



# **Liquid-Phase Selective Oxidation of Methane to Methane Oxygenates**

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**Abstract:** Methane is an abundant and relatively clean fossil fuel resource; therefore, its utilization as a chemical feedstock has a major impact on the chemical industry. However, its inert nature makes direct conversion into value-added products difficult under mild conditions. Compared to the gas-phase selective oxidation of methane, there have been several recent advances in the liquid-phase conversion of methane. This review categorizes the reports on the liquid-phase selective oxidation of methane according to the solvent and oxidant used. The advantages and disadvantages of each approach are discussed. High yields of methyl bisulfate as a methanol precursor can be achieved using SO<sub>3</sub> in sulfuric acid; however, more attention should be paid to the separation process and overall economic analysis. However, the aqueous-phase selective oxidation of methane with in situ generated  $H_2O_2$  is quite promising from an environmental point of view, provided that an economical reducing agent can be used. Based on the current state-of-the-art on this topic, directions for future research are proposed.

**Keywords:** methane; liquid-phase oxidation; catalyst; methanol; methane oxygenates; formic acid; selective oxidation

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# 1. Introduction

Methane is abundant in nature and is the main component of natural gas, shale gas, coal bed methane, associated gases, biogas, and gas hydrates [1]. As these resources are relatively clean compared to other fossil resources, including oil and coal, methane is considered a promising feedstock for the chemical industry. However, because methane exists as a gas in nature, its utilization is limited as it must either be utilized on-site or transported to consumers in the form of liquefied or pipelined natural gas. In addition, many natural gas resources are not sufficiently large to be economically transported by conventional means; therefore, they are flared away or left unutilized [2].

Methane is primarily used as a fuel due to having the highest calorific value of combustion per carbon of any hydrocarbon and emitting less carbon dioxide from any fossil fuel while producing the same amount of heat. However, the demand for methane as a fuel is expected to decrease as renewable energy becomes more prevalent. It is more economical to convert methane into high-value chemicals than to use it as a fuel. However, its utilization as a chemical feedstock is limited because of its inertness in chemical reactions.

In general, methane activation is difficult because of its very high C-H bond dissociation energy (BDE) of 439 kJ/mol (Figure 1) [3,4]. Additionally, the target product (e.g., methanol) is more reactive than methane itself, as the C-H BDE of methanol is ~402 kJ/mol (Figure 1) [4]. Therefore, it is difficult to achieve high selectivity for the target product with a high methane conversion. Furthermore, when comparing the ionization potential, proton affinity, electron affinity, highest occupied molecular orbital, and water solubility (applicable to liquid-phase reactions), which are measures of reaction activity, methane is expected to have a lower reactivity than methanol (Figure 1) [4]. Accordingly, even if methane is activated and oxidized, over-oxidation or complete oxidation to  $CO_2$  of the reaction intermediate occurs easily, making it difficult to select a catalyst and set the reaction conditions for the partial oxidation of methane (POM) to achieve high yields of reaction intermediates. Consequently, the yield of the target product is low, making it costly to separate the product and recover the unreacted methane.



**Figure 1.** Various quantitative measures of the reactivity of methane, ethylene, and methanol [4]. Copyright 2017, American Chemical Society.

The current commercial routes for methane conversion rely on an indirect methane conversion pathway involving the initial synthesis of syngas, a mixture of H<sub>2</sub> and CO, through processes such as methane steam reforming (CH<sub>4</sub> + H<sub>2</sub>O  $\rightleftharpoons$  CO + 3H<sub>2</sub>,  $\Delta$ G<sup>0</sup><sub>298K</sub> = 142 kJ/mol,  $\Delta H_{298K}^0$  = 206 kJ/mol), methane autothermal reforming (CH<sub>4</sub> + 1/3O<sub>2</sub> + 1/3H<sub>2</sub>O  $\rightleftharpoons$  $CO + 7/3H_2$ ,  $\Delta G^{0}_{298K} = -10.5 \text{ kJ/mol}$ ,  $\Delta H^{0}_{298K} = 45 \text{ kJ/mol}$ ), or methane dry reforming  $(CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2, \Delta G^0_{298K} = 171 \text{ kJ/mol}, \Delta H^0_{298K} = 247 \text{ kJ/mol})$ . The syngas produced is further processed using well-established C1 chemical processes, including methanol synthesis [5] and Fischer–Tropsch synthesis [6], to produce various chemicals, including methanol, olefins, and synthetic fuels. Because this indirect methane conversion process includes an energy-intensive syngas synthesis step, it is only economically viable at a large scale [7]. It has several drawbacks, such as high production costs, significant energy consumption, and substantial capital investments. As a result, there has been growing interest in exploring direct methane conversion methods as alternatives to current indirect routes. The direct conversion of methane has the potential for more cost-effective and energy-efficient processes, making it an attractive option for producing value-added products from methane.

Direct methane conversion can be broadly categorized into gas- and liquid-phase pathways (Figure 2). The gas-phase routes encompass the POM (CH<sub>4</sub> + 1/2O<sub>2</sub>  $\rightarrow$  CH<sub>3</sub>OH,  $\Delta G^{0}_{298K} = -112 \text{ kJ/mol}, \Delta H^{0}_{298K} = -126 \text{ kJ/mol}$ ), selective halogenation (CH<sub>4</sub> + 1/2X<sub>2</sub>  $\rightarrow$  CH<sub>3</sub>X, X = Cl, Br, and I) with subsequent hydrolysis (CH<sub>3</sub>X + H<sub>2</sub>O  $\rightleftharpoons$  CH<sub>3</sub>OH + HX, X = Cl, Br, and I), oxidative coupling of methane (OCM) (CH<sub>4</sub> + 1/2O<sub>2</sub>  $\rightarrow$  1/2C<sub>2</sub>H<sub>4</sub> + H<sub>2</sub>O,  $\Delta G^{0}_{298K} = -144 \text{ kJ/mol}, \Delta H^{0}_{298K} = -141 \text{ kJ/mol})$ , dehydroaromatization (DHA) (CH<sub>4</sub>  $\rightarrow$  1/6C<sub>6</sub>H<sub>6</sub> + 3/2H<sub>2</sub>,  $\Delta G^{0}_{298K} = 72.1 \text{ kJ/mol}, \Delta H^{0}_{298K} = 89 \text{ kJ/mol})$ , and non-oxidative coupling of methane (NOCM) (CH<sub>4</sub>  $\rightarrow$  1/2C<sub>2</sub>H<sub>4</sub> + H<sub>2</sub>,  $\Delta G^{0}_{298K} = 84.7 \text{ kJ/mol}, \Delta H^{0}_{298K} = 101 \text{ kJ/mol})$ . In contrast, the liquid-phase reactions involve two representative routes: the direct oxidation of methane to methane oxygenates (e.g., methanol, formalde-

hyde, and formic acid) and methanol synthesis via a stable methanol precursor (e.g., methyl bisulfate (MBS) and methyl trifluoroacetate (MeTFA)) in strong acids (e.g., sulfuric acid ( $H_2SO_4$ ) and trifluoroacetic acid (HTFA)). The POM has a typical characteristic in which the selectivity to the value-added methane oxygenates decreases with increasing methane conversion [8,9]. However, recent noticeable progress has been made in the liquid-phase direct conversion of methane [9,10]. Therefore, this review focuses on liquid-phase selective oxidation of methane to methane oxygenates using various oxidants in different solvents.



**Figure 2.** Direct conversion of methane to various chemicals. The red and blue arrows mean endothermic and exothermic reactions, respectively.

#### 2. Liquid-Phase Partial Oxidation of Methane in Strong Acids

Over the last few decades, homogeneous organometallic catalysts have been investigated for the selective oxidation of methane in strong acids [4,10]. Because methane has a strong C-H bond, the choice of the central metal and ligand is important for the activation of methane. In addition, an appropriate choice of oxidizing agent is important to activate C-H bonds, oxidize low-valent central metals to high-valent ones, and avoid the overoxidation of methane oxygenates and ligand degradation. The use of strong acids (e.g., H<sub>2</sub>SO<sub>4</sub> and HTFA) is beneficial for stabilizing the reaction intermediates (MBS and MeTFA) because these methanol precursors are more resistant to electrophilic attack than the methanol itself.

The Shilov system can be introduced as a homogeneous organometallic catalyst for the selective functionalization of methane. The reaction follows the Shilov cycle (Figure 3), which is composed of three major steps: electrophilic activation of the C-H bond, oxidation of the complex, and nucleophilic oxidation of the alkane substrate [11]. Therefore, an alkane (RH) is selectively oxidized to an alcohol (ROH) or alcohol precursor (RCl) catalyzed by  $Pt^{II}Cl_2$  with an oxidant ( $[Pt^{IV}Cl_6]^{2-}$ ). Considerable research has been conducted to increase the productivity of methanol precursors and make the entire process more economical through changes in catalysts, oxidants, and solvents.



Figure 3. Shilov cycle for functionalization of C–H bond in alkanes [11].

# 2.1. HTFA

# 2.1.1. Potassium Persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>)

 $K_2S_2O_8$  is a radical initiator and strong oxidizing agent. It has been frequently used for methane oxidation in the presence of metal catalysts, and the reduced catalysts can be reoxidized with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Electrophilic transition-metal compounds have been reported for the C-H bond activation of alkanes, including methane, in HTFA [12]. In particular, the Pd(II) complex is an attractive choice because of its strong electrophilic properties and ease of reoxidation to Pd(II) ions using  $K_2S_2O_8$  as the oxidant (entry 1, Table 1). N-Heterocyclic carbene (NHC)-Pd complexes were examined for the POM using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (entry 2, Table 1) [13–15]. Despite the high activity of the catalysts with bromide ligands, the reaction of Pd-NHC with iodide ligands did not produce any product [13]. On the other hand, when Pd was substituted with Pt, which is already known as an active metal for the POM, decomposition of the Pt complex and aggregation to form Pt black were observed. PdCl<sub>4</sub><sup>2–</sup>-HTFA systems with large amine-based cations, such as tetramethylammonium ([Me<sub>4</sub>N]<sup>+</sup>), 1,2,3-trimethylimidazolium ([TMIm]<sup>+</sup>), and 1,1,3,3-tetramethylguanidine ([TMG]<sup>+</sup>), have also been used for the POM with  $K_2S_2O_8$  [16]. Among the various PdCl<sub>4</sub><sup>2-</sup> catalysts, [Me<sub>4</sub>N]<sub>2</sub>[PdCl<sub>4</sub>] showed the best catalytic activity. During the reaction (entry 3, Table 1),  $PdCl_4^{2-}$  is first converted to  $PdTFA_4^{2-}$ , which can activate the C-H bond in methane, and Pd(II) is oxidized to Pd(IV) with  $H_2S_2O_8$ . Finally, reductive elimination produces MeTFA (Figure 4). Generally, metals are easily leached, and most conventional supports degrade in HTFA, making it difficult to heterogenize homogeneous metal complexes for this reaction. Recently, Zhang et al. [17] immobilized Pd species in the porous organic polymer Pyr-POPs(pyridine-based porous organic polymers), which can predominantly capture methane, and reported high catalytic activity for this reaction (entry 4, Table 1).



**Figure 4.** Plausible reaction mechanism for methane oxidation using  $PdTFA_4^{2-}$  [16]. Adapted with permission. Copyright 2022, Elsevier.

In addition to Pd complexes, various transition metal salts (e.g., Ti, Fe, Cr, Mn, and Cu) have been tested for this reaction. Among these, Cu(OAc)<sub>2</sub> appeared to be the most effective catalyst for the production of MeTFA and methyl acetate from a mixture of HTFA and trifluoroacetic anhydride (TFAA) (**entry 5**, Table 1) [18]. A redox cycle between Cu(I) and Cu(II) and the participation of a methyl radical are proposed in the reaction mechanism (Figure 5).



**Figure 5.** Possible mechanism for the partial oxidation of methane catalyzed by Cu(II) cation [18]. The red and blue letters mean chemical species related to HTFA and  $K_2S_2O_8$ , respectively. Adapted with permission. Copyright 2000, Wiley.

Recently, a simple CuO catalyst was reported for the POM with  $K_2S_2O_8$  in HTFA/TFAA (entry 6, Table 1) [19]. The copper species dissolved in the solvent and generated KSO<sub>4</sub> radicals from  $K_2S_2O_8$ . This radical abstracts H from methane to form a methyl radical, which further reacts to produce MeTFA. Ultraviolet–visible spectra showed the reoxidation of reduced copper oxide (Cu<sub>2</sub>O) after the reaction with persulfate. Table 1 compares the activities of some active catalyst systems based on Pd and Cu complexes for POM with  $K_2S_2O_8$  in HTFA. Even though relatively high turnover frequencies (TOFs) can be obtained at low temperatures ( $\leq 100$  °C), there are some critical problems in this system.  $K_2S_2O_8$  is not regenerative and HTFA is decomposed in the presence of  $K_2S_2O_8$  [16].

Table 1. Comparison of catal	ytic systems for the p	partial oxidation of met	hane using K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> in HTFA.
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Entry	Catalyst	Temp. (°C)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (mmol)	Gas Composition (bar)	TON	TOF (h <sup>-1</sup> )	Ref.
1	Pd(CH <sub>3</sub> COO) <sub>2</sub>	80	21	$CH_4 = 20$	3.8	0.2	[13]
2	Pd-NHC *	90	21	$CH_{4} = 30$	30	2.1	[13]
3	[Me <sub>4</sub> N] <sub>2</sub> [PdCl <sub>4</sub> ]	80	10	$CH_{4} = 20$	330	22.0	[16]
4	Pyr-POPs-Pd *	80	20	$CH_{4} = 1$	664	33.2	[17]
5	Cu(CH <sub>3</sub> COO) <sub>2</sub>	100	5	$CH_4:N_2 = 5:25$	30.4	1.5	[18]
6	CuO	90	2.8	$CH_4 = 5.2$	33	1.9	[19]

\* NHC: N-doped heterocyclic carbene. Pyr-POPs: pyridine-based porous organic polymers.

# 2.1.2. Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>)

Hydrogen peroxide ( $H_2O_2$ ) is an environmentally friendly oxidant because it emits only water after oxidation. The conventional commercial process for  $H_2O_2$  synthesis is based on the use of anthraquinone (AQ) [20]. Recently, the synthesis of  $H_2O_2$  directly from  $H_2$  and dioxygen ( $O_2$ ) has been actively investigated [21–24]; however, it is not yet competitive.

 $H_2O_2$  was used instead of  $K_2S_2O_8$  for the POM in a Pd/TFA catalytic system with excess TFAA to remove the  $H_2O$  formed from  $H_2O_2$  [18,19,25–28]. In the absence of TFAA, MeTFA was further hydrolyzed to  $CH_3OH$ , which was readily oxidized to  $CO_2$ .  $H_2O_2$ can be added directly to the reaction medium or synthesized in situ from  $H_2$  and  $O_2$ . Lin et al. [29] used a  $CO/O_2/H_2O$  system instead of an  $H_2/O_2$  system to synthesize  $H_2O_2$ in situ at relatively high temperatures (70–100 °C) to oxidize methane to MeTFA (entry 1, Table 2). In the  $CO/O_2/H_2O$  system, the water–gas shift reaction ( $CO + H_2O \rightleftharpoons CO_2 + H_2$ ) occurs over Pd/C, and  $H_2$  and  $O_2$  can be combined to produce  $H_2O_2$  over Pd/C. The addition of CuCl<sub>2</sub> to the  $CO/O_2/H_2O$  system resulted in the formation of methanol and its derivative (MeTFA) as the main products [29]. The presence of Cl<sup>-</sup> ion is essential for the conversion of methane to methanol and its ester. The yield of MeTFA was affected by the halide ions and decreased in the order  $Cl^- > Br^- > I^-$ . The POM was further examined over Pd/C with various metal ions (Cu, V, etc.) in the CO/O<sub>2</sub>/H<sub>2</sub>O system (**entries 2–5**, Table 2) [27,28,30]. It was found that the nature of the co-catalyst (mainly Cu and V species), the presence of Cl<sup>-</sup>, and the composition of the solvent significantly impacted the structure of Pd species and consequently influenced the yield of MeTFA.

**Table 2.** Comparison of catalytic systems for the partial oxidation of methane using  $H_2O_2$  and  $H_2O_2$  generated in situ from a  $CO/O_2/H_2O$  or an  $H_2/O_2$  system in HTFA/TFAA.

Entry	Catalyst	Temp. (°C)	H <sub>2</sub> O <sub>2</sub> (mmol)	Gas Composition (bar)	Solvent Composition (vol.%)	TON	TOF (h <sup>-1</sup> )	Ref.
1	$CuCl_2 + Pd/C$	90	-	CH <sub>4</sub> :O <sub>2</sub> :CO = 61:6.8:13.6	$HTFA:H_2O = 75:25$	30	0.33	[29]
2	H <sub>4</sub> PVMo <sub>11</sub> O <sub>40</sub>	80	10	$CH_4 = 50$	TFAA = 100	260	10.8	[31]
3	5%Pd/C + Cu(OAc) <sub>2</sub>	80	-	CH <sub>4</sub> :O <sub>2</sub> :H <sub>2</sub> = 34:6.8:6.8	HTFA/TFAA = 80:20	20	4	[28]
4	5%Pd/C + NH4VO3	80	-	CH <sub>4</sub> :O <sub>2</sub> :H <sub>2</sub> = 34:6.8:6.8	HTFA/TFAA = 80:20	3.7	0.7	[28]
5	Cu(OAc) <sub>2</sub>	80	10	CH <sub>4</sub> :N <sub>2</sub> = 34:13.6	TFAA = 100	1.0	0.5	[28]

TFAA must be used in conjunction with TFA when using  $H_2O_2$  directly or when generated in situ. Otherwise, the produced MeTFA hydrolyzes to methanol, which can easily be further oxidized to HCOOH and CO<sub>2</sub>, resulting in lower yields of methanol and its derivatives. Therefore, an additional unit for the synthesis of TFAA from TFA via dehydration was required for the synthesis of methanol from methane using  $H_2O_2$  as an oxidant.

# 2.1.3. O<sub>2</sub>

 $O_2$  is an ideal oxidant for selective oxidation of hydrocarbons. However, the POM with  $O_2$  is a spin-forbidden reaction because methane and  $O_2$  exist in the singlet and triplet states, respectively. Therefore, this reaction is generally performed at relatively high temperatures, even in the presence of a catalyst.

The POM using  $O_2$  was examined in the presence of various metal-trifluoroacetate salts, including Pd, Mn, Fe, Co, Cu, and Pb, in HTFA at 180 °C [32]. Mn and Co salts showed 30 and 90% yields of MeTFA based on the amount of catalyst added, respectively. Furthermore, a 50% yield of MeTFA based on the amount of methane introduced was obtained at 180 °C in the presence of Co salts using  $O_2$  as an oxidant in TFA/TFAA solution [33].

Recently, Blankenship et al. [34] demonstrated the conversion of aerobic methane to methyl esters in the presence of dilute TFA in perfluorohexane over a  $Co/SiO_2$  catalyst. Among the catalytic systems using  $O_2$  as the sole oxidant, this catalyst exhibited the highest MeTFA productivity, and the spent catalyst could be easily reactivated by heat treatment. The catalytic activity of supported Mn catalysts was recently reported by the same group [35]. The higher methyl ester productivity (c.a. 1000  $\mu$ mol/g<sub>cat.</sub>/h) than  $Co/SiO_2$  has been reported for supported Mn catalysts. However, the leaching of the active metal from the catalyst surface and deactivation of the catalyst to MnF<sub>2</sub> have also been reported.

There have only been a few reports on the aerobic oxidation of methane in HTFA; however, all reactions require relatively high temperatures, resulting in the decomposition of HTFA. The problem of corrosion caused by HTFA cannot be overlooked from a practical perspective and raises concerns from an economic perspective.

## 2.2. $H_2SO_4$

Oleum, also known as fuming  $H_2SO_4$ , has sulfur trioxide (SO<sub>3</sub>) in  $H_2SO_4$ . SO<sub>3</sub> is commercially produced through the oxidation of SO<sub>2</sub> with O<sub>2</sub> and can be hydrolyzed to

 $H_2SO_4$ .  $SO_3$  can act as an oxidizing agent for POM [36] during the conversion to  $SO_2$ , which can then be converted back to  $SO_3$  via an oxidation reaction with  $O_2$ . Throughout the entire process, oxygen was indirectly utilized for the POM with  $SO_3$ . MBS was produced as a methanol precursor during the POM with  $SO_3$  in  $H_2SO_4$  (Figure 6a). This MBS was more stable against further oxidation than methanol, similar to MeTFA in the HTFA system.



**Figure 6.** (a) Overall scheme for methanol synthesis via MBS. The blue and pink letters mean chemical species related to methane and HSO<sub>4</sub>, respectively. (b) Proposed reaction mechanism for the oxidation of methane over Pt complex [36]. Adapted with permission. Copyright 1998, American Association for the Advancement of Science.

Periana et al. [37] reported a high yield (43%) of MBS during the POM using Hg(II) triflate in triflic acid and H<sub>2</sub>SO<sub>4</sub> at 180 °C (entry 1, Table 3). They also observed that thallium (Tl) and gold (Au) salts converted methane to MBS but their reduced forms could not be reoxidized with SO<sub>3</sub>. In a subsequent study, they reported high yields ( $\geq$ 70%) of MBS based on the moles of methane over Pt<sup>II</sup>(bpym)Cl<sub>2</sub> (bpym = 2,2'-bipyrimidinyl) using SO<sub>3</sub> as an oxidant in the oleum system [36] (Figure 6b). They claimed that the key role of the ligand was to prevent the aggregation and reduction of the active Pt species to inactive Pt(0).

Table 3. Comparison of catalytic systems for the partial oxidation of methane using SO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub>.

Entry	Catalyst	Temp. (°C)	SO <sub>3</sub> (mmol)	P <sub>CH4</sub> (bar)	TON <sup>c</sup>	TOF (h <sup>-1</sup> )	Ref.
1	HgSO <sub>4</sub>	180	-	34.5	10.8	3.6	[37]
2	$K_2$ PtCl <sub>4</sub>	215	70	72	n.d.	22,998	[38]
3	(DMSO) <sub>2</sub> PtCl <sub>2</sub> <sup>a</sup>	180	75	35	19,125	6375	[39]
4	Pt black	180	75	35	1982	661	[40]
5	K <sub>2</sub> [PtCl <sub>4</sub> ]-CTF <sup>b</sup>	215	103	40	201	80.4	[41]
6	Pt-CTF <sup>b</sup>	215	103	40	246	98.4	[41]

<sup>a</sup> DMSO: dimethyl sulfoxide. <sup>b</sup> CTF: covalent triazine-based framework; <sup>c</sup> TON(turnover number) = [moles of MBS produced]/[moles of catalyst introduced].

Zimmermann et al. [38,42] compared the catalytic activity for the POM over (bpym)PtCl<sub>2</sub>, PtCl<sub>2</sub>, Pt(acac)<sub>2</sub>, and K<sub>2</sub>PtCl<sub>4</sub> and found that simple platinum salts were stable, selective, and unprecedently active for the POM in oleum. The extremely high TOF exceeding 20,000 h<sup>-1</sup> was obtained with low concentrations of the catalyst (**entry 2**, Table 3) [38]. It was also proven that when the concentration of the catalysts was sufficiently high, higher MBS formation rates were achieved with (bpym)PtCl<sub>2</sub>, indicating that catalyst solubility is a key factor in this catalytic system. To enhance the stability of chloride-ligated Pt catalysts, Dang et al. [39] introduced the DMSO (dimethyl sulfoxide) ligand to the Pt catalysts and

obtained an 84% yield of MBS at 180 °C (entry 3, Table 3). (DMSO)<sub>2</sub>PtCl<sub>2</sub> was deactivated to PtCl<sub>2</sub> although it could be reactivated by adding excess DMSO. They also investigated the POM over Pt black in the presence of 20 wt.% oleum at 180 °C and found that the dissolved Pt was active but the decomposition of MBS to CO<sub>2</sub> occurred on Pt(0) (entry 4, Table 3) [40] (Figure 7).



**Figure 7.** Proposed mechanism of Pt black catalyzed methane oxidation to methyl bisulfate (MBS) [40]. Adapted with permission. Copyright 2019, Elsevier.

Compared with homogeneous catalysts, heterogenized homogeneous or heterogeneous catalysts have practical advantages [43]. They can be easily separated from the reaction medium to decrease separation costs. However, it is difficult to develop stable and highly active POM catalysts for the highly corrosive and oxidizing oleum. Palkovits et al. [41,44] and Soorholtz et al. [41,44] synthesized a covalent triazine-based framework (CTF) containing multiple bipyridyl structural units utilizing 2,6-dicyanopyridine as a monomer and succeeded in providing coordination sites similar to the platinum coordination sites found in (bpym)PtCl<sub>2</sub> (entries 5 and 6, Table 3).

The separation of MBS from  $H_2SO_4$  requires distillation at high temperatures or depressurization up to 100 mbar, which in turn decomposes the MBS to  $SO_3$ , dimethyl ether, and dimethyl sulfate [40]. In the case of the direct hydrolysis of MBS in  $H_2SO_4$ , the addition of water wastes a large amount of diluted  $H_2SO_4$ . According to Ahlquist et al. [3], the methanol concentration cannot be higher than 10 µM in  $H_2SO_4$  as methanol undergoes additional oxidation. Accordingly, the MBS produced should be separated from  $H_2SO_4$ before it is converted to methanol [45]. Im et al. [46] proposed a modified reactive distillation process in which HTFA was used as a mediator to form MeTFA and  $H_2SO_4$  from MBS to facilitate the separation of methanol from a mixture of MBS and  $H_2SO_4$  (Figure 8).



**Figure 8.** Reaction scheme for the direct synthesis of methanol from methane with SO<sub>3</sub> using HTFA as a mediator in the separation. The blue letters mean chemical species related to methane [46].

#### 3. Liquid-Phase Partial Oxidation of Methane in Water

From an environmental perspective, water is an ideal solvent for organic synthesis. Moreover, the use of  $O_2$  as an oxidant for the partial oxidation of substrates in water is more desirable than the direct use of  $H_2O_2$  as an oxidant. Therefore, the direct oxidation of methane to methanol using  $O_2$  is called the chemist's dream reaction. In nature, methanotrophic bacteria, using enzymes called methane monooxygenases (MMOs), can directly and selectively convert methane to methanol using  $O_2$  under mild conditions. MMOs utilize two reducing equivalents to split the O-O bonds of  $O_2$  [47].

$$CH_4 + O_2 + 2H^+ + 2e^- \rightarrow CH_3OH + H_2O$$

There are two types of MMOs: particulate MMO (pMMO) and soluble MMO (sMMO). While most methanotrophs rely solely on pMMO for methane oxidation, a few express sMMO under Cu-starved conditions [48]. sMMO consists of three main components: the hydroxylase component, MMOH, with non-heme diiron active sites; the reductase, MMOR, which reduces the diiron site using the nicotinamide adenine dinucleotide cofactor; and the regulatory protein, MMOB. The active site of sMMO, termed compound Q, contains a dinuclear Fe<sup>IV</sup> cluster (Figure 9) [49]. The reaction mechanism of MMO in Figure 9 was proposed by Lippard et al. [50]. Electron transfer to the iron species initiates the diiron center to activate  $O_2$  and hydrocarbon hydroxylase.



**Figure 9.** Catalytic cycle of sMMO. R<sub>red</sub>: reduced, R<sub>OX</sub>: oxidized reductase MMOR, respectively, P\*: intermediate before H<sub>peroxo</sub>, and B: the regulatory component MMOB [50]. Copyright 2015, American Chemical Society.

On the contrary, the membrane-bound, copper-dependent pMMO enzyme consists of three subunits encoded by PmoA ( $\alpha$ ), PmoB ( $\beta$ ), and PmoC ( $\gamma$ ) to form an  $\alpha\beta\gamma$  protomer [51]. The crystal structures of pMMO from multiple methanotrophic species revealed the presence of three Cu-binding sites: bis-His, CuB, and CuC [52]. Computational studies have suggested that both dinuclear and mononuclear copper sites located at this specific location can catalyze methane oxidation [53–55]. Therefore, Fe-based and Cu-based heterogeneous catalyst systems have been actively investigated for the POM in liquid and gas phases.

# $3.1. H_2O_2$

# 3.1.1. Fe-Zeolite

Inspired by sMMO, Fe zeolites have been investigated for the POM with  $H_2O_2$  in water. Rahman et al. [56] reported the synthesis of methane oxygenates (mainly formic acid) over H-ZSM-5 using  $H_2O_2$  at 100 °C (entry 1, Table 4). Soon after, Hammond et al. [57] reported that very small amounts of Fe species incorporated unintentionally into the zeolite framework were responsible for this reaction (entry 2, Table 4). Regarding the active Fe species, their research group observed that hydrothermally prepared Fe-silicalite-1 with an MFI structure possessed catalytic activity for the POM after heat treatment (entry 3, Table 4) and that the migration of Fe species from isolated framework sites to isolated or oligonuclear extra-framework sites occurred after calcination of the catalysts at high temperatures [58–60]. They proposed a dihydroxodiiron center as the active Fe species [61–65]. A good correlation was also reported between the catalytic activity of Fe/ZSM-5 and the peak intensity of the band (corresponding to the extra-framework Fe<sup>2+</sup> species) at ~1880 cm<sup>-1</sup> in the Fourier-transform infrared spectrum after NO adsorption [66,67].

In contrast, Zhu et al. [68] suggested the presence of a single Fe active site for the Fe/ZSM-5 catalyst (**entry 4**, Table 4). They observed only atomically dispersed Fe species in 0.03% Fe/ZSM-5 using high-angle annular dark-field scanning transmission electron microscopy (HAADF-TEM) images and claimed that mono- and diiron species were active species. Theoretical calculations of the reaction mechanism over mono- and binuclear Fe-O species showed that both iron species are possible active centers for the C-H bond dissociation of methane, with a moderate energy barrier. Oda et al. [69] also proposed mono-iron species with four coordination numbers of Fe-O as the active Fe species based on an extended X-ray absorption fine structure (EXAFS) study (**entry 5**, Table 4). Furthermore, Yu et al. [70] also suggested the monomeric Fe complex [(OH)<sub>2</sub>-Fe<sup>III</sup>-(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>. The single Fe = O species can activate the C-H bond of methane, and the activated CH<sub>3</sub>• radical reacts with OH• radicals to produce methanol (Figure 10). Al-Shihri et al. [71] proposed another reaction mechanism. They reported the formation of diols (hydrated HCHO) and polyoxomethylene along with CH<sub>3</sub>OOH, CH<sub>3</sub>OH, and HCOOH over H-ZSM-5 (**entry 6**, Table 4). They also reported H<sub>2</sub> formation owing to the oxidation of HCHO to HCOOH [72].

The substitution of Si<sup>4+</sup> with Al<sup>3+</sup> or Ga<sup>3+</sup> in MFI zeolites (ZSM-5 and silicalite-1) increased the number of cation exchange sites, resulting in higher POM activity over the [Fe,Al]- and [Fe,Ga]-MFI catalysts than over [Fe]-MFI [73]. Shahami and Shantz also reported that the MFI zeolite with Ga<sup>3+</sup> in the framework showed higher reaction activity than those with Al<sup>3+</sup> and B<sup>3+</sup> (**entries 7 and 8**, Table 4) [74]. They observed that MFI catalysts with Al<sup>3+</sup> and Ga<sup>3+</sup> possessed a higher acid density than those with B<sup>3+</sup> and that the catalyst with lower acidity showed much lower oxygenate productivity. Furthermore, when H<sup>+</sup> ions in the MFI catalysts were replaced with Na<sup>+</sup> ions, the catalytic activity significantly decreased. This means the Brønsted acid sites are essential for the methane oxidation reaction.

In addition to MFI zeolites, other zeolites have been examined for this reaction. Kalamaras et al. [75] compared the catalytic activities of Fe/zeolites (MFI, BEA, and FAU) and found that Fe/ZSM-5 was the best (**entry 9**, Table 4). Fang et al. [76] prepared various catalysts, including supported Fe catalysts on MOR,  $Al_2O_3$ , SBA-15, and  $SiO_2$ , and found that MOR showed the best catalytic performance for POM (**entry 10**, Table 4).

The inertness and low solubility of methane result in low methane conversion in aqueous-phase reactions. Xiao [77] found that the utilization of sulfolane, a very stable aprotic polar solvent, could enhance the catalytic activity of POM. When sulfolane was used as an admixture in the reaction media, the yield of methane oxygenates increased significantly (entries 11 and 12, Table 4).



**Figure 10.** Proposed reaction scheme of the reaction pathway for direct methane oxidation to methanol over Cu - Fe(2/0.1)/ZSM-5 using  $H_2O_2$  as the oxidant. Red, purple, gray, and white balls represent O, Fe, C, and H atoms, respectively [70]. Adapted with permission. Copyright 2021, American Chemical Society.

Table 4. Comparison of catalytic systems for the partial oxidation of methane over Fe-zeolites using  $H_2O_2$  in water.

Entry	Catalyst	Temp. (°C)	H <sub>2</sub> O <sub>2</sub> (mmol)	CH <sub>4</sub> (bar)	Total Productivity (mmol/g <sub>cat.</sub> /h)	Product Selectivity (%)	Ref.
						CH <sub>3</sub> OH: 0.1	
1	H-ZSM-5	100	122	26	2.3	HCOOH: 55	[56]
						CO <sub>2</sub> : 45	
			_			CH <sub>3</sub> OH: 10	r1
2	2.5%Fe/ZSM-5	50	5	30.5	16.8	HCOOH: 72	[57]
						CO <sub>2</sub> : 17	
_			_			CH <sub>3</sub> OH: 19	
3	Fe-silicalite-1	50	5	30.5	9.5	HCOOH: 67	[62]
						CO <sub>2</sub> : 9	
						CH <sub>3</sub> OH: 1	
4	0.03%Fe/ZSM-5(66)	80	5	30	54.1	HCOOH: 84	[68]
						CO <sub>2</sub> : 5	
						CH <sub>3</sub> OH: 2	
5	0.45%Fe-ZSM-5	50	5	30	45.2	HCOOH: 92	[69]
						$CO_2: 0$	
						CH3OH: 11	
6	ZSM-5(30)	50	5	10	26.7	HCOOH: 54	[71]
						CO <sub>2</sub> : 1	
						CH <sub>3</sub> OH: 5	
7	Ga,Fe-MFI(50)	55	5	30	51.2	HCOOH: 90	[74]
						CO <sub>2</sub> : 3	

Entry	Catalyst	Temp. (°C)	H <sub>2</sub> O <sub>2</sub> (mmol)	CH <sub>4</sub> (bar)	Total Productivity (mmol/g <sub>cat.</sub> /h)	Product Selectivity (%)	Ref.
8	Al,Fe-MFI(50)	55	5	30	44.0	CH <sub>3</sub> OH: 5 HCOOH: 87 CO <sub>2</sub> : 7	[74]
9	Fe/ZSM-5	50	5	30.5	3.5	- - -	[75]
10 <sup>b</sup>	Fe-MOR	80	10	28.5	8.9	CH <sub>3</sub> OH: 17 HCOOH: 37 CO <sub>2</sub> : 9 CH <sub>2</sub> OH: 84	[76]
11 <sup>a,b</sup>	Fe-MFI	50	27	30	11.3	HCOOH: 11 CO <sub>2</sub> : 0	[77]
12 <sup>b</sup>	Fe-MFI	50	27	30	13.1	CH <sub>3</sub> OH: 1 HCOOH: 35 CO <sub>2</sub> : 63	[77]

Table 4. Cont.

 $^{\rm a}$  The mixture of sulfolane and  $\rm H_2O$  (50:50) was used as the reaction medium.  $^{\rm b}$  The data were inferred from the figure.

# 3.1.2. Promoted Fe-Zeolites

Various promoters have been applied to Fe-zeolites to increase methane conversion and methanol selectivity. Among these, copper is the most frequently reported promoter. Hutchings et al. [57] reported an increase in methanol selectivity as formic acid selectivity decreased with the addition of copper species to Fe-ZSM-5 without any change in methane conversion (**entry 1**, Table 5). Yu et al. [70] observed that the OH radical signal was enhanced by adding Cu to Fe/ZSM-5 based on electron paramagnetic resonance (EPR) radical trapping studies, implying that Cu species facilitated the production of OH radicals from H<sub>2</sub>O<sub>2</sub>. However, there have been a few reports on the contrary. Al-Shihri et al. [72] reported that as the amount of Cu introduced increased from 0 to 2  $\mu$ mol, the amount of total product decreased from 464 to 5  $\mu$ mol. They claimed that the addition of Cu to the reaction liquid accelerated the decomposition of HCOOH to CO<sub>2</sub> and H<sub>2</sub> as well as the decomposition of H<sub>2</sub>O<sub>2</sub>. Leaching of Cu species from Cu-Fe/ZSM-5 was observed during this reaction, which increased the H<sub>2</sub>O<sub>2</sub> decomposition and CO<sub>2</sub> selectivity [78].

**Table 5.** Comparison of catalytic systems for the partial oxidation of methane over promoted Fezeolites using  $H_2O_2$  in water.

Entry	Catalyst	Temp. (°C)	H <sub>2</sub> O <sub>2</sub> (mmol)	CH4 (bar)	Total Productivity (mmol/g <sub>cat.</sub> /h)	Product Selectivity (%)	Ref.
1	2.5%Cu-2.5%Fe/ZSM-5	50	5	30.5	16.5	CH <sub>3</sub> OH: 85 HCOOH: 0 CO <sub>2</sub> : 15	[57]
2	0.5%LaFe-ZSM-5(H <sub>2</sub> )	50	5	30.5	59.5	CH <sub>3</sub> OH: 6 HCOOH: 90 CO <sub>2</sub> : 4	[79]
3	0.5%LaFeCu-ZSM-5(H <sub>2</sub> )	50	5	30.5	12.6	CH <sub>3</sub> OH: 85 HCOOH: 0 CO <sub>2</sub> : 15	[79]
4	0.5%LaFeCu-ZSM-5(Air)	50	5	30.5	4.6	CH <sub>3</sub> OH: 51 HCOOH: 43 CO <sub>2</sub> : 2	[79]
5	0.1%Ir0.6%Fe/ZSM-5	50	5	28.5	3.5	CH <sub>3</sub> OH: 16 HCOOH: 71 CO <sub>2</sub> : 8	[80]

Entry	Catalyst	Temp. (°C)	H <sub>2</sub> O <sub>2</sub> (mmol)	CH4 (bar)	Total Productivity (mmol/g <sub>cat.</sub> /h)	Product Selectivity (%)	Ref.
6	0.7%Fe/ZSM-5	50	5	28.5	1.0	CH <sub>3</sub> OH: 17 HCOOH: 54 CO <sub>2</sub> : 4	[80]
7	0.01%Pd/ZSM-5	50	5	30	8.0	CH <sub>3</sub> OH: 7 HCOOH: 54 CO <sub>2</sub> : 14	[81]

Table 5. Cont.

The introduction of La to H-ZSM-5 and CuFe/ZSM-5 catalysts was reported to lower the strong Brønsted acid sites, resulting in the reduction of  $H_2O_2$  decomposition and an increase in the  $H_2O_2$  utilization efficiency (entry 2, Table 5) [79]. The reductive pretreatment with 5%  $H_2$ /Ar was more beneficial for the catalytic activity than that with air because of the higher fraction of extra-framework Fe species (entries 3 and 4, Table 5).

The promotional effect of Ir on Ir-Fe/ZSM-5 was also observed in terms of methane oxygenation productivity and  $H_2O_2$  efficiency (entries 5 and 6, Table 5) [80]. This was ascribed to the formation of an Ir-O-Fe complex, which induced increased radical production from  $H_2O_2$  decomposition.

Huang et al. [81] reported the unique catalytic performance of singly dispersed Pd/ZSM-5 catalysts (entry 7, Table 5). The  $Pd_1O_4$  structure in 0.04 wt.% Pd/ZSM-5 was confirmed by an extended EXAFS study. Increasing the Pd content in the Pd/ZSM-5 catalysts did not significantly improve the production of methane oxygenates (entry 7, Table 5). This lack of enhancement can be attributed to the aggregation of Pd particles in the catalyst structure. However, there has been no discussion on Fe impurities, which have been previously reported as active sites for selective methane oxidation.

#### 3.1.3. Metal–Organic Framework (MOF)-Based Catalysts

Metal–organic frameworks (MOFs) have recently been utilized for the POM [82]. Szécsényi et al. [83] reported MOF-mediated POM using  $H_2O_2$  as an oxidant. The Mössbauer spectra and EXAFS studies showed that MIL-53 facilitates the formation of catalytically active Fe species in diiron complexes. MIL-53 (Al,Fe) catalysts showed high methane oxidation activity with TOFs of 90 h<sup>-1</sup> and a methane oxygenate selectivity of ca. 80% (entry 1, Table 6). After further characterization of the catalysts and DFT calculations, they concluded that the isolated Fe sites in the MOFs catalyzed the direct conversion of methane to methanol.

**Table 6.** Comparison of catalytic systems for the partial oxidation of methane over MOF-based catalyst using  $H_2O_2$  in water.

Entry	Catalyst	Temp. (°C)	H <sub>2</sub> O <sub>2</sub> (mmol)	Feed Composition (bar)	Total Productivity (mmol/g <sub>cat.</sub> /h)	Product Selectivity (%) <sup>a</sup>	Ref.
1 <sup>b</sup>	MIL-53(Al,Fe)	40-60	5	CH <sub>4</sub> = 30.5	7.8	CH <sub>3</sub> OH: 44 HCOOH: 21 CO <sub>2</sub> :36	[82]
2	UiO-66(2.5TFA)-Fe	50	3	CH <sub>4</sub> = 30	4.9	CH <sub>3</sub> OH: 13 HCOOH: 63 CO <sub>2</sub> : 2	[84]
3	Cu-ZIF-7	50	5	CH <sub>4</sub> = 28.5	1.1	CH <sub>3</sub> OH: 22 HCOOH: 0 CO <sub>2</sub> : 71	[85]

	1	able 6. Cont.					
Entry	Catalyst	Temp. (°C)	H <sub>2</sub> O <sub>2</sub> (mmol)	Feed Composition (bar)	Total Productivity (mmol/g <sub>cat.</sub> /h)	Product Selectivity (%) <sup>a</sup>	Ref.
4	CuCZ8-20	40	10	CH <sub>4</sub> = 30	0.5	CH <sub>3</sub> OH: 41 HCOOH: 0 CO <sub>2</sub> : 49	[86]
5	CuNC-600	50	5	$CH_4 = 30$	4.0	CH <sub>3</sub> OH: 80 HCOOH: 0 CO <sub>2</sub> : 11	[87]

Table 6. Cont.

<sup>a</sup> CH<sub>3</sub>OH selectivity = (sum of concentrations of CH<sub>3</sub>OH and CH<sub>3</sub>OOH)/(sum of concentrations of total products)  $\times$  100. <sup>b</sup> The data were inferred from the figure.

Fe-O clusters anchored on the Zr<sub>6</sub> nodes of UiO-66 and modulated with acetic acid (AA) or HTFA have also been investigated [84]. Among these non-modulated, AA-modulated, and HTFA-modulated Fe-UiO-66 catalysts, one catalyst with HTFA showed the highest methane oxygenates productivity of 4799  $\mu$ mol/g<sub>cat.</sub>/h (only 105  $\mu$ mol/g<sub>cat.</sub>/h of CO<sub>2</sub> was obtained) (**entry 2**, Table 6). An EPR study showed that the addition of Fe-UiO-66(TFA) gave rise to •OH radical signals in the presence of H<sub>2</sub>O<sub>2</sub>. Theoretical calculations indicated that the introduction of HTFA to the Fe-UiO-66 catalysts lowered the energy for H<sub>2</sub>O<sub>2</sub> activation compared to the higher activation energy for Fe-UiO-66 without HTFA.

Recently, regarding copper-doped zeolitic imidazolate framework-7 (Cu/ZIF-7), it was reported that the mononuclear cupric ion (Cu<sup>2+</sup>) coordinated to four nitrogen ligands (CuN<sub>4</sub>) displayed catalytic activity for methane oxidation to methanol, methyl hydroperoxide, and hydroxymethyl hydroperoxide, and formic acid using H<sub>2</sub>O<sub>2</sub> (entry 3, Table 6) [85]. The facile synthesis of multiple mononuclear CuN<sub>4</sub> active centers is highly appealing because of its simplicity and clear preparation process. However, it is imperative to address the ongoing challenge of oxidative degradation of benzimidazole to further enhance its application. The same research group reported a single-atom Cu catalyst with a Cu<sub>1</sub>N<sub>4</sub> structure on N-doped carbon prepared by the carbonization of Cu/ZIF-8 (entry 4, Table 6) and a Cu<sub>1</sub>N<sub>3</sub> structure on N-doped carbon (entry 5, Table 6) prepared by the carbonization of a polymeric copper–dibenzimidazole complex [86,87].

# 3.1.4. Other Catalysts

Hutchings et al. [88] observed that Au-Pd nanoparticles supported on  $TiO_2$  showed catalytic activity in the POM using  $H_2O_2$  (entry 1, Table 7). From the EPR study, it was concluded that the reaction was catalyzed over the Au-Pd catalyst via radical pathways, generating CH<sub>3</sub> radicals from methane. The catalytic activity of the Au-Pd nanoparticle catalysts without any support was further investigated (entry 2, Table 7) [89]. The moles of the total product reached 16.8 µmol after 30 min of the reaction at 50 °C with a methane oxygenates selectivity of 90% for the Au-Pd colloid, which surpassed that of Au-Pd/TiO<sub>2</sub> (1.6  $\mu$ mol, 26%). Upon the addition of 5 bar of O<sub>2</sub> as an additional oxidant, the product yield further increased to 28.3 μmol while maintaining a high selectivity of 88%. Notably, using only 50  $\mu$ mol of H<sub>2</sub>O<sub>2</sub> and 5 bar of O<sub>2</sub> as the oxidant, the Au-Pd colloid still achieved a substantial total product yield of 20 µmol with an oxygenates selectivity of 92%. Furthermore, experiments employing isotopically labeled oxygen  $(O_2)$  as the oxidant in the presence of  $H_2O_2$  demonstrated that a significant fraction (70%) of the resulting CH<sub>3</sub>OH originated from the gas-phase  $O_2$  (Figure 11). The effect of additional  $O_2$  as an oxidant was also demonstrated by Xu et al. [90] in their isotopically labeled  $O_2$  experimental study on the partial oxidation of methane using  $H_2O_2$  over a Au-Pd@ZIF-8 catalyst (entry 3, Table 7).



**Figure 11.** Proposed reaction scheme for methane oxidation in the presence of  $H_2O_2$  and molecular  $O_2$ . The red letters mean oxygen related to <sup>16</sup>O [89]. Adapted with permission. Copyright 2017, American Association for the Advancement of Science.

After optimization of the Au-Pd catalytic system, the methane oxidation reaction exhibited an impressive productivity value of 74.4 mmol/g<sub>cat.</sub>/h [91]. This signifies the remarkable intrinsic activity of the unsupported Au-Pd nanoparticles specifically for this reaction. Furthermore, this productivity value significantly surpasses those of methane monooxygenase (MMO) and Fe-Cu/ZSM-5 catalysts, which demonstrate productivities of 5.1 mmol/g<sub>cat.</sub>/h [92] and 16.5 mmol/g<sub>cat.</sub>/h [57,61], respectively (**entry 2**, Table 7).

Yan et al. [93] investigated the effect of pH on the  $H_2O_2$  efficiency of the POM over an AuPd colloid. They conducted the reaction in a pH range of 1–8 and found that not only the amount of primary oxygenates, such as CH<sub>3</sub>OH and CH<sub>3</sub>OOH, but also the efficiency of  $H_2O_2$  (defined as [moles of  $H_2O_2$  consumed]/[moles of total product]) were the highest at pH 3 (entry 3, Table 7).

Bao et al. [94] reported room-temperature methane conversion using Fe species confined in graphene nanosheets (GNs) (entry 4, Table 7). The unique FeN<sub>4</sub> structure on the GNs was prepared by simple ball milling of graphite flakes with iron phthalocyanine, and the structure was confirmed by EXAFS. The single iron atom O-FeN<sub>4</sub>-O structure on the GNs could activate the C-H bond of methane to a methyl radical with a low energy barrier of 0.79 eV and produce CH<sub>3</sub>OH and CH<sub>3</sub>OOH. These primary products were further converted to HOCH<sub>2</sub>OOH and HCOOH, as confirmed by time-of-flight mass spectrometry (TOF-MS) and <sup>13</sup>C-nuclear magnetic resonance spectroscopy (NMR).

A similar study using N-doped carbon-supported Fe species was reported by Lin et al. [95]. They prepared Fe/N-doped carbon by treating activated carbon under the flow of NH<sub>3</sub> gas at 600 °C and impregnating iron precursor on it. The TOF which is defined as [moles of total products] [moles of Fe introduced]<sup>-1</sup> [reaction time (h)]<sup>-1</sup> was higher than 5 (**entry 5**, Table 7), and the recycling test was stably conducted.

A non-noble single-metal catalyst for the partial oxidation of methane was also reported by Shen et al. [96]. The well-dispersed Cr atoms supported on  $TiO_2$  nanoparticles showed methane oxygenates yield of 57.9 mol/mol<sub>Cr</sub> (8.8 mmol/g<sub>cat.</sub>/h with a methane oxygenates selectivity of 92.8%) at 50 °C (entry 6, Table 7). The presence of Cr<sup>III</sup> and Cr<sup>VI</sup> species was confirmed. However, Cr<sup>VI</sup> species disappeared after the reaction, and the catalytic activity decreased severely in the reuse test. This implies that the Cr<sup>VI</sup> species play a vital role in the POM.

**Table 7.** Comparison of catalytic systems for the partial oxidation of methane over other catalysts using  $H_2O_2$  in water.

Entry	Catalyst	Temp. (°C)	H <sub>2</sub> O <sub>2</sub> (mmol)	Feed Composition (bar)	Total Productivity (mmol/g <sub>cat.</sub> /h)	Product Selectivity (%) <sup>a</sup>	Ref.
1	Au-Pd/TiO <sub>2</sub>	90	5	CH <sub>4</sub> = 30.5	1.9	CH <sub>3</sub> OH: 88 HCOOH: 0 CO <sub>2</sub> : 12	[88]
2	Au-Pd colloid	50	1	CH <sub>4</sub> :O <sub>2</sub> = 30:5	53.6	CH <sub>3</sub> OH: 88 HCOOH: 6 CO <sub>2</sub> : 5	[89]

Entry	Catalyst	Temp. (°C)	H <sub>2</sub> O <sub>2</sub> (mmol)	Feed Composition (bar)	Total Productivity (mmol/g <sub>cat.</sub> /h)	Product Selectivity (%) <sup>a</sup>	Ref.
3	AuPd@ZIF-8	50	0.5	CH <sub>4</sub> :O <sub>2</sub> = 30:5	4.5	CH <sub>3</sub> OH: 59 HCOOH: 26 CO <sub>2</sub> : 14	[90]
4	2.7%FeN4/GN	25	49	CH <sub>4</sub> :N <sub>2</sub> = 18:2	0.2	CH <sub>3</sub> OH: 39 HCOOH: 29 CO <sub>2</sub> : 6	[94]
5	2.5%Fe/NC-HH	25	5	$CH_4 = 40$	1.6	CH <sub>3</sub> OH: 29 HCOOH: 51 CO <sub>2</sub> : 20	[95]
6	Cr/TiO <sub>2</sub>	50	5	$CH_{4} = 30$	4.4	CH <sub>3</sub> OH: 48 HCOOH: 5 CO <sub>2</sub> : 0	[96]

Table 7. Cont.

<sup>a</sup> CH<sub>3</sub>OH selectivity = (sum of concentrations of CH<sub>3</sub>OH and CH<sub>3</sub>OOH)/(sum of concentrations of total products)  $\times$  100.

#### 3.2. In Situ Generated $H_2O_2$

Direct utilization of  $H_2O_2$  as an oxidant is uneconomical because it is more expensive than methanol. This cost disparity poses a significant challenge to the practical implementation of  $H_2O_2$ -based processes on a large scale. The synergistic integration of in situ  $H_2O_2$  generation and selective oxidation reactions in a single process greatly enhances the environmental and economic attractiveness of utilizing  $H_2O_2$  as a green oxidant on an industrial scale. This tandem reaction not only improves safety by eliminating the need for  $H_2O_2$  storage and transport but also reduces capital and operating costs. Therefore, the direct synthesis of hydrogen peroxide (DSHP) from  $H_2$  and  $O_2$  was investigated. Pd-based catalysts with various supports and secondary metals were tested for DSHP from  $H_2$  and  $O_2$  [22–24]. To enhance the yield of  $H_2O_2$ , acids and halide ions are frequently utilized as they increase the stability and selectivity of  $H_2O_2$ .

Because  $H_2O_2$  is unstable and decomposes in the presence of a catalyst, a mineral acid is required to inhibit its decomposition of produced  $H_2O_2$ . Choudhary et al. [97,98] reported that oxidized Pd catalysts can facilitate the production of  $H_2O_2$ , even in a water-based environment, albeit with lower selectivity for  $H_2O_2$ . Conversely, the Pd<sup>0</sup> catalysts exhibit minimal generation of  $H_2O_2$  in non-acidic aqueous media. This was mainly due to the rapid decomposition of the  $H_2O_2$  formed in the reaction. The incorporation of any of the mineral acids, including  $H_2SO_4$ , HCl, HNO<sub>3</sub>,  $H_3PO_4$ , and HClO<sub>4</sub>, resulted in improved  $H_2O_2$ selectivity compared to a non-acidic aqueous medium [97]. However, the use of liquid acid can cause corrosion of the reactor and the leaching of active metals. For this reason, numerous studies have been conducted on the reaction over catalysts supported on acidic carriers, including sulfated SiO<sub>2</sub> [99–101], zeolites [97,102–104], heteropoly acids [105,106], and acid-functionalized polymers [107].

The use of halide ions, including  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$ , as promoters has also been investigated to enhance the conversion of H<sub>2</sub> and selectivity to H<sub>2</sub>O<sub>2</sub> in DSHP reactions. Halide ions have been utilized by directly adding them to the reaction liquid or depositing them onto solid catalysts. Choudhary and Samanta [108] investigated the effects of halide ions on the DSHP reaction using supported Pd catalysts. Bromide or chloride ions at optimum concentrations promote H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation, causing a drastic increase in H<sub>2</sub>O<sub>2</sub> formation, but only in the presence of protons (protic acids). Regarding the H<sub>2</sub>O<sub>2</sub> decomposition reaction, it seems that the presence of Br<sup>-</sup> or Cl<sup>-</sup> highly inhibits the decomposition rate of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O. Too high concentrations of halide ions can cause the leaching of active metals and also deactivate the catalysts by adsorption on the active species [109]. The utilization of halide ions was also studied by incorporating them onto the catalyst surface. The Pd-based catalysts supported on SO<sub>4</sub><sup>2-</sup>-, Cl<sup>-</sup>-, F<sup>-</sup>-, and Br<sup>-</sup>-doped ZrO<sub>2</sub> were tested for DSHP [110]. The best overall  $H_2O_2$  selectivity was observed with F- and Br-dopants, followed by  $SO_4^{2-}$ . Subsequently,  $Cl^-$  and the non-doped sample exhibited lower  $H_2O_2$  selectivity.

# 3.2.1. Pd-Based Catalyst and Transition Metal-Based Catalyst

Kang and Park [111] demonstrated the POM using iron salts and Pd/C for methane oxidation and DSHP of H<sub>2</sub> and O<sub>2</sub>, respectively. H<sub>2</sub>O<sub>2</sub> was either added directly to the reaction liquid or synthesized in situ from  $H_2$  and  $O_2$ , and the pH of the reaction liquid was adjusted using  $H_2SO_4$  to increase the stability of  $H_2O_2$ . In this process,  $Fe^{2+}$  ions act as catalysts. When combined with  $H_2O_2$ , they can generate hydroxyl radicals (OH·). These hydroxyl radicals play a crucial role in the oxidation of methane. Methane reacts with hydroxyl radicals, resulting in the formation of methane oxygenates, such as  $CH_3OOH$ , CH<sub>3</sub>OH, and HCOOH (entry 1, Table 8). The reduction of  $Fe^{3+}$  to  $Fe^{2+}$  was accelerated by the dissociation of atomic hydrogen from molecular hydrogen on Pd. Fe-ZSM-5 catalysts have been used as substitutes for iron salts under acidic conditions [112]. However, severe leaching of Fe species was observed with high yields of methane oxygenates at low pH values, indicating that homogeneous Fe species were responsible for this reaction. The same group also performed the POM over Fe-ZSM-5 using  $H_2O_2$  generated in situ over acidfunctionalized porous polymer-supported Pd catalysts in the absence of liquid acid [113]. Metal leaching from Fe-ZSM-5 was not observed because of the absence of liquid acids in the reaction system. The cooperation between Pd/c-s-HCPP and Fe-ZSM-5 resulted in a total productivity of 3.7 mmol/g<sub>cat.</sub>/h and selectivity to methane oxygenates of 89% at 50 °C (entry 2, Table 8). Moreover, a one-body Pd-Fe/ZSM-5 catalyst was used for aqueousphase POM in the presence of  $H_2$  and  $O_2$  [114]. The Pd-Fe/ZSM-5 catalysts exhibited significantly better catalytic performance than the physical mixture of the Pd/ZSM-5 and Fe/ZSM-5 catalysts (entry 3, Table 8). This implies that the intimate contact between Pd and Fe is important for methane oxidation with in situ generated  $H_2O_2$  from  $H_2$  and  $O_2$ . The effect of halide ions on the catalytic activity of aqueous-phase POM using H<sub>2</sub>O<sub>2</sub> generated in situ over Pd/C was also examined [115]. Among various halide ions, including  $F^-$ , Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> were effective for the synthesis of  $H_2O_2$  from  $H_2$  and  $O_2$ , resulting in the synthesis of methane oxygenates from methane over Fe/ZSM-5. Compared with Br<sup>-</sup>, the higher product yield was obtained with a much lower concentration of I<sup>-</sup>, guaranteeing that no detectable leaching of metal from Fe/ZSM-5 and Pd/C was found (entry 4, Table 8).

Zhong et al. [116] investigated various M-Pd/ZSM-5 catalysts (M = Cu, Fe, Co, and Ni) for the partial oxidation of methane in tandem with the direct synthesis of  $H_2O_2$  in the presence of  $H_2$  and  $O_2$ . Among those bicomponent Pd-M catalysts, PdCu/ZSM-5 showed the highest productivity of 1178 mmol/g<sub>metal</sub>/h with a methane oxygenates selectivity of 95% at 120 °C (entry 5, Table 8). Based on the control experiments and EPR study, it was proven that PdO nanoparticles facilitated the generation of  $H_2O_2$ , whereas Cu single atoms accelerated the generation of OH• radicals and the consequent homolytic cleavage of methane by OH• to produce CH<sub>3</sub>• radicals.

Pd-containing phosphomolybdates, which are activated by molecular hydrogen (H<sub>2</sub>), have been reported to convert methane and O<sub>2</sub> to methanol at room temperature [117]. The highest activity reached 67.4  $\mu$ mol/g<sub>cat.</sub>/h (**entry 6**, Table 8). In this catalytic system, Pd enables rapid H<sub>2</sub> dissociation and H spillover to the phosphomolybdate for Mo reduction, whereas facile O<sub>2</sub> activation and subsequent methane activation occur at the reduced phosphomolybdate sites. The continuous production of methanol from methane was also achieved by concurrently introducing H<sub>2</sub>, O<sub>2</sub>, and methane to the system.

# 3.2.2. Pd-Au-Based Catalyst

Hutchings et al. [88] observed a lower overall productivity of the tandem system (0.12 mmol/g<sub>cat.</sub>/h) (**entry 7**, Table 8) compared with the direct  $H_2O_2$  injection system (0.28 mmol/g<sub>cat.</sub>/h). He et al. [118,119] tested the catalytic activity of Pd-Au nanoparticles

on carbonaceous materials for the POM using  $H_2O_2$  generated in situ. Among supports such as activated carbon (AC), reduced graphene oxide (rGO), and carbon nanotubes (CNTs), Pd-Au supported on CNTs exhibited the highest catalytic activity (entry 8, Table 8). They proposed that the strong interaction between the Pd and Au nanoparticles and AC and rGO suppressed methane activation. In addition, methane oxygenates, including CH<sub>3</sub>OH, CH<sub>3</sub>OOH, and HCOOH, were obtained over Pd/CNT and Au/CNT.

An impressive methane oxygenate yield of 91.6 mmol/ $g_{AuPd}$ /h was achieved by Xiao et al. [120] over AuPd catalyst encapsulated in hydrophobic sheath-modified ZSM-5 at 70 °C (entry 9, Table 8). The AuPd catalysts were prepared by modifying AuPd@ZSM-5 with an organosilane. These organic chains appear to allow the diffusion of H<sub>2</sub>, O<sub>2</sub>, and CH<sub>4</sub> to the catalyst active sites while trapping the H<sub>2</sub>O<sub>2</sub> generated inside the catalyst pores to enhance the reaction probability.

The direct utilization of  $O_2$  in the absence of any reducing agent was initially reported. Qi et al. [121] reported that Au nanoparticles supported on ZSM-5 could oxidize methane to CH<sub>3</sub>OH and CH<sub>3</sub>COOH with a small amount of CO<sub>2</sub> while using O<sub>2</sub> as the sole oxidant in an aqueous solution. The relatively low product yields and high operating temperatures are still problems to be solved in this case.

**Table 8.** Comparison of catalytic systems for the partial oxidation of methane using  $H_2O_2$  generated in situ from  $H_2$  and  $O_2$  in water.

Entry	Catalyst	Temp. (°C)	Feed Composition (bar)	Total Productivity (mmol/g <sub>cat.</sub> /h)	Product Selectivity (%) <sup>a</sup>	Ref.
1	FeSO <sub>4</sub> + Pd/C	20	CH <sub>4</sub> :H <sub>2</sub> :Air = 15:3:10	64.2 <sup>b</sup>	CH <sub>3</sub> OH: 5 HCOOH: 61 CO2: 34	[111]
2	Fe/ZSM-5 + Pd/c-s-HCPP <sup>c</sup>	50	CH <sub>4</sub> :H <sub>2</sub> :Air = 15:3:10	3.4	CH <sub>3</sub> OH: 28 HCOOH: 61 CO <sub>2</sub> : 11	[112]
3	Pd-Fe/ZSM-5	50	CH <sub>4</sub> :H <sub>2</sub> :Air = 15:3:10	0.5	CH <sub>3</sub> OH: 52 HCOOH: 37 CO2: 11	[114]
4	Fe/ZSM-5 + Pd/AC	50	CH <sub>4</sub> :H <sub>2</sub> :Air = 15:3:10	3.5	CH <sub>3</sub> OH: 34 HCOOH: 45	[115]
5	Pd-Cu/ZSM-5 <sup>d</sup>	120	CH <sub>4</sub> :H <sub>2</sub> :O <sub>2</sub> = 73:24:9	2.2	CH <sub>3</sub> OH: 55 HCOOH: 40	[116]
6	Pd/CsPMA-H <sup>e</sup>	25	CH <sub>4</sub> :O <sub>2</sub> = 20:0.3	0.067	CH <sub>3</sub> OH: 100	[117]
7	AuPd/TiO <sub>2</sub>	50	CH <sub>4</sub> :H <sub>2</sub> :O <sub>2</sub> :N <sub>2</sub> = 30.5:0.3:0.7:8.7	0.14	CH <sub>3</sub> OH: 83 HCOOH: 0 CO <sub>2</sub> : 17	[88]
8	Pd-Au/CNTs	50	CH <sub>4</sub> :H <sub>2</sub> :O <sub>2</sub> :Ar = 15.5:1.3:2.6:13.5	0.4	CH <sub>3</sub> OH: 78 HCOOH: 22	[118]
9	AuPd@ZSM-5-C16	70	CH <sub>4</sub> :H <sub>2</sub> :O <sub>2</sub> :Ar = 0.5:0.9:1.8:27	5.0	CH <sub>3</sub> OH: 95 HCOOH: 5 CO <sub>2</sub> : 0	[120]

<sup>a</sup> CH<sub>3</sub>OH selectivity = (sum of concentrations of CH<sub>3</sub>OH and CH<sub>3</sub>OOH)/(sum of concentrations of total products)  $\times$  100. <sup>b</sup> The total productivity is the turnover frequency based on moles of Fe species. <sup>c</sup> HCPP: hyper cross-linked porous polymer. <sup>d</sup> The data were inferred from the figure. <sup>e</sup> CsPMA: Cs-exchanged phosphomolybdate catalyst.

# 4. Summary and Outlook

The current indirect route for utilizing methane as a chemical feedstock via syngas is economically applicable only to large methane gas fields. To exploit the many small- and medium-sized methane resources, highly efficient direct methane conversion technologies must be developed. Among the various direct methane conversion pathways, the POM is the most attractive because it is thermodynamically feasible and has successful examples in nature, such as MMOs. This review discussed liquid-phase POM in strong acids and water according to the oxidant and catalyst used. As summarized in Table 9, higher yields of methanol precursors (MeTFA or MBS) were generally obtained in strong acids (HTFA or  $H_2SO_4$ ) than in water. However, the instability of HTFA (entry 1, Table 9) and additional requirements of TFAA (entries 2 and 4, Table 9) are significant drawbacks of using  $K_2S_2O_8$  and  $H_2O_2$  as oxidants in the HTFA system. The direct synthesis of MBS from methane in oleum, subsequent esterification with HTFA, and hydrolysis of MeTFA could compete with the current indirect method for methanol synthesis from methane. However, the co-production of methanol and  $H_2SO_4$  is inevitable (entry 6, Table 9), which would need to be market acceptable.

Entry	Solvent	Oxidant	Advantages	Disadvantages
1	CF <sub>3</sub> COOH	$K_2S_2O_8$	Relatively high yields of MeTFA	Corrosive solvent Solvent decomposition Waste (KHSO <sub>4</sub> ) from an oxidant
2	CF <sub>3</sub> COOH	$H_2O_2$	Relatively high yields of MeTFA	Corrosive solvent TFAA is required H <sub>2</sub> O <sub>2</sub> is expensive
3	CF <sub>3</sub> COOH	CO/H <sub>2</sub> O/O <sub>2</sub>	Relatively high yields of MeTFA $O_2$ can be indirectly used	Corrosive solvent CO is required Waste (CO <sub>2</sub> ) from an oxidant
4	CF <sub>3</sub> COOH	$H_2/O_2$	Relatively high yields of MeTFA O <sub>2</sub> can be indirectly used	Corrosive solvent H <sub>2</sub> and TFAA are required
5	CF <sub>3</sub> COOH	O <sub>2</sub>	O <sub>2</sub> can be directly used	Corrosive solvent Relatively high reaction temperatures Very low yields of MeTFA Solvent decomposition
6	$H_2SO_4$	SO <sub>3</sub>	High yields of MBS O <sub>2</sub> can be indirectly used	Corrosive solvent Inevitable H <sub>2</sub> SO <sub>4</sub> co-production
7	H <sub>2</sub> O	$H_2O_2$	Relatively low product yields with an exception (Table S1) No waste from an oxidant	$H_2O_2$ is expensive
8	H <sub>2</sub> O	$H_2/O_2$	Relatively low product yields with an exception [119] O <sub>2</sub> can be indirectly used No waste from an oxidant	H <sub>2</sub> is required
9	H <sub>2</sub> O	CO/H <sub>2</sub> O/O <sub>2</sub>	Relatively low product yields O <sub>2</sub> can be indirectly used	CO is required Waste (CO <sub>2</sub> ) from an oxidant
10	H <sub>2</sub> O	O <sub>2</sub>	O <sub>2</sub> can be directly used No waste from an oxidant	Very low product yields

Table 9. Comparison of different catalytic systems for the liquid-phase partial oxidation of methane.

Compared with the POM in strong acids, the methanol yields for POM in water are generally much lower. Similar to MMO, which requires a reducing agent, methane can be oxidized by  $H_2O_2$  generated in situ from  $H_2$  and  $O_2$ . In particular, well-designed AuPd nanoalloys encapsulated in nanocages with controlled surface hydrophobicity provided excellent methanol yields under mild conditions [120]. The synergistic and cooperative effect between active centers and supports should be considered and sought in future studies. This approach paves the way for the development of a direct methanol synthesis process that is cost-competitive with conventional methanol processes based on indirect methane conversion. The hydrogen required for this process can be supplied by water electrolysis powered by renewable energy sources.

However, the direct conversion of methane to methane oxygenates without a reducing agent cannot be sufficiently stressed. Since the direct oxidation of methane and  $O_2$  is a

spin-forbidden reaction, relatively high reaction temperatures are required for thermal catalysis. In view of this, additional energy sources for the activation of methane and  $O_2$ , as well as well-designed thermal catalysts, must be continuously sought.

Recently, (photo)electrochemical [122,123] and photocatalytic [124–126] direct methane conversions have been actively investigated. Although these are still in the early stages of research and development, their performance should be monitored as thermal methane conversion technologies develop.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal14030167/s1, Table S1: The catalytic performance for selective oxidation of methane with  $H_2O_2$  over 0.38 wt.% Fe-ZSM-5 under different conditions. Figure S1: UV–Vis spectra of 0.38 wt.% Fe-ZSM-5 [57,63,127,128].

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