct methane conversion to methanol. [60]

In all cases, the addition of catalysts improves the selectivity of methanol. Bi et al. reported 93% methanol selectivity in the liquid phase and the highest production rate 56.7 mmol $g_{cat}^{-1} h^{-1}$ which is five times greater than could be obtained without catalyst addition [62]. Tang et al. achieved 86% methanol selectivity using a copper-mordenite zeolite (Cu-MOR) catalyst. However, during prolonged reaction time, Cu₂-(μ -O)²⁺ was reduced to Cu⁺ and Cu (II) hydroxide, causing carbon deposition and decreased catalyst activities [64]. Fathollahi et al. reported that increasing the oxygen flow rate in the DBD reactor with an inner Cu electrode led to the formation of OH radicals that increased methane conversion and methanol selectivity [64]. They noticed that when the plasma power was increased from 10W to 152W, the electric field inside the reactor rose, creating

electrons with sufficient energy to break the C–H bond (8.8 eV) and O–O bond (5.1 eV). This leads to an increased methane conversion and methanol selectivity, but selectivity decreases when the power is 78W, leading to the dominant production of heavy hydrocarbons. The combined highest methanol selectivity and methane conversion of 36.2% and 76% were achieved.

So far, plasma technology has shown great promise of being expanded to the industrial level, but no literature has reported its utilization for the direct conversion of methane to methanol yet.

2.4. Direct conversion of methane to methanol via electrochemical method

Direct electrochemical conversion of methane to methanol is one of the very promising ways to avoid the energy-intensive syngas/FTS route. However, CH_4 is a very stable molecule that is very difficult to activate, and methanol on the other is considerably reactive. As a recap, the CH_4 molecule consists of four C-H bonds in a symmetrical tetrahedral structure. The molecule has a low electron affinity (1.9 eV) and polarizability ($2.8 \times 10-40 \text{ C}^2\text{m}^2\text{J}^{-1}$). However, its ionization energy (12.6 eV) [5] is high, meaning that it requires 439 kJmol⁻¹ to break one of the C-H bonds. In contrast, CH_3OH is significantly more reactive and can be easily transformed into formaldehyde (HCHO) or formic acid (HCOOH) under mild conditions. Table 2 shows the standard electrode potential values, E^0 for CH_4 conversion to CH_3OH , and other possible products in aqueous solution [68].

| S/N | Reaction | E ⁰ (V) vs. NHE (pH = 0, T = 298 K) |
|-----|---|--|
| 1 | $CH_4(g) + H_2O(l) \rightarrow CH_3OH(a) + 2H^+(aq) + 2e^-$ | 0.58 |
| 2 | $CH_4(g) + H_2O(l) \rightarrow HCHO(a) + 4H^+(aq) + 4e^-$ | 0.48 |
| 3 | $CH_4(g) + 2H_2O(l) \rightarrow HCOOH(a) + 6H^+(aq) + 6e^-$ | 0.26 |
| 4 | $CH_4(g) + H_2O(l) \rightarrow CO(g) + 6H^+(aq) + 6e^-$ | 0.26 |
| 4 | $CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$ | 0.17 |

 Table 2. Some possible electrode reactions related to CH₄ conversion

It can be seen that the anodic potential for the CH₄ conversion to CH₃OH is 0.58 V (vs. a normal hydrogen electrode (NHE)), which is smaller than that of the oxygen evolution reaction (OER) of 1.229 V. This indicates that the interfering OER can be eliminated under reasonable electrolysis conditions. However, the E^0 values for CH₄ conversion to HCHO, HCOOH, CO, and CO₂ are smaller than 0.58 V and their generation at the anode will be favored over the generation of CH₃OH. This means that then direct electrochemical methane conversion to methanol will suffer from high energy barriers required to activate the methane molecule to enable its conversion, and also suffer from low methanol selectivity. Therefore, the first approach to direct electrochemical conversion of methane to methanol lies in the development of a suitable and highly selective electrocatalyst that can activate the methane molecule and enable its conversion.

Due to the above reasons, research in the direct electrochemical conversion of methane to methanol focuses on developing efficient catalysts to improve the selectivity of methanol with high Faradaic efficiency. The study conducted by Sun's group in 2020 used platinum wire as the cathode and porous hollow nickel-based fibers coated with a NiO active layer as the anode (NiO/Ni electrode) to drive the conversion of methane to methanol [78]. 54% Faradaic efficiency (FE) was obtained for methanol at an anodic potential of 1.44 V (vs. a reversible hydrogen electrode (RHE)), with a current density of 20 mA cm⁻². 85% FE of ethanol was also at an anodic potential of 1.46 V (vs. RHE) 40 mA cm⁻² current density. The catalytic effect of NiO/Ni on CH₄ activation was explained based on the peak current increment due to Ni^{II} \rightarrow Ni^{III} in the presence of CH₄ as observed in the linear sweep voltammetry (LSV) curves. They further explained based on the density functional theory (DFT) calculations that the chemisorbed CH₄ on the Ni(200)/Ni(111) interface has a high tendency to go through a C–C non-oxidative coupling process, resulting in the favorable production of ethanol over methanol.

Sarno et al. synthesized a NiO-V₂O₅/Rh catalyst with dispersed single atoms of Rh in the NiO-V₂O₅ phase and used it to convert methane to methanol at 50-200°C using Nafion membranes [70]. 650 μ mol g⁻¹ h⁻¹ CH₃OH was obtained at 91% faradaic efficiency and 97.9% product selectivity at 100 °C with a charging current of 100 mA. V₂O₅ oxygen activation capability, methane adsorption on Rh single atoms inclusions dispersed in the catalyst matrix, and NiO adjuvant action. Were responsible for the excellent performance of NiO–V₂O₅/Rh. Another study reported a methanol production rate of 752.9 μ mol g⁻¹ h⁻¹ with 77% product selectivity using CuO/CeO₂ mixed oxides as anodic catalysts and carbonate solution as the supporting electrolyte [71]. LaCo0.5Fe0.5O3 was also used in ionic liquid [BMIM]BF4 to directly convert methane to methanol [72]. The formation rate of methanol obtained was 39.3 µmol gcat⁻¹h⁻¹ with an FE of 92.4% when electrolyzed in the electrolyte content 0.5 molL⁻¹ water at an anodic potential of 0.8 V (vs. Ag/Ag+), and 93.2 µmol gcat⁻¹h⁻¹ with the FE of 54.8% at 2 mol L⁻¹ water content when the anodic potential was 1.0 V. Other catalysts such as ZrO_2/Co_3O_4 , TiO₂/RuO₂, NiO@NiHF, V₂O₅/SnO₂, Au–Pd/C, V₂O₅/TiO₂/RuO₂, and NiO/Ni with reasonable product selectivity and formation rate [73].

2.5. Conversion of methane to methanol using supercritical water technology

Methane conversion using supercritical water oxidation (SCWO) has been achieved and has been proven to be one of the most promising methods of direct methane to methanol conversion. The conversion of methane to methanol via supercritical water technologies involves the use of water as a solvent, oxidant, and catalyst to activate and oxidize methane to methanol in a single step. Supercritical water is water that is above its critical point of 374 °C and 22.1 MPa, where it exhibits unique properties such as high density, low viscosity, high diffusivity, and enhanced solvation.

Lee et al. reported the direct conversion of methane to methanol under isothermal conditions using SCWO in a laminar reactor [74]. 1–3% methane conversion and 35% highest methanol production was achieved at temperatures of 400–410 °C. Methane partial oxidation to methanol was also reported by Dixon et al. over Cr_2O_3 in SCWO with excellent conversion rate and good methanol selectivity [75]. When the concentration of the supercritical water (SCW) is high, it saturates the methanol and prevents it from further conversion to methane of other hydrocarbons. This increases the yield and selectivity of methanol. The presence of Cr_2O_3 increases the initial methane conversion rate and hence the overall efficiency of the SCWO technology. The performance of supercritical water technology however depends on the type of reactor and other factors [76].

3. CHALLENGES OF DIRECT CONVERSION OF METHANE TO METHANOL AND FUTURE PROSPECTS

Direct conversion of methane has shown to be a promising alternative method that could replace the energy-intensive syngas/FTS route for producing methanol. It offers several advantages in terms of economic and environmental suitability. However, this method has not been implemented industrially due to difficulties in scaling up to an industrial level. Different methods of directly converting methane to methanol have limitations and drawbacks. As mentioned earlier in each section, the common issue with all methods is the inability to achieve excellent methanol selectivity with a good methane conversion rate.

The strong C-H bond of methane requires high energy and selective catalysts for activation. Methanol, which is the target product, is more reactive at the conditions feasible for methane conversion and tends to oxidize further to other products. This makes it challenging to obtain both high methanol selectivity and excellent methane conversion rates simultaneously under ambient conditions comparable to the indirect syngas/FTS route. At high temperatures or reactive environments where methanol conversion becomes favorable, direct conversion of methane to methanol will continue to be inefficient.

Direct methane conversion to methanol methods such as low-temperature heterogeneous catalystmediated routes, plasma technology, SCWO technology, electrochemical method, and photocatalytic conversions have shown promising results in terms of methane conversion rates and methanol selectivity under ambient conditions. To advance research in this field, future efforts should focus on optimizing reactor design, and process control, and developing novel catalysts such as metal-containing zeolites - that can achieve high activity, selectivity, yield, and stability for the reaction. This will enhance the scalability and feasibility of the process for commercial use.

4. CONCLUSION

Direct conversion of methane to methanol has been examined for decades to replace the indirect energy-intensive syngas/FTS method. However, the method has not been used in the industry yet because of the issues with simultaneously obtaining high yield and selectivity of methanol and methane conversion rate. The indirect syngas/FTS method still works better than the direct method at the moment. Therefore, further research is needed in this area to enhance the scalability and feasibility of the process for industrial-level applications.

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