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REVIEW

Metal Incorporated Zeolites as Heterogeneous Catalysts in the Selective Partial Oxidation of Methane to Methanol: A Review

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Methane, being a potential greenhouse gas, is a very serious environmental concern nowadays. The valorization of methane to valuable chemicals like methanol has long been considered as an effective remedy to this problem. But, in spite of several attempts, the production of methanol directly from methane remains largely challenging, both in laboratory scale and in industrial level, because of low reactivity of methane and challenges in product recovery. In present review, the developments in the application of different heterogeneous catalysts in oxidation of methane to produce methanol directly, the 'holy grail' reaction in chemistry is discussed, with the main focus on the metal exchanged porous zeolite matrices as heterogeneous catalysts. The different reaction parameters like the nature of oxidants, reaction conditions, zeolite pore sizes, the metal loading ratio are also critically reviewed.

Keywords: Methane, Methanol, Zeolite, Heterogeneous catalyst, Selective oxidation.

INTRODUCTION

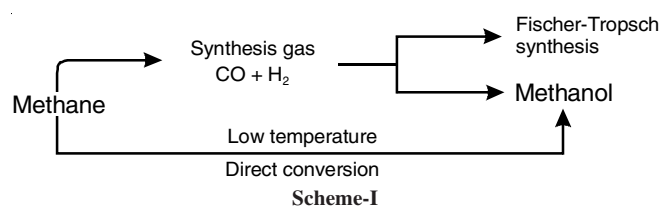
Methane (CH₄), the simplest hydrocarbon, occurs in our planet as one of the principal components of the natural gas. The concentration of methane in natural gas is estimated to be within 70% to 90% by volume [1-6]. Although the global natural gas reservoirs offer considerable supply till date, it becomes important to rethink about the innovative methods for converting methane into more valuable chemicals and fuels amidst the imperative of addressing change in global climate and striving for attaining net-zero carbon emissions [1]. The global warming potential (GWP) of CH₄ is estimated as 28-36 over 100 years (CO₂ has GWP 1). Here, it should be mentioned that the human activity is found to be the second most important contributor towards the emission of methane after CO₂ [4]. The fact which needs immediate attention is that about 24% of all anthropogenic methane emission comes from oil and natural gas related facilities [1,6]. At this moment, the major fraction CH₄ produced undergoes combustion for generation of heat or electricity. However, in many instances, particularly at oil fields, recovered methane is frequently directly flared, thereby leading to significant CO₂ emissions. There is an increasing urgency, along with

emerging commitments, to drastically reduce this practice by 2030 [6]. Hence, the need to convert methane into a beneficial and environmentally sustainable chemical alternative, rather than simply flaring it and generating CO₂, is becoming increasingly evident. Methanol (and its derivatives) will continuously be gaining importance in the world. Currently, they are almost completely produced from natural gas (~65%) and coal (~35%, in China) [5]. In 2021, global CH₃OH demand was 106 million tonnes [6], which is almost double than its previous decade. It is expected that the demand will be growing strongly [5]. Presently, even greater than 60% of current CH₃OH demand is for its use as chemical feedstock, majorly for the olefins (32%) production, formaldehyde (23%) manufacturing and also acetic acid (8%) production. Methanol is further used *via* methyl *tert.*-butyl ether (MTBE) in transport fuel (11%), in biodiesel (3%) and by direct blending or substitution in gasoline (11%), which is growing very fast [6]. So to meet the stringent environmental restrictions, the chemistry involved in these processes should be extremely efficient for arresting majority of carbon and they have to be cost effective also. In effect even a low-cost but inefficient conversion of associated gas will be observed as only partially lowering the flaring and emission. The major diffi-

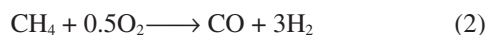
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culty to the exploitation of natural gas appears from the difficulties in approachability of reserves of crude oil. Long-distance transportation through pipelines for a long distance in gaseous form is not at all practical solution for natural gas. The boiling point of methane is 109 K at 1 atmosphere pressure, and so liquefaction is also not a feasible option. To liquefy the gas by cooling to some acceptable temperature is also not sustainable for the duration of transport. On-site conversion of methane is also very tedious and difficult because of chemical inertness of methane. It is quite clear that these difficulties in methane processing make its valorization financially unviable, leaving us with the only option of flaring. The scientific community and industries have been interested in extracting valuable chemicals from natural gas for over a century, due to its potential as an underutilized resource [7].

Now, because of its inertness ($\Delta H_{C-H} = 438.8 \text{ kJ mol}^{-1}$), and also due to low reactivity, methane activation looks very challenging, and so the present industrial utilization of methane depends on some indirect and energy intensive pathways. For instance, a pivotal step towards transforming to a methanol economy involves converting methane into methanol. This process typically begins with either steam reforming of methane or partial oxidation of methane to produce synthesis gas *i.e.* syngas (CO/H_2), a step which necessitates large-scale operations, so that the process becomes economically viable. Syngas can then be further converted into methanol through catalytic processes. In another route, there may be catalytic transformation of syngas into various other significant hydrocarbon products. Therefore, the production of methanol directly from methane has emerged as an attractive prospect, because it presents one of the most promising pathways for utilizing remote natural gas sources directly (**Scheme-I**).



Both partial oxidation of methane to methanol (eqn. 1) and over-oxidation of methane to CO (eqn. 2) are exothermic reactions, but at above 600 K, thermodynamically favoured pathway is CO formation [8].



So, if methanol has to be main product, it will be obvious to maintain the reaction temperature at less than 500 K [8,9] (Table-1). From the last century, many research groups have attempted to study and tried to understand the oxidation of CH_4 to CH_3OH by using many different catalyst-free and homogeneous processes [10-15], but till now, these methodologies could only be successfully used in a small-scale in distant sites areas with plentiful methane resource [1,16,17]. In recent times, some researchers reported high conversion of methane and selectivity towards methanol with homogeneous catalysts in

TABLE-1
GIBBS FREE ENERGIES OF METHANE OXIDATIONS
AT DIFFERENT TEMPERATURES [22]

Reactions	ΔG_T (kJ mol ⁻¹)	
	298 K	650 K
$\text{CH}_4 + 1/2\text{O}_2 \rightarrow \text{CH}_3\text{OH}$	-111	-93
$\text{CH}_4 + \text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-288	-294
$\text{CH}_4 + 3/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$	-544	-573
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-801	-800

liquid phase, especially in H_2SO_4 /oleum liquid system [7]. There are many detailed reviews on these partial oxidation in liquid phase with homogeneous catalysts by some research groups [18-21].

However, as is evident in homogeneous catalysis, it becomes tedious to isolate, recycle and reuse these catalysts. Also the enzymatic catalytic processes [23-25] inspired and drove the attention towards the development of new functional heterogeneous catalytic materials for the selective production of methanol by oxidation of methane in recent times, both in gas and liquid phases [1]. In this review, the main emphasis will be on the synthesis and application of heterogeneous catalysts in the selective oxidation of methane to methanol, the 'holy grail' of chemistry. There has been tremendous progress of the heterogeneously catalysed methane oxidation to methanol based on porous materials like zeolites. It is well known that heterogeneous catalysts have advantages in these types of reactions due to their easy separation and the ability to be recycled and reused in further reactions, thereby making the process more sustainable [26,27]. Also, as the biomimetic heterogeneous catalysts use the principle of enzymatic reactions in many cases, methane oxidation by enzymes is also considered for discussion.

Methane oxidation using enzymes: At the primary stage of metabolism of methane, methanotrophic bacteria employ a type of enzyme methane monooxygenases (MMOs) for oxidation of methane to methanol. Methane is utilized as their solo energy source. Two types of MMO are (i) soluble form (sMMO) having a di-iron active centre and (ii) a particulate form (pMMO) containing a copper active site. Major studies have been found on sMMOs because obtaining pure form of pMMOs is very difficult, in spite of the fact that pMMOs are the predominant form of MMOs [23,28-30].

sMMO is a multi-constituent enzyme and constituted of three major components, for example a hydroxylase (MMOH) that transforms methane to methanol, a reductase (MMOR) is there which transfers the oxygen to the active centre of hydroxylase after activating it, and the methane's entrance to hydroxylase active site is regulated by a regulatory protein (MMOB). This active site lies deeply embedded within the organization. Methane and oxygen reach this active site *via* the hydrophobic cavity running through the center. Once methanol is produced, its hydrophilic nature facilitates its expulsion from the enzyme, preventing excessive oxidation. This mechanism is cyclic in nature and most of the chemo-catalysts try to mimic the di-iron active site of the MMO [23,28,31,32]. However, replicating the unusual oxidation state of iron, specifically Fe(IV), in a

laboratory setting is challenging. This state is stabilized by the amino acids located near the active site, making it difficult to duplicate.

There are different other monooxygenases [23] that activate a large number of hydrocarbons and application of these enzymes will be intriguing. Recently, the potential of using sMMO to produce methanol as part of a gas-to-liquids process has been reviewed [33]. Numerous challenges have been identified, including limitations in gas-liquid mass transfer and the risk of enzyme poisoning by impurities in the natural gas.

There are three subunits in pMMO, (PmoA, PmoB and PmoC) [34]. The active site here is copper based and is considered to be located in PmoC [34]. This copper site, referred to as CuC, is linked with two other copper centers in PmoB, though not all pMMOs contain these centers [35]. The activity of this methane monooxygenase relies on the preservation of active center's structure, which is significantly affected when removed from its original membrane environment. This explains the prominence of sMMO in the literature.

Presently, the promising heterogeneous catalytic methodologies mimic the idea from homogeneous or biocatalysis. There are metal complexes, which may cleave methane and other hydrocarbons C-H bonds under homogeneous catalytic conditions with high selectivity at lower temperatures. These are discussed in the reviews by Shilov & Shul'pi [36], Periana *et al.* [37] and Horn & Schlögl [38]. Under the conditions of 180 °C and a 20 mM concentration of $\text{Hg}(\text{HSO}_4)_2$ in sulfuric acid, methanol yields exceeded 40% with a selectivity of over 90%. Later, Periana [39] described a catalyst based on platinum, dichloro-(η -2-[2,2'-bipyrimidyl])platinum(II) *i.e.* [(bpy₂m)PtCl₂]. This catalyst showed remarkable performance by giving 90% methane conversion with 81% selectivity to methyl bisulfate. This methyl bisulfate can be hydrolyzed to methanol and sulphuric acid. Palkovits *et al.* [40] developed a covalent triazine-based framework (CTF) using Periana's molecular template, achieved by trimerizing 2,6-dicyanopyridine in molten ZnCl₂. This solid ligand coordinates with PtCl₂, creating a solid analog to Periana's system. The Pt-CTF demonstrates activity in methane oxidation in oleum, producing methyl bisulfate, which can be converted to methanol after workup. Despite an initial activation period, the catalyst achieves turnover numbers (TONs) exceeding 250. This study demonstrates a mechanism for methane oxidation using a low-temperature heterogeneously catalyzed process. It also emphasizes whether concepts from homogeneous catalysis might improve the efficiency of heterogeneous catalysis.

The methane selective oxidation in the gas phase to produce oxygenates like methanol and formaldehyde underwent extensive research, particularly during the 1980s and 1990s. Characteristically, this method involved elevated temperatures and often utilized metal oxide catalysts. Numerous historical investigations on this topic have been previously reviewed [41-44]. Methane oxidation at high temperature has been explored for many years [45]. Many co-workers [46-48] successfully extended the heterogeneous catalytic routes from previous researches. Under around 180 bar pressure, utilizing natural gas and oxygen concentrations ranging from 4.1% to 12.0%, copper exhibited

a remarkable effectiveness as a catalyst in enhancing methanol production. Under these operational settings, it was observed that on the copper catalysts surface, Cu₂O was formed, suggesting that the oxygen from Cu₂O acted as the primary oxidizing agent for methane. However, it is pertinent to mention that any sulphur traces in the reaction mixture enormously impaired the activity of the catalyst.

Various catalysts have been investigated for the high temperature gas phase partial oxidation of methane, with the goal of producing oxygenates. For instance, in a seminal study Dowden *et al.* [49] introduced a theoretical framework proposing a virtual mechanism. According to this model, the preliminary interaction of methane with the catalyst surface led to its dissociation, forming methylene and methyl species. Importantly, it was crucial to inhibit further dehydrogenation of methyl and methylene species, as it would result in carbon oxides formation. Hence, catalysts favouring the production of methyl species were preferred, directing attention towards metal oxides rather than metals.

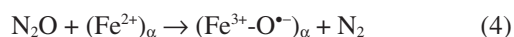
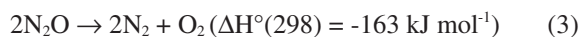
Catalysts with weak dehydrogenation properties, typically associated with d^0 , d^1 , d^5 , d^{10} or d^4 electron configurations, were found suitable. Moreover, the oxygen insertion characteristics of typical n-type metal oxides were deemed essential. Recommended constituents included TiO₂, V₂O₅, Fe₂O₃, MoO₃ and ZnO [1,50]. Results were reported for MoO₃/ZnO, MoO₃/Fe₂O₃, MoO₃/VO₂ and MoO₃/UO₂ supported on 1/3Al₂O₃/SiO₂ with a *ca.* 0.1 m² g⁻¹ surface area of and a packing of 5% oxide. The most effective catalyst was MoO₃/Fe₂O₃, which achieved a combined selectivity of 80% for CH₃OH and HCHO at a methane conversion rate of 3.5%, producing 869 g kgcat⁻¹ h⁻¹ of methanol and 100 g kgcat⁻¹ h⁻¹ of formaldehyde. To sustain high yields, experimental conditions necessitated around 30 bar pressure and 430 to 500 °C temperature range. Additionally, a rapid liquid water injection was employed to swiftly lower the reactor effluent temperature within 0.3 seconds after exiting the catalyst surface.

In some other studies single metal oxides have been exploited for the activation of the reactants (methane and oxygen) and production of methanol. A good potential catalyst was MoO₃ due to the fact that in spite of being effective for selective oxidation of methanol to formaldehyde, at higher temperatures, only minimal further oxidation to carbon oxides was observed [51]. Isotopic exchange experiments between CH₄ and deuterium have been regarded as the initial indicator of catalytic activation of CH₄ [52]. A catalyst synthesized by physical mixing of 1:1 Ga₂O₃/MoO₃ demonstrated a significant performance in methane oxidation and selectivity was towards formaldehyde [53]. By mimicking the cytochrome P450 enzymes, Lyons *et al.* [54] developed a high temperature catalyst for gas phase reaction. The catalyst was a microporous framework (sodalite) where framework Al³⁺ was substituted by >10 wt.% Fe at exchangeable sites. The material had to be calcined at 550 °C to produce the best catalyst. The XRD and EPR results suggested that Fe was driven from framework sites into the exchangeable positions due to the partial collapse of framework, these were associated with remaining framework Fe to produce active centre. About 5.7% methane conversion with 70% methanol selectivity was obtained under reaction conditions 3:1 CH₄: air at 416 °C, under

53 bar pressure and a gas hourly space velocity (GHSV) of 530 h^{-1} . Betteridge *et al.* [55] used Fe-sodalite catalyst in same reaction conditions, achieved at 3.1% conversion along with 33% methanol selectivity. Similarly, Stroud [56] reported one of the most active dual component catalysts with MoO_3 as one of the component.

The mechanism of the selective oxidation of methane over the metal oxide catalysts is quite complex. A number of different mechanisms over different catalysts have been postulated. There may be involvements of both gas phase homogeneous and heterogeneous reactions. The observation of requirement of high reaction temperature, and the beneficial role of increasing the pressure makes this proposal more probable. Enhancing the selectivity of methane oxidation catalysts becomes more challenging with the inclusion of gas phase reactions. Therefore, strategies that enable the activation of methane at lower temperatures and promote reactions on the surface while reducing reactions in gas phase would present more efficient approach for crafting superior methane selective oxidation catalysts [1].

For oxidation of methane over polyoxotungstates [57] or silica supported catalysts, and majorly over iron incorporated zeolites, the application of nitrous oxide (N_2O) as an oxidant has recently received great attention [58]. The desirable properties like thermal stability, capability to incorporate mono- or bi-nuclear active sites and also confinement effects make zeolites a unique host matrix [59-61]. Iron and copper containing zeolites are best examples of catalysts of this kind. They have been used both in liquid phase oxidation as well as in gas phase [60,62,63]. The decomposition of N_2O [64] (eqn 3) have been reported over different catalysts including iron containing zeolites like Fe containing H-ZSM-5 [63,65-68]. In this process, the active metal centre undergoes an oxidation which facilitates the oxidation of methane through the generation of an active α -oxygen species (eqn. 4).



Several researchers [68,69] studied the different reaction conditions required for decomposition of N_2O over zeolite based catalysts. In an important study, Melian-Cabrera *et al.* [70] reported the comparison of the different iron containing zeolite structures in N_2O decomposition. They reported that Fe-ZSM-5 (Si:Al ratio of 11.4) showed impressive 95% decomposition of N_2O at 500 °C. However, Fe-BEA zeolites only achieved a 20% conversion, even at a higher temperature of 575 °C. However, N_2O breakdown at high temperatures differs from previous studies on methanol or phenol formation [71]. Instead, these systems are better understood as stoichiometric transfer reagents but as it is known that α -oxygen can be formed at even below 200 °C, so, at least in theory, catalytic partial oxidation of methane at low temperature should be achievable. The ratio of Si/Al is another crucial feature for N_2O decomposition over catalyst for producing active oxygen in oxidation of methane. The Si/Al ratio may also govern the loading of metal. It has been observed that low Si:Al ratio should provide accommodations greater concentration of active sites in Fe containing zeolite catalysts [72].

Iron incorporated zeolites: The generation of active α -oxygen site for the oxidation of methane is related to that postulated for N_2O decomposition, where the active oxygen species produced upon the decomposition of N_2O should remain on an active iron site and not recombine. Therefore, to enhance the decomposition of N_2O at lower temperature, addition of a reductant in feed stream is essential, because it can promote the abstraction of the oxygen from the oxidized active site [73-76]. Initially, the active site was suggested to be mono- or di-nuclear iron sites for disintegration of N_2O and generation of active oxygen [77-79]. In both cases, the extra-framework iron is proposed as active site for the formation of α -oxygen species [80-85], which is produced by decomposition of N_2O over a reversible redox $\alpha\text{-Fe}^{2+}$ site [86,87]. After addition of oxygen it has been proposed that either mononuclear $\text{Fe}^{4+}=\text{O}^{2-}$ (or $\text{Fe}^{3+}\text{-O}^\bullet$) or dinuclear Fe as an oxo-bridged $\text{Fe}^{3+}\text{O}^{2-}\text{Fe}^{3+}$ species were the most suitable candidates for the α -oxygen active site [87].

A reactive intermediate known as high spin $\text{Fe}^{4+}=\text{O}$ species has been identified, with the methane being confined in the zeolite pores, thereby enhancing the perceived reactivity. Additionally, to gain insight about the active site structure of Fe-ZSM-5, Mössbauer spectroscopy was very helpful, which revealed that during the N_2O decomposition in Fe-ZSM-5, the active oxygen and the adjacent Fe^{2+} ions both were present as mononuclear species. Furthermore, Bols *et al.* [88] reported about a Fe-containing zeolite synthesis, where over 70% of the Fe was in $\alpha\text{-Fe}^{2+}$ form. Panov and co-workers [87,89,90] investigated extensively the proposal by Ovanesyan *et al.* [91] that an α -oxygen species was accountable for the production of methanol. They found that Fe-ZSM-5 activated methane by α -oxygen species which is formed on the active Fe centre upon using N_2O as an oxidant. The effect of surface acidity on this catalytic processes was examined by Chow *et al.* [92] over MFI zeolites. The presence of aluminium was very important to produce the active cationic form of the Fe species. Nevertheless, methanol was not stable over Brønsted acid sites, lowering the methanol selectivity and yield. Co-feeding water with CH_4 and N_2O thereby facilitated the detachment of methanol from these catalyst, enhancing the stability. A secondary beneficial role of water in the feed lies in the decrease of C2 compounds in the post-reactor stream [93].

The effect of framework structure, remoteness of Fe-Fe/O/Si, pore dimensions and Si:Al ratio on the extraction of methanol processes have been studied extensively over different zeolitic materials like MFI, beta (BEA), chabazite (CHA), both experimentally and computationally. It was found that addition of iron post synthesis produced more effective catalysts. The Fe-ZSM-5 (%) showed greater methanol yield [94-96]. Fe-ZSM-5 (Fig. 1a), Fe-BEA and Fe-FER zeolite catalysts were compared for the activity as well as product distribution by Zhao *et al.* [97]. Different parameters like composition, framework acidity, characteristics of the pores were judged on the basis of methanol yield as well as N_2O decomposition. The outcomes of these experiments advocated that greater aluminium content of Fe-FER was playing a pivotal role to stabilize the active iron centre, as a result, higher yield of methanol (with 200 mg catalyst, the

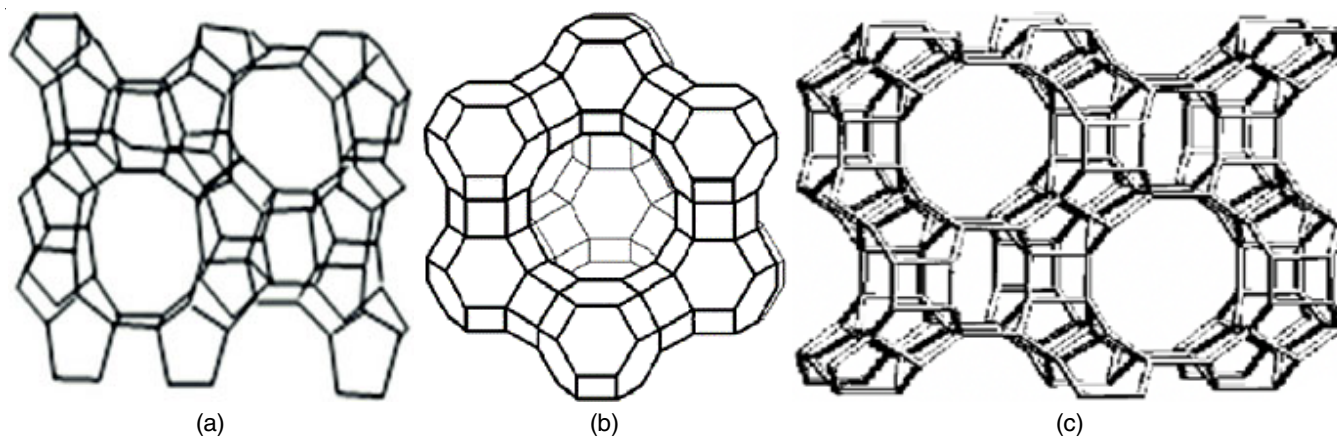


Fig. 1. Crystalline structure of (a) ZSM-5, (b) zeolite Y, (c) mordenite

TOF CH_4 was 125 h^{-1} at 350°C) was obtained. For Fe-ZSM-5 catalyst, the smaller pore sizes and lower Lewis acidity produced higher amount of coking and therefore subsequent deactivation (with 200 mg catalyst, TOF CH_4 was 88.1 h^{-1} at 350°C) was obtained. Two catalyst preparation methods were compared to demonstrate the variations in the catalysts which were formed *via* solid state ion exchange (SSIE) and liquid ion exchange (LIE). The N_2O conversion was higher for the Fe-FER-LIE catalyst at 360°C . Although the conversion of methane was low ($<2\%$), the major products were CO and dimethyl ether (DME), whereas the Fe-FER-SSIE catalyst demonstrated greater selectivity to dimethyl ether (DME) [98].

Two types of iron-fauzite (Y) (Fig. 1b) were synthesized, one by solid state ion exchange (Fe-Y-O) and another by incipient wetness impregnation (Fe-Y-I) methods by Zhu *et al.* [99] to examine the effect of the procedure of catalyst preparation on selective methane oxidation. It was proposed that incipient wetness impregnation created a greater number of Fe_2O_3 particles and that was confirmed by TEM. However, the Fe-Y-I samples did not have these entities. The results explain about the presence of 63% higher concentration of α -Fe sites for the Fe-Y-O sample with respect to the Fe-Y-I catalyst and also the fact that the yield of methanol was significantly greater over Fe-Y-O. However, further insights suggested that extra-framework dinuclear Fe^{2+} complexes are the active sites in this catalyst.

Li *et al.* [100] in another study on mordenite (MOR) zeolites reported that there is an increase in the α -Fe sites density upon the addition of extra-framework Al. In this synthetic strategy, aluminium nitrate and ferrocene were added to zeolite before the activation. ^{27}Al MAS-NMR was utilized to characterize three such samples after different stages of treatment and it was found out that the zeolite structure could actually support more aluminium in the extra-framework positions. Comparison of quantities of extra-framework Al (*i.e.* octa-hedrally coordinated) and framework Al (*i.e.* tetrahedral) showed that there is an increase in concentration of extra framework sites, but the framework aluminium concentration did not increase. Subsequently, Fe-MOR catalyst having the highest aluminium content showed highest selectivity to methanol and DME.

Conclusively, many factors like the framework structure, surface acidity (both Brønsted and Lewis), Fe/Al ratio and

pore characteristics have great contributions towards efficient methanol production. The catalyst's efficiency can be correlated with the six-membered rings density in the zeolite structure [88], because this configuration is assumed to produce the best stabilization of the active site. Progressing this tools requires preparation of zeolite having the highest α -Fe loading possible, alongside optimizing reaction conditions to enhance methanol yields while minimizing CO or carbon deposits.

Microporous materials in aqueous media: The effectiveness of methane monooxygenase in liquid-phase methane oxidation (using water as solvent at 50°C) is well-documented and comparable to that of chemo-catalyst-mediated processes under similar conditions. Thus, drawing inspiration from these biological pathways, numerous research endeavors have delved into exploring low-temperature methane oxidation. Analogies have been drawn between the restricted space of active site of the enzyme and the precisely structured pore sizes of zeolites which are inorganic microporous materials [60,101].

A greater number of oxidants can be used in the aqueous media at low temperatures. H_2O_2 has been a popular reagent in these systems because the oxidation side product is water ($\text{CH}_4 + \text{H}_2\text{O}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$). Indeed, Sorokin *et al.* [102, 103] employed μ -nitridoironphthalocyanine complex immobilized on silica for activation of methane with H_2O_2 in mild acidic condition and reported that this condition promoted catalytic activity. However, Forde *et al.* [104] found the catalyst to have quite low activity (TOF $\sim 2 \text{ h}^{-1}$) and reported that it is not stable under this type of reaction conditions of oxidation of methane.

Iron incorporated ZSM-5 with H_2O_2 : Hutchings *et al.* [60] established that methane can be converted to the oxygenates extremely effectively by commercial ZSM-5 in aqueous systems with H_2O_2 as oxidant. A crucial step for the production of effective catalyst was the calcination at 550°C for 3h. Formic acid was the major product with approximately 54% selectivity, detailed time-online analyses showed methyl hydroperoxide (CH_3OOH) to be the initial primary product. The selectivity towards formic acid (HCOOH) increased with a longer reaction time, proving that HCOOH is partly produced by the successive oxidation of CH_3OOH and CH_3OH . Iron impurities in ZSM-5 (140 ppm) [60,101,105-107] were found to be active species in these reactions.

An additional amount of iron can be incorporated on ZSM-5 either in the synthetic procedures or afterwards to produce more active catalyst than bare ZSM-5 or silicalite-1 supports. But for zeolites like β , Y or ferrierite, this process did not work, which shows that the zeolitic framework bears a serious role in the catalytic reaction. It was also proposed that Al^{3+} or other trivalent cations (*e.g.* Ga^{3+}) induced Brønsted acidic sites in the zeolite. This factors are important for the active iron species dispersion. However, when the Si/Al ratio in ZSM-5 is too low (like 12.4) [108] or when there is a high iron loading, both scenarios were found to be counterproductive. This could be attributed to the unproductive decomposition of H_2O_2 by the zeolite acidic sites or the agglomeration of iron oxide units. Interestingly, it has been discovered that upon incorporation of Cu^{2+} into the reaction alongside the Fe/ZSM-5 catalyst as both homogeneous or heterogeneous components [Cu-Fe-ZSM-5 or Cu-silicate-1 or even $\text{Cu}(\text{NO}_3)_2$] distinctly improves the selectivity to CH_3OH (> 80%), while the activities of the catalyst does not alter significantly. A comparative study has been made to compare the catalytic performances of iron and copper incorporated zeolites in oxidation of methane using H_2O_2 as oxidant (Table-2). It is pertinent to mention that Cu^{2+} alone in the zeolite have not been found to activate methane, $\cdot\text{OH}$ radicals (produced due to decomposition of H_2O_2) were not observed in the EPR spectra. So it was proposed that $\cdot\text{OH}$ radicals may have been eliminated by copper ions in the system. In an optimized reaction, Cu/silicalite-1 and Fe/silicalite-1 catalysts were physically blended and used with 1 M H_2O_2 , 3 bar CH_4 at 70 °C. The amount of catalyst utilized was double than that of the standard condition. This setup resulted in a significant methane conversion rate of 10% and an impressive selectivity of 93%. Notably, in presence of H_2O_2 and the zeolite, methanol will be further oxidized under these reaction conditions. So, to stabilize the product, the presence of excess amount of CH_4 , is needed. This stability arises probably through competing for catalytic active sites. Although many research groups successfully reproduced the excellent catalytic activity of Cu/Fe/ZSM-5 system, the real characteristics of the catalytic active sites and the actual role of Cu have still not been fully recognized and as a result it has created a lot of controversy in the scientific community. However, recently Yu *et al.* [109,110] used Mössbauer spectroscopy and quantified different types of active iron species in the catalyst. They observed that there is a positive relationship of the turnover rates of methanol with only the mononuclear Fe species in catalysts with diverse Fe loadings. Hence they proposed that isolated mononuclear iron species are the actual active sites. In a time-online analysis comparing two catalysts 0.1 wt.% Fe/ZSM-5 and 2 wt.% Cu-0.1 wt.% Fe/ZSM-5, it was shown that different intermediates were produced and products in the oxidation of methane.

Hydrogen peroxide has been explored as oxidant for selective oxidation of methane over many other types of catalysts apart from zeolites containing extra-framework iron species (Table-2). Kwon *et al.* [111] described a 0.3 wt.% Rh/ZrO₂ catalyst and achieved a 0.3 mol CH_3OH kg cat⁻¹ h⁻¹, using H_2O_2 as oxidant at 70 °C. There was no formation of HCOOH and the catalyst showed positive results even at 300 °C with oxygen as oxidant. In another study, Cui *et al.* [112] reported a single iron atom catalyst confined in graphene to show 0.47 mol mol Fe⁻¹ h⁻¹ of oxygenates at room temperature. Catalysts containing other 3d transition metals like Co, Ni, Cu and Mn were not found to be active. Zhou *et al.* [113] activated methane by single atom nickel catalyst on N-doped amorphous carbon. Under optimized conditions, conversion of methane was >1 mol kgcat⁻¹ h⁻¹ and selectivity to methanol was >90%. Single atom catalysts like isolated Fe sites on MOF [114,115], Cr catalysts on TiO₂ [116] have been employed for producing methanol from methane, but none of them are comparable to so far the best reported catalyst Cu-Fe/ZSM-5 [110].

Copper modified zeolite for methane oxidation to methanol: Cu-zeolites are among most widely used catalysts for selective oxidation of CH_4 to CH_3OH now, in gas phase. In general, two types of oxidants are majorly applied for the methane selective oxidation on Cu zeolites, for example NO/ N_2O and O_2 . Like the iron modified zeolites, the productivity of methanol on Cu-zeolites hinge on upon factors like catalyst synthetic procedures and catalytic paths, which are intricately related to the zeolitic support and their properties [117,118] such as the morphological constraints, and the Si:Al ratio.

Groothaert *et al.* [117] oxidized CH_4 with a high selectivity to CH_3OH by ZSM-5 and MOR zeolites modified with copper. The catalysts were activated in O_2 or N_2O . In this process, in the first step, Cu-zeolite was activated by O_2 at a more than 300 °C, which produced a highly activated bis(μ -oxo)di-copper active species. Then CH_4 was allowed to mix onto the activated catalyst at minimum 125 °C. A highly selective methanol (98%) product was obtained upon extracting the catalyst with water and acetonitrile. When the desorption temperature was increased to 300 °C, there was over oxidation to CO_2 . This showed that desorption of methanol from the catalyst is a concern in this type of process. It was also reported previously that preparation procedures of Cu-zeolites also affects their catalytic activities. The Cu/Al ratio in the range of 0.1-0.32 depicted a linear relation in methanol production. A Cu/Al ratio range of 0.32-0.58 produced a maximum value of *ca.* 9 $\mu\text{mol g}^{-1}$ on the oxygen activated (450 °C) Cu-ZSM-5 catalysts in oxidation of methane (175 °C). So, all the Cu species did not perform as active sites for activation of methane. Less than 5% of copper atoms in Cu-ZSM-5, where Cu: CH_3OH stoichiometric ratio was 2:1, was active in methanol production. In this catalyst,

TABLE-2
COMPARISON OF METHANE OXIDATION BY H_2O_2 OVER Fe- AND Cu-BASED ZEOLITE IN BATCH REACTOR MODEL [60]

Catalyst	Methane conversion (%)	Methanol selectivity (%)	Other product (formic acid and CO_2) selectivity (%)
ZSM-5	0.3	19	59
2.5%Fe-ZSM-5	0.7	12	89
2.5% Fe-2.5% Cu-ZSM-5	0.7	85	15

Cu:Al ratio was 0.32117 and observed that Cu-mordenite (MOR) catalyst (where Si/Al = 8.8, Cu/Al = 0.43) showed better performance (methanol yield $11.34 \mu\text{mol g}^{-1}$) than Cu-ZSM-5. In same reaction, zeolite Y (with Si/Al = 2.7, Cu/Al = 0.05 and 0.29) and amorphous silica (Si/Al = 141, 2 wt.% Cu) demonstrated very low yield of methanol (below $1 \mu\text{mol g}^{-1}$). The Si/Al ratio also governs the catalytic performances of Cu-zeolites. The productivity of methanol progressively reduced with growing Si/Al ratios on Cu-ZSM-5 [118]. For catalysts with a Si/Al ratio in the range within 12 to 120, methanol yield was found to have a linear correlation. But, on Cu-MOR zeolites there is an increase in methanol productivity with Si/Al ratio of 5.3 and 8.8, just contrary to Cu-ZSM-5 catalytic systems.

Extensive investigations have been done on the reaction conditions for transformation of methane to methanol. When the reaction temperature was decreased from 175 to 150 °C, there was no noticeable effect on the productivity of methanol on Cu-ZSM-5, but for Cu-MOR, there has been a sharp drop in methanol yield. Both Cu-ZSM-5 [119] and Cu-MOR zeolites [118] showed a higher yield when the temperature was increased to 200 °C. When the pressure of methane was increased to 8 bar, there was a considerable increase in catalytic performance for copper modified MOR, ZSM-5 and BEA zeolites. Methanol yield was highest ($119 \mu\text{mol g}^{-1}$) with Cu-MOR, while with Cu-BEA the highest methanol selectivity was observed (98%). For Cu-ZSM-5 catalyst, the methanol productivity was $16 \mu\text{mol g}^{-1}$ and selectivity of 52% were observed [120]. Further, increase the reaction temperature resulted in sharp decline in methanol productions on these catalysts.

Cu-Y zeolites were traditionally regarded as ineffective for converting methane to methanol under standard conditions. However, van Bokhoven *et al.* [120] employed Cu-Y zeolite in the oxidation of methane at 360 °C after activating the catalyst at 400 °C in oxygen at ambient methane pressure. The yield of methanol was remarkably high ($90 \mu\text{mol g}^{-1}$) with selectivity of 92%. An extraordinary high methanol yield of 303 and 360 $\mu\text{mol g}^{-1}$ were observed when the methane pressure was increased to 8 bars and 15 bars respectively, and the selectivity was 90%. The Cu-zeolites which were synthesized by traditional liquid-phase ion exchange procedure showed low methanol productivity even under strong O₂ activation conditions [121, 122]. A Cu-MOR catalyst prepared by a solid-state ion-exchange (SSIE) approach showed greater productivity of methanol by raising the temperature up to 650 °C [123]. It is pertinent to mention here that Cu-MOR catalysts which are synthesized by SSIE, showed a higher activity in methane oxidation than conventional liquid-phase ion exchange prepared Cu-MOR even upon activation in O₂ at 450 °C. While zeolites like ZSM-5, MOR and Y have been traditionally used, other zeolites with varying properties and pore sizes have been explored. The Cu-

modified EMT, FER, BEA and omega zeolites displayed poor productivity of methanol under specific conditions, unlike the aforementioned zeolites. However, small-pore zeolites such as Cu-SSZ-13, Cu-SSZ-16, Cu-SSZ-39 and Cu-SAPO-34 showed better performance for methane to methanol conversion, with usually higher methanol productivity compared to medium pore ZSM-5 and large-pore MOR under similar reaction conditions [118,120,124]. A comparative study of methane partial oxidation to methanol by iron and copper containing zeolites under flow reactor has been presented in Table-3. Research by Groothaert *et al.* [118] revealed that even after extraction of methanol, the residual methanol is converted to CO₂ at 300 °C over Cu-ZSM-5 zeolite. This is due to existence of methanol in zeolite samples due to incomplete extraction and oxidation of this methanol to CO₂ upon increasing the temperature. Online methanol desorption with wet inert gas stream at higher temperature was more effective methanol desorption route. van Bokhoven *et al.* [120] conducted a comparative study of two methanol desorption methodologies on Cu-Y catalyst. Their findings demonstrated that the yield of methanol achieved by double extraction with 2-4 mL of pure water is comparable to that obtained by desorption with a wet stream of helium (2.6 vol% H₂O, 40 mL min⁻¹, 1 bar).

The use of sodium form of zeolites has been a subject of interest. A series of Cu-zeolites were prepared using Na-form zeolites as the supports [124]. The amount of methanol produced on Cu-Na-ZSM-5 and copper exchanged H-ZSM-5 were equivalent. Different cases were reported on Na-MOR zeolites with different Si:Al ratios, Na-Y, Na-FER and Na-SSZ-13. It has been proved that Na⁺ ions have a negligible influence on the active Cu sites in zeolites.

In the conventional methane to methanol two-step reaction, Cu-zeolites were activated with oxygen at around 450 °C and subsequently, the reaction with methane was carried out at a lower temperature (*e.g.* 200 °C). Finally methanol was recovered by extraction with water at ambient temperature or by desorption by steaming at an elevated temperature. An effective way to improve methanol production is the cyclic operation of the two-step stoichiometric reaction. A representative study of two step catalytic methane oxidation over copper containing zeolites has been presented in Table-4. van Bokhoven *et al.* [122] activated Cu-MOR at 200 °C and also Cu-eronite (ERI) system at 300 °C and showed that low temperature activation of O₂ was sufficient for Cu-zeolites to convert methane into methanol [122]. These findings prompted the development of an isothermal process for converting methane to methanol over Cu-zeolites, where both oxygen activation and methane reaction occur at the same temperature. The effect of oxygen and methane pressures on methanol yield was analyzed on Cu-MOR catalyst. The results obtained in the two processes namely, isothermal

TABLE-3
COMPARISON OF METHANE OXIDATION BY H₂O₂ OVER Fe- AND Cu-BASED ZEOLITE IN FLOW REACTOR MODEL

Catalyst	Methane conversion (%)	Methanol selectivity (%)	Other product (formic acid and CO ₂) selectivity (%)
ZSM-5	0.5	9	90
1.5% Fe-ZSM-5	0.2	15	85
1.5% Fe-1.5% Cu-ZSM-5	0.5	92	8

TABLE-4
TWO STEP CATALYTIC METHANE TO METHANOL REACTIONS AND
PERFORMANCES OF SOME REPRESENTATIVE Cu INCORPORATED ZEOLITES

Zeolite	Si/Al ratio	Cu/Al ratio	O ₂ activation T (K)	Methane reaction T (K)	Methane pressure (bar)	Methanol productivity (μmol g ⁻¹)	Methanol selectivity (%)	Ref.
ZSM-5 ^a	12	0.58	723	448	1	8.2	98	[117]
ZSM-5 ^a	11.6	0.53	673	473	8	31	52	[120]
MOR ^a	10.5	0.39	673	473	8	119	91	[120]
Y ^b	2.6	0.41	673	633	15	360	93	[120]
BEA ^a	12.4	0.4	673	473	8	55	98	[120]
SSZ-13 ^b	12	0.35	723	473	1	31	–	[119]

^aMethod of preparation: Ion-exchange. Ambient temperature methanol extraction with water.

^bMethod of preparation: Ion-exchange. Methanol desorption at ≥ 200 °C with wet inert gas stream.

and two-step stoichiometric conditions were comparable [120]. Kim *et al.* [125] were able to obtain 4% enhancement in the productivity of methanol on Cu-MOR by optimizing the preparation, pre-treatment and reaction conditions for methane conversion. Alvarez *et al.* [126] developed a three-step cyclic procedure on Cu-MOR catalyst. In this system, in the adsorption step, methane was fed at 200 °C. Secondly, methanol was desorbed by a flow of water in nitrogen gas at 150 °C and finally, the catalyst was activated by oxygen or air at 450 °C. Ambient pressure of 1 bar was maintained for all three steps. They found that the activation and desorption conditions have great influence on the yield of methanol. To avoid the over oxidation of methane to CO₂, water was used as soft oxidant for methane oxidation on Cu-MOR zeolite [127]. The stepwise cyclic reaction of methane-to-methanol with oxidants (*e.g.* O₂ or H₂O) on Cu-zeolites creates the commercial difficulties because of its stoichiometric property and the requirement of frequent temperature variations.

Upon using O₂ as oxidant, Roman-Leshkov *et al.* [128] reported that active Cu sites in zeolite matrices can directly convert methane to methanol. These values were higher than that reported with Cu-Na-ZSM-5 using the extraction gas without use of methane or those found by Lobo *et al.* [129] and Grouthaert *et al.* [117] using an off-line solution extraction. This signifies that there may be oxidation of methane in the extraction gas to methanol as well. Therefore there may be an increase in the productivity of methanol. Lobo *et al.* [129] executed methane to methanol oxidation reaction over SSZ-13 with N₂O as oxidant instead of O₂. The results suggested that N₂O produced higher methanol yield than O₂ at 200 and 300 °C. Upon studying in details, it could be observed that crystalline, microporous structure of zeolites with small pores are better for catalytic conversion of methane to methanol. The structure of active Cu sites in zeolites is one of the key parameters which influences the activity in the methane to methanol reaction. That is why, extensive research has been pursued to study the copper sites in Cu-zeolites [117,118,130,131]. EPR, XAFS and FTIR studies experimentally proved the existence of monocopper species like Cu⁺, Cu²⁺ and [CuOH]⁺ [130,132]. However, Kulkarni *et al.* [133] predicted the Cu species to be comprised of 53% of 8-membered ring (8MR) Cu-H₂O, 33% of 6-membered ring (6MR), MR-Cu and 11% of 8-membered ring 8MR-Cu-OH by using equilibrium analysis and Gibbs formation energies at 450 °C with 5% water partial pressure.

Based on Wulfers's data [119], only 3-9% of total Cu species was involved in the oxidation of methane in Cu-CHA zeolites which suggested that 8MR-Cu-OH species are the actual active species in this type of reaction.

At first, it was assumed that a *bis*(μ-oxo)di-copper site having a specific UV-vis signal at 22,700 cm⁻¹ is the active site. However, more recent combined Raman DFT study showed that the site actually is a mono(μ-oxo)di-copper site [134]. After studying the linear correlation of the intensity of the band and the amount of methanol extracted, it was suggested that the di-copper core is the only active site in the conversion over Cu-ZSM-5 [121], Cu-MOR also has same UV-vis nature, featuring μ-oxo di-copper site, but there may be other active sites responsible for the formation of methanol. Beznis *et al.* [121] suggested that particles on the outer surface of Cu-ZSM-5 particles are inactive. The catalytic systems of Cu-ZSM-5 and Cu-MOR have been studied most thoroughly compared to other catalysts.

Conclusively, there may be many types of active sites over which methane is converted to methanol. However, only a part has been identified experimentally so far. More extensive research is required in selectively stabilizing and identifying active sites. Despite considerable spectroscopic effort and the growing evidence that there may not be one universal active site, further detailed *in situ* studies are needed to investigate about the existence of copper oligomers and whether other active species exist as the reaction proceeds.

Conclusion

Research in the field of selective partial oxidation of methane to methanol has been a challenge for the chemists for almost over a century now. It is also significant that in present context of climate change and global warming, conversion of a potent greenhouse gas into some valuable chemicals will be a double benefit for all. Although methane monooxygenase (MMOs) perform this dream reaction at ambient condition, it not applicable for a large scale because of its low specific activity. Heterogeneous catalysts prepared by metal exchanged zeolites or porous matrices has been employed as mimic to this biological systems. Iron and copper exchanged zeolites have been found to activate methane at relatively low temperature to produce methanol but still, selectivity has been one of the major challenges. Because of the high zeolite acidity, desorption of methanol become more tedious and there is probability of over oxidation

of methanol to some over oxidized product like formaldehyde, thereby lowering methanol yield. Many types of the reaction conditions, different types of oxidants and different metal exchanged zeolites have been applied. Copper-exchanged zeolites have performed as best catalyst for this reaction, both in terms of methanol productivity and methanol selectivity. But there remains many questions yet to be answered, like the exact nature of the active sites, the zeolitic parameters are also to be understood in more detail. The demand for methanol is increasing and so there is necessity of developing new strategies to convert methane to methanol. Heterogeneous catalysts have played a crucial role in this research. So, there is every reason to be optimistic for generation of new functional heterogeneous catalytic materials in near future where this grand challenge can be solved through innovative catalyst design and engineering techniques.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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