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Metal-zeolite catalysts promoting low-temperature methane oxidation to oxygenates

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Abstract

Catalytic conversion of methane (CH₄) into value-added chemicals provides a viable path to reduce dependency on crude oil. Despite the challenges associated with activating methane's C–H bond and limiting side reactions, low-temperature oxidation of methane to oxygenates has emerged as a promising approach, often hailed as a “grail reaction”. Zeolite-based metal (metal-zeolite) catalysts facilitate methane oxidation at low temperatures, converting methane into oxygenates while minimizing the complete oxidation to carbon dioxide (CO₂). This review highlights recent achievements in metal-zeolite catalysts for methane partial and coupling oxidation. With zeolite as the core, we explore the synthesis methods, metallic active sites, reaction mechanisms, and zeolite descriptors of metal-zeolite catalysts for methane partial oxidation. Additionally, we examine the critical role of mono- and bi-metallic species in metal-zeolite catalysts for methane coupling oxidation with carbon monoxide (CO). Finally, we discuss the challenges and opportunities for metal-zeolite catalysts in methane oxidation under mild conditions, proposing future directions for rational design of metal-zeolite catalysts, revealing reaction mechanisms through *operando* or *in situ* techniques, and leveraging artificial intelligence (AI) for enhanced catalytic efficiency.

Keywords: Metal-zeolite catalysts, low-temperature oxidation, methane conversion, oxygenated products



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INTRODUCTION

Natural gas, containing 70%-90% methane (CH_4), is estimated to have global reserves exceeding 190 trillion cubic meters and is recognized as a clean and abundant resource^[1,2]. Conventional methane utilization relies on reforming and Fischer-Tropsch processes, which are both energy-intensive and costly^[3,4]. Recently, low-temperature methane oxidation to oxygenates, including methanol (CH_3OH), formic acid (HCOOH), and acetic acid (CH_3COOH), has been identified as an ideal alternative pathway^[5]. These methane-derived oxygenated products are significant platform compounds for producing commodity chemicals, which enhances natural gas utilization efficiency and reduces dependence on petroleum-based chemicals^[6-11]. However, the generated oxygenates are more reactive than methane and can be easily over-oxidized to carbon monoxide (CO) and carbon dioxide (CO_2), posing a challenge for high activity and selectivity^[12]. Thus, highly active and selective metal species are essential for efficient low-temperature methane oxidation. Various homogeneous and heterogeneous catalysts, including metal oxides^[13,14], metal complex^[15-17], and metal-organic frameworks (MOFs)^[18,19], have been used for low-temperature methane oxidation in the presence of N_2O or H_2O_2 as oxidants^[20,21]. Compared to the above-mentioned catalytic systems, zeolite materials provide unique spatial nanoconfinement effects within their microporous channels for constructing enzyme-like metal species with high activity, surpassing most homogeneous and heterogeneous metal-containing catalysts for low-temperature methane oxidation^[22].

Zeolites are crystalline materials with uniform micropores (typically less than 2 nm), high surface areas, tunable framework compositions, and good (hydro)thermal stabilities, which are constructed by corner-sharing TO_4 tetrahedra (T represents Si, Al, P, etc.)^[23]. The TO_4 tetrahedra can be connected in different ways to form various zeolite topologies, each of which is assigned a three-letter code by the International Zeolite Association (IZA)^[24]. In this review article, chabazite (CHA), ferrierite (FER), mordenite (MOR), faujasite (FAU), and Mobil-five (MFI) are mainly discussed. Zeolites are widely used for industrial applications in catalysis and separation^[25]. Incorporation of trivalent metal atoms, such as Al and Ga, into the zeolite lattice yields a negatively charged framework, which is balanced by extra-framework cations or protons toward electrical neutrality. Diverse metallic species can be incorporated into zeolite channels via ion exchange or *in situ* synthesis methods. The isolation of metal cations at ion-exchange (IE) sites and the unique spatial nanoconfinement effect in zeolites impart metallic species with unique electronic structures and thus distinctive catalytic performances. The microporous structure of zeolite effectively restricts side reactions, thus enhancing the yield of the desired products^[26]. Additionally, the strong acidity of zeolites plays a crucial role in light alkane conversions^[27,28]. Specifically, iron (Fe) and copper (Cu) ions within zeolites exhibit remarkable activity in the methane conversion to oxygenates. Furthermore, zeolite-encapsulated metal clusters and nanoparticles (e.g., Au, AuPd, and Pd) have been employed to achieve high activity for the production of methanol from methane^[29-32]. Zeolite-based metal (metal-zeolite) catalysts significantly promote the conversion of methane to oxygenates, positioning them as highly promising candidates for catalysis^[33-40]. Methane oxidation establishes the links between natural gas, flare gas, shale gas, biogas and value-added chemicals such as olefin, fuel, solvent, etc., which is significant for pursuing a sustainable supply of chemicals and energy^[41] [Figure 1].

In this review, recent advancements in metal-zeolite catalysts containing various metallic species for low-temperature methane oxidation were summarized. We provide a comprehensive overview of synthesis methods, metallic active sites, reaction mechanisms, and zeolite descriptors that promote both direct methane oxidation and methane coupling oxidation with CO to form oxygenates. This highlights the efficient catalytic system arising from the synergy between metal species and zeolite framework. The outlook section addresses challenges and opportunities faced by metal-zeolite catalysts in catalyzing low-temperature methane oxidation, aiming to advance research in low-carbon alkane oxidation and inspire the improvement of metal-zeolite catalysts.

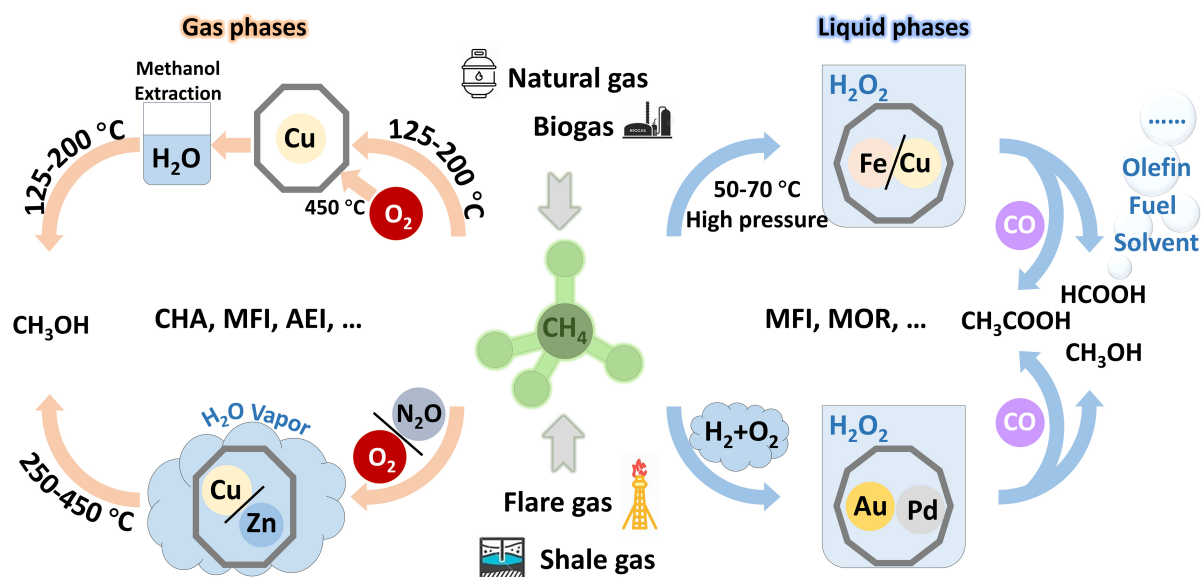


Figure 1. Schematic of catalytic processes of methane oxidation to produce oxygenates under (left) gas and (right) liquid phases over metal-zeolite catalysts.

METHANE TO OXYGENATES OVER METAL-ZEOLITE CATALYSTS

Low-temperature methane oxidation to oxygenates has garnered significant interest as a potential route for substantially reducing the processing cost^[42-47]. Over the past two decades, several processes have been developed: (i) continuous conversion under moderate conditions using metal-zeolite catalysts with N₂O/O₂^[48-53]; (ii) chemical looping systems employing metal-zeolite catalysts with O₂^[54,55]; and (iii) methane oxidation to oxygenates utilizing H₂O₂/(H₂ + O₂)/O₂ at low temperatures in aqueous conditions^[56] [Figure 1]. Metallic species, Fe, Cu, Co, etc., at the IE sites of zeolites^[57-61] have successfully mimicked soluble and particulate methane monooxygenases (sMMO and pMMO)^[62-67], facilitating methane conversion to oxygenates under mild conditions. These catalysts have emerged as attractive options in catalytic oxidation research^[68-75]. This section will explore the metal-zeolite catalysts for direct partial methane oxidation from the views of synthesis methods, active metallic sites, reaction mechanisms, and zeolite descriptors.

Fe-containing zeolite catalysts

Modulating synthesis methods to promote low-temperature methane oxidation

It is widely recognized that mononuclear and binuclear Fe located at the IE sites exhibit exceptional activity for the oxidation of methane in hydrogen peroxide (H₂O₂) systems, owing to their structural similarity to methane monooxygenase^[28]. In addition to active mononuclear and binuclear species, metallic clusters and nanoparticles are experimentally confirmed to exist in Fe-containing zeolites, which display limited activity in low-temperature methane oxidation. Therefore, it is crucial to deliberately increase the proportion of active species during catalyst design. The synthesis method of metal-zeolite catalysts significantly influences the active species and thus the catalyst activity and selectivity.

Post-treatment strategy

Various post-treatment methods have been employed to prepare metal-containing zeolites^[60,76]. These methods include wet impregnation (WI), aqueous phase IE, and solid-state ion-exchange (SSIE). Taking Fe-

containing zeolite catalysts as an example, compared with IE and SSIE methods, the WI method generally leads to the formation of larger metal species with poor dispersion [Figure 2]. In 2012, Hammond *et al.* reported that Fe-containing ZSM-5 zeolites synthesized by SSIE enabled partial methane oxidation to oxygenates (primarily HCOOH) using H_2O_2 as an oxidant^[77]. Additionally, Fe/MOR zeolite consisting of binuclear Fe sites was also successfully prepared using the SSIE method^[78]. Similarly, Yu *et al.* compared Fe/ZSM-5 catalysts synthesized by WI, IE, and SSIE methods^[79]. They employed scanning transmission electron microscopy (STEM), ultraviolet-visible diffuse reflectance (UV-vis DR), and ^{57}Fe Mössbauer spectroscopy for visualization and quantitative analysis of Fe species and provided a semi-quantitative estimation of their distribution. The proportion of mononuclear Fe species decreases in the order of $\text{Fe/ZSM-5}_{\text{SSIE}} > \text{Fe/ZSM-5}_{\text{IE}} > \text{Fe/ZSM-5}_{\text{WI}}$. The results indicated that the WI and IE processes led to unavoidable aggregation of Fe species during the hydrolysis and drying processes under an aqueous condition. In contrast, the SSIE method mitigated these issues by employing the solvent-free synthesis process, which effectively suppressed the aggregation of Fe species and prevented the formation of large Fe oxides. In another work, Kim *et al.* compared different synthesis methods and concluded that the IE method produced isolated or oligonuclear extra-framework Fe species more effectively than SSIE, chemical vapor infiltration (CVI), hydrothermal synthesis, and WI methods^[80]. Consequently, the IE samples showed superior catalytic activity compared to those synthesized by other techniques. It should be noted that the differences in particle size, hierarchical structure, framework Si/Al ratio, location of framework Al atoms of zeolite supports significantly affect the nuclearity and distribution of extra-framework metallic species that are introduced via post-treatment methods. In addition, with rising Fe content of Fe-ZSM-5 catalyst synthesized by post-treatment strategy, the proportion of low-activity Fe clusters and nanoparticles would increase, leading to metal aggregation on the crystal surface and adversely affecting the catalyst performance.

In situ strategy

In situ introduction method enhances Fe dispersion and increases the proportion of active species. For instance, Cheng *et al.* introduced Fe source into the seed-directed template-free synthesis system of ZSM-5 zeolite (Fe-HZ5-TF)^[81]. This organic-template-free approach enabled introduction of more Fe atoms into the zeolite framework. These framework Fe atoms have a strong propensity to migrate out of the framework to form isolated extra-framework Fe species under thermal treatment, leading to the formation of Fe-HZ5-TF catalyst (0.39 wt% of Fe loading). Overall, Fe-HZ5-TF demonstrated three times the number of active sites compared to conventional Fe-ZSM-5 catalysts. The resultant Fe-HZ5-TF achieved a high C1 oxygenate yield of $109.4 \text{ mmol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ during methane oxidation using 0.5 M hydrogen peroxide at 75 °C. Recently, Zhang *et al.* adopted an amino acid-assisted hydrothermal synthesis method to prepare a framework aluminum-rich ZSM-5 zeolite with a Si/Al ratio of 9 ($\text{Z-L}_{0.3}\text{H}_6\text{-9}$)^[82]. The Fe source was directly introduced to the synthesis system of $\text{Z-L}_{0.3}\text{H}_6\text{-9}$ zeolite, leading to $0.44\text{Fe@Z-L}_{0.3}\text{H}_6\text{-9}$ catalysts (0.44 represents the Fe loading of 0.44 wt%). The resultant $0.44\text{Fe@Z-L}_{0.3}\text{H}_6\text{-9}$, consisting of 73% mononuclear Fe^{3+} and 27% binuclear Fe^{3+} species, exhibited exceptional oxygenate yield and turnover frequency (TOF) of $41.3 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$ and 526 h^{-1} , respectively, which surpasses the performance of $0.48\text{Fe/Z-L}_{0.3}\text{H}_6\text{-9}$ ($32.8 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$ and 383 h^{-1}) synthesized through SSIE method.

Modulating zeolite descriptors to promote methane conversion

Framework trivalent atoms

The active Fe^{3+} species in zeolites are typically anchored by negatively charged MO_4 ($\text{M} = \text{Al}, \text{Ga}$) tetrahedra in the zeolite framework. Therefore, it is highly desirable to increase the concentration of framework trivalent atoms, which is effective in maximizing mononuclear and/or binuclear Fe^{3+} sites^[25]. Hammond *et al.* demonstrated that the copresence of Al^{3+} and Ga^{3+} is essential for enhanced catalytic activity^[60]. Firstly,

Post-treatment strategies:

Wet impregnation (WI); Aqueous phase ion-exchange (IE); Solid-state ion-exchange (SSIE)

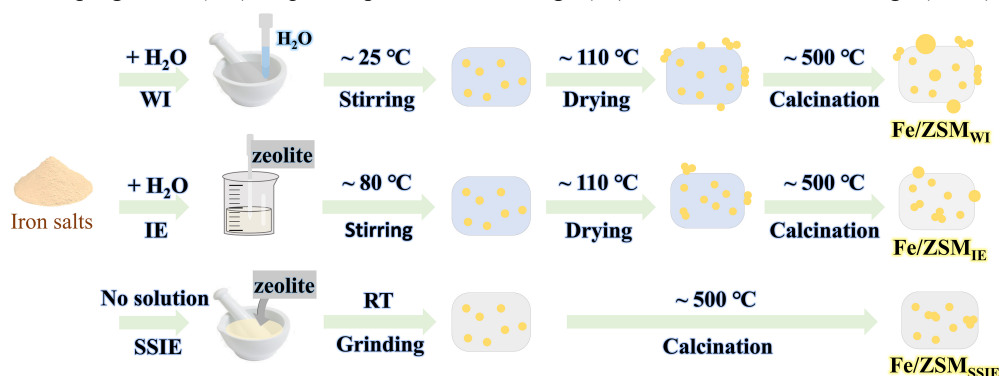
**In situ strategies:** Seed-directed template-free synthesis; Amino acid-assisted synthesis

Figure 2. Schematic illustration of post-treatment and *in situ* synthesis methods of Fe-containing zeolite catalysts. Compared to IE, SSIE, and *in situ* synthesis methods, the WI method tends to cause metal particle agglomeration. IE: Ion-exchange; SSIE: solid-state ion-exchange; WI: wet impregnation.

the copresence of framework Al^{3+} or Ga^{3+} enhances the formation of extra-framework Fe species. Secondly, the capability of stabilizing and retaining the distribution of active Fe species is promoted. In addition, Brønsted acid sites derived from framework trivalent atoms provide a synergistic effect with metal species. For instance, Shahami and Shantz employed several trivalent atoms (Ga, Al, B) in Fe-MFI zeolites for catalytic methane oxidation in the liquid phase^[83]. Using NH_3 temperature-programmed desorption and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of pyridine, they probed the acidity strength and revealed that strong acidity is crucial for hydrogen peroxide activation and enhanced product selectivity. The formation rate of formic acid and the total oxygenated products correlated with total acidity; samples with lower acidity exhibited reduced oxygenate production and selectivity to methanol. Similarly, Zhang *et al.* utilized the framework aluminum-rich ZSM-5 to anchor more active Fe sites for enhanced productivity and TOF as mentioned above^[82]. The synthesis of mononuclear and binuclear Fe species in zeolites is closely tied to the location of framework Al atoms. Computational studies suggested that mononuclear Fe sites form readily on proximal AlO_4 pair sites, whereas binuclear sites are favored on two AlO_4 tetrahedra located at a specific distance within the opened cage structure. Oda *et al.* successfully synthesized ZSM-5 zeolite with varied Si/Al ratios by hydrothermal synthesis using only tetrapropyl ammonium (TPA^+) ion as the structure-directing agent (SDA) [Figure 3A(i)-(iv)]^[84]. The resultant ZSM-5 zeolite has a large number of proximal framework AlO_4 tetrahedra to fix mononuclear Fe species while suppressing the cogeneration of oligomeric Fe sites. HCOOH was the major product over the as-prepared Fe/ZSM-5 catalysts. When the Fe content was set below 0.43 wt%, the oxygenate yields rose with increasing Fe content. By contrast, the oxygenate yield exhibited a decrease when the Fe content exceeds 0.43 wt%. At a high Fe content (0.46–1.1 wt%), the resulting catalyst showed TOF values of 988–

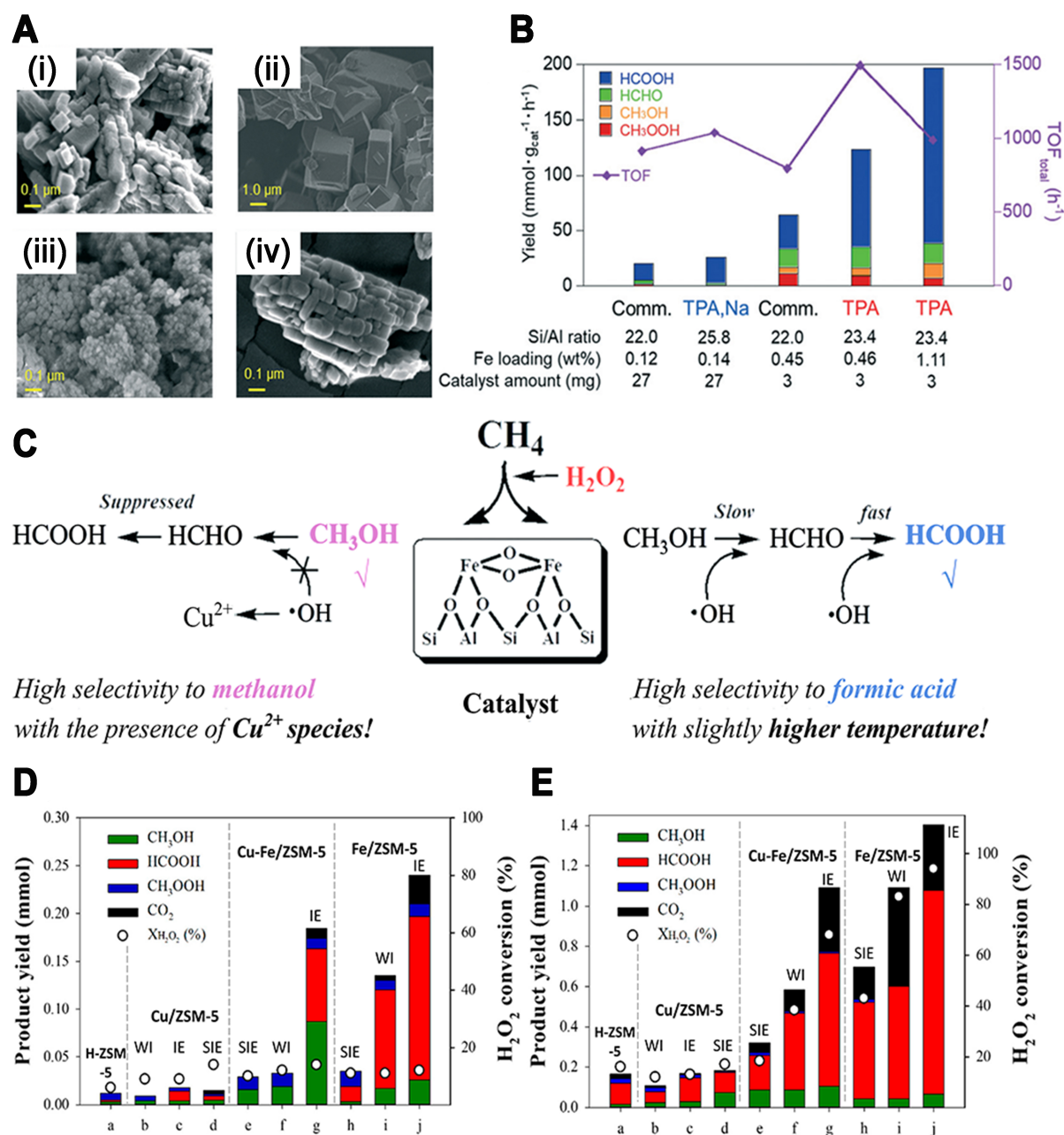


Figure 3. SEM images of ZSM-5 zeolites with varied Si/Al ratios of [A(i)] 12.4, [A(ii)] 22.0, [A(iii)] 50.3, and [A(iv)] 19.6; (B) Comparisons of the catalytic performances of various Fe/ZSM-5 samples. Reprinted with permission from ref^[84]. Copyright 2022. The Royal Society of Chemistry; (C) Proposed reaction pathway controlling the oxidation of methane into methanol and formic acid using H_2O_2 over the Fe/MOR catalyst. Reprinted with permission from ref^[78]. Copyright 2019. The Royal Society of Chemistry. Partial oxidation of methane over different metal-containing ZSM-5 catalysts. Reaction conditions: 50 mg catalyst, 31 bar CH_4 , 0.277 M H_2O_2 , liquid volume = 30 mL, reaction temperature = 30 °C (D), 50 °C (E). Reprinted with permission from ref^[86]. Copyright 2022. MDPI. SEM: Scanning electron microscopy.

1,497 h^{-1} , producing 124–197 $\text{mmol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ of C1 oxidation products at 50 °C [Figure 3B].

Extra-framework copper cations

Copper ions (Cu^{2+}) exhibit a synergistic effect with Fe species in zeolite, enhancing methanol selectivity^[85].

Fang *et al.* demonstrated that the addition of Cu^{2+} effectively enhances the methanol selectivity towards 71.3%^[78]. This is because Cu^{2+} reacts with hydroxyl radicals to prevent the over-oxidation of methanol, thereby promoting methanol selectivity [Figure 3C]. Kim *et al.* investigated the copper-promoted Fe/ZSM-5 catalyst by preparing Cu/ZSM-5, Cu-Fe/ZSM-5, and Fe/ZSM-5 using WI, SSIE, and IE methods [Figure 3D and E]^[86]. Their study examined the influence of copper species on methane oxidation in H_2O_2 . Characterization of the catalysts through UV-vis spectroscopy, nitrogen physical adsorption, hydrogen programmed temperature reduction, and Fourier transform infrared (FTIR) spectroscopy confirmed that copper promoted the methanol selectivity over the Cu-Fe/ZSM-5 catalyst. The resultant Cu/ZSM-5 exhibited low catalytic activity, with oxygenate product yield below 0.05 and 0.4 mmol at 30 and 50 °C, respectively [Figure 3D and E]. This indicates that Cu ions are not the active sites for methane conversion in the aqueous H_2O_2 solution. Fe/ZSM-5 prepared via IE method showed an enhanced oxygenate yield (~0.20 mmol at 30 °C and 1.0 mmol at 40 °C) but high selectivity toward formic acid and CO_2 due to the over-oxidation of methanol, in which the methanol selectivity is below 10%. Notably, the addition of Cu to Fe/ZSM-5 (Cu-Fe/ZSM-5) improved the methanol selectivity with a value approaching ~55%. However, copper species loss was observed during the reaction, with the released homogeneous copper species accelerating H_2O_2 decomposition and increasing CO_2 selectivity. These results highlight the critical role of Cu ions in regulating the selectivity of liquid products.

Pore window size of zeolites

Zeolite pore apertures influence the activity of metallic species, diffusion efficiency of molecules, and product selectivity^[87-90]. This is because the spatial nanoconfinement effects differ in different zeolite topologies, which can significantly alter the intermediate stability and reaction kinetics. Recently, Snyder *et al.* demonstrated that similar active sites exhibit markedly different reactivity with methane when hosted in zeolites with varied pore sizes ('BEA and CHA')^[91]. In large-pore zeolites ('BEA'), active sites deactivate completely after a single turnover, whereas in small-pore zeolites (CHA), 40% of the active sites are maintained, which enables a catalytic cycle. Density functional theory (DFT) calculations combined with spectroscopic characterizations revealed that limited diffusion in small-pore zeolites suppresses the release of CH_3 radicals after C-H activation, which facilitates radical recombination to generate methanol instead of deactivated Fe-OCH₃ species at other sites in the lattice.

Active sites and reaction mechanisms of Fe-containing zeolites

The active site was initially proposed as an extra-framework binuclear Fe species, inspired by methane monooxygenase^[52]. This hypothesis was supported by the results from X-ray absorption fine structure (XAFS), UV-vis, and Raman spectroscopies. The computational model indicated that binuclear Fe sites exhibit exceptional reactivity for H-abstraction from CH_4 ^[92]. Additionally, recent studies revealed that mononuclear Fe is also highly active in the direct methane oxidation to CH_3OH and HCOOH in aqueous solutions^[93-96]. Table 1 summarizes the catalytic performance of reported Fe-containing zeolite catalysts for the selective oxidation of methane using hydrogen peroxide as an oxidant under mild reaction conditions, focusing on metal loading, preparation method, oxygenate yield, and TOF value. The reaction mechanisms for converting methane to CH_3OH and HCOOH in H_2O_2 using Fe-containing zeolite catalysts typically begin with the formation of highly oxidized Fe species through the activation by H_2O_2 , which then oxidizes CH_4 . However, there is a lack of *in situ* characterizations to directly analyze the structures of mono-/binuclear Fe species and their intermediates during catalysis. Current research on the reaction mechanisms often relies on DFT calculations.

Binuclear Fe species

Fang *et al.* identified the extra-framework binuclear $[\text{Fe}_2(\mu\text{-OH})_2\text{O}_2]$ as the active site for methane oxidation

Table 1. Catalytic performance of reported Fe-containing zeolite catalysts for the selective oxidation of methane using hydrogen peroxide as oxidant under mild conditions

Catalysts	Metal loading (wt%)	Nuclearity	Synthesis method	Oxygenates yield ^a (mol·kg _{cat.} ⁻¹ ·h ⁻¹)	TOF ^b (h ⁻¹)	Ref.
Fe-ZSM-5 (WI)	Fe (0.54)	Mononuclear	WI	2.8	28.6	[80]
Fe-ZSM-5 (HT)	Fe (0.59)	Mononuclear	<i>In situ</i>	3.5	33.0	[80]
Fe-ZSM-5 (SIE)	Fe (0.50)	Mononuclear	SSIE	6.8	58.2	[80]
Fe-ZSM-5 (IE)	Fe (0.43)	Mononuclear	IE	17.1	223.0	[80]
Fe-ZSM-5 (84) ₅₅₀	Fe (0.49)	Binuclear	<i>In situ</i>	13.5	154.0	[60]
Fe/ZSM-5(23)	Fe (2.79)	Binuclear	SSIE	8.0	16.1	[97]
Fe-HZ5-TF	Fe (0.40)	Mononuclear	<i>In situ</i>	59.3	849.0	[81]
Ga,Fe-MFI(50)	Fe (1.63)	Extra-framework	<i>In situ</i>	49.4	170.0	[83]
0.5%Fe/ZSM-5	Fe (0.57)	Mononuclear	WI	8.9	88.0	[98]
1%Fe/ZSM-5	Fe (1.10)	Mononuclear	WI	11.0	56.0	[98]
0.03wt%Fe/ZSM-5(66)	Fe (0.028)	Mononuclear	IE	16.6	3,104.0	[92]
Fe ³⁺ /ZSM-5(30) _{COMM}	Fe (2.50)	Mononuclear	SSIE	16.7	37.5	[95]
Cu-Fe/ZSM-5 (30)	Fe (2.50)	Binuclear	SSIE	14.0	31.3	[77]
Cu-Fe(2/0.1)/ZSM-5	Fe (0.13)	Mononuclear	WI	1.7	75.2	[85]
0.44Fe@Z-L _{0.3} H ₆ -9	Fe (0.44)	Mononuclear	<i>In situ</i>	41.3	526.0	[82]

^aOxygenates yield is calculated as moles (total liquid oxygenates) / mass (catalyst) / time; ^bTOF is calculated as moles (total liquid oxygenates) / moles (active metal) / time (hour). TOF: Turnover frequency; WI: wet impregnation; HT: hydrothermal; SIE or SSIE: solid-state ion-exchange; IE: ion-exchange.

in the H₂O₂ solution over Fe/MOR^[78]. The methanol formation mechanism involves a CH₃OOH intermediate pathway: CH₄ adsorbs and reacts with the terminal oxygen species in [Fe₂(μ-OH)₂O₂] to form CH₃O[•]. Then, CH₃O[•] reacts with H₂O₂[•] to generate CH₃OOH[•]. The extraction of one oxygen from CH₃OOH[•] yields CH₃OH[•], which eventually desorbs as methanol [Figure 4A]. Szécsényi *et al.* investigated the methane oxidation on binuclear Fe species in ZSM-5 using periodic DFT calculations^[96]. Their study demonstrated the initial model [(H₂O)₂-Fe(III)-(μ-O)₂-Fe(III)-(H₂O)₂]²⁺ [Figure 4B], which formed Fe(III)-oxo and Fe(IV)-oxo complexes when reaction with H₂O₂. The findings revealed that these sites were catalytically active, with Fe(III) promoting heterolytic and Fenton-type reactions and Fe(IV) facilitating homolytic reactions. Hammond *et al.* proposed a binuclear Fe complex, [Fe₂(μ₂-OH)₂(OH)₂(H₂O)₂]²⁺, along with a preliminary reaction pathway based on this binuclear model^[77]. In this mechanism, two Fe atoms are oxidized to Fe=O and Fe-OOH, facilitating the oxidation of the CH₄ molecule on Fe=O, which combines with Fe-OOH to form methyl hydroperoxide (CH₃OOH) as the first intermediate product.

Mononuclear Fe species

Yu *et al.* identified mononuclear Fe species as the active sites in Fe/ZSM-5 for methane oxidation^[98]. The sample containing 0.1 wt% Fe (0.1% Fe/ZSM-5) primarily consists of mononuclear Fe with octahedral coordination. As seen from Figure 4C(i)-(iv), single-site Fe species are uniformly distributed across the zeolite crystal. *In situ* XAFS analysis provided evidence of the interaction between CH₄ molecular and isolated Fe active centers. Moreover, *in situ* FTIR spectroscopy indicated a strong interaction between Fe³⁺ and CH₄ molecular, which weakens the interaction between Brønsted acid sites and CH₄ molecular. During the oxidation of methane, CH₃OOH and CH₃OH were first generated from CH₄, with CH₃OH further converted to hydroxymethyl hydroperoxide (HOCH₂OOH) and subsequently to HCOOH. In addition, Cheng *et al.* synthesized Fe-ZSM-5 catalysts featuring mononuclear Fe (Fe-HZ5-TF)^[81]. Electron paramagnetic resonance (EPR) spectroscopy and *in situ* DRIFTS results showed that initial mononuclear Fe(III) species are oxidized by H₂O₂, generating Fe(IV)=O species and hydroxyl (•OH) radicals. CH₄ is

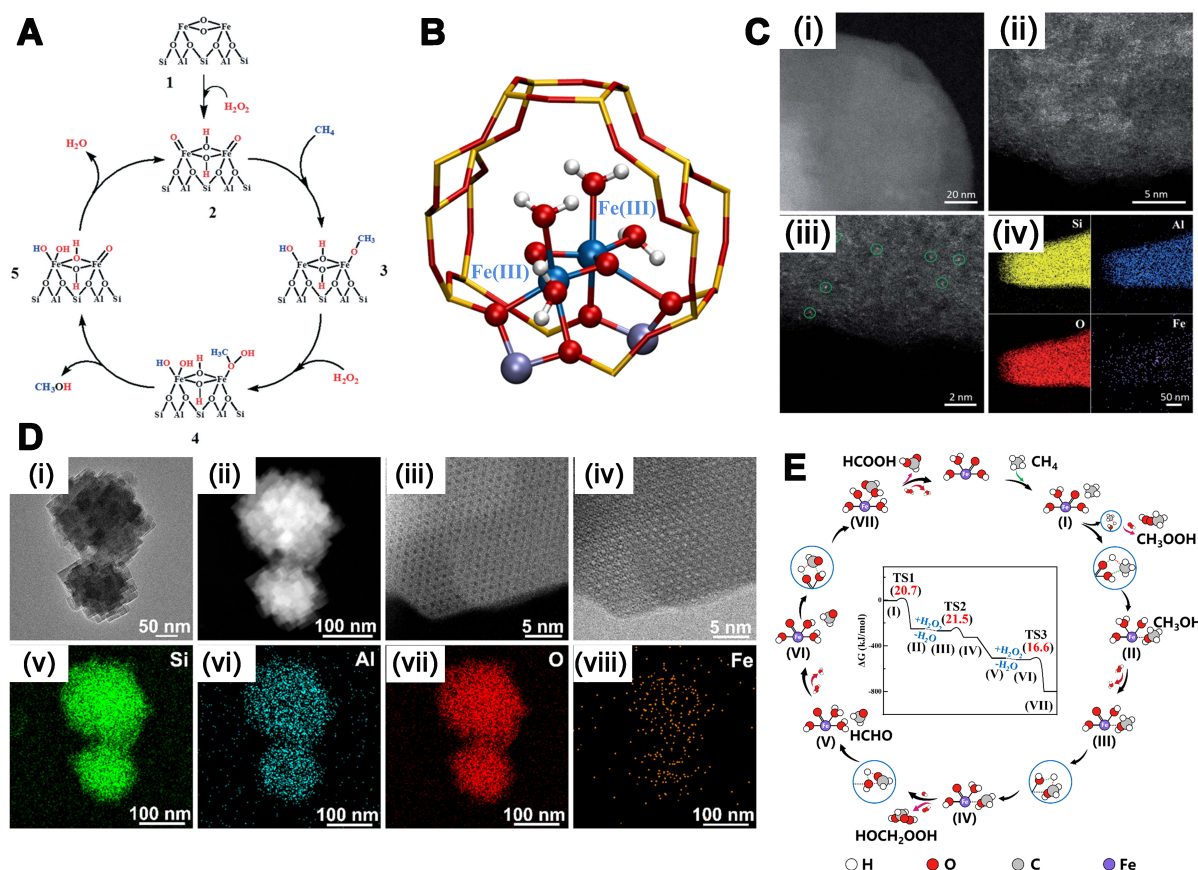


Figure 4. (A) Catalytic cycle for the liquid-phase oxidation of methane to methanol over the binuclear Fe³⁺ species in MOR. Reprinted with permission from ref.^[178]. Copyright 2019. the Royal Society of Chemistry; (B) [(H₂O)₂-Fe(III)-(μ-O)₂-Fe(III)-(H₂O)₂]²⁺ model in ZSM5 zeolite. Reprinted with permission from ref.^[196]. Copyright 2018. American Chemical Society; [C(i)-(iii)] STEM images of the 0.1% Fe/ZSM-5. [C(iv)] Elemental mapping images of the 0.1% Fe/ZSM-5. Reprinted with permission from ref.^[198]. Copyright 2021. The Royal Society of Chemistry; Low-magnification [D(i)] TEM, [D(ii)] STEM, and C₅-corrected. [D(iii)] STEM-ADF and [D(iv)] STEM-ABF images of 0.44Fe@Z-L_{0.3}H₆-9. [D(v)-(viii)] Elemental mappings for Si, Al, O, and Fe elements; (E) Proposed reaction mechanisms and schematic illustrations for the selective oxidation of methane on the mononuclear Fe³⁺. Reprinted with permission from ref.^[182]. Copyright 2024. The Chinese Chemical Society. STEM: Scanning transmission electron microscopy; TEM: transmission electron microscopy; ADF: annular dark-field; ABF: annular bright-field.

consequently adsorbed on the Fe(IV)=O sites, followed by the homolytic cleavage of a C–H bond to generate Fe(III)–OH and methyl (•CH₃) radicals. Subsequently, these •CH₃ radicals combine with peroxy (•OOH) and •OH radicals to form CH₃OOH and CH₃OH. The Fe(III)–OH can be reoxidized to form Fe(IV)=O in the presence of H₂O₂, thereby restarting the catalytic process. Recently, Zhang *et al.* successfully regulated the ratio of mononuclear and binuclear Fe³⁺ sites in aluminum-rich ZSM-5 by varying the Fe content [Figure 4D(i)-(viii)]^[182]. They combined advanced characterizations and catalytic results with DFT calculations to map out the reaction networks for methane conversion into oxygenates over both mononuclear and binuclear Fe³⁺ species. Focusing on the pathway of CH₄ to HCOOH on the [(H₂O)O=Fe^V–(OH)₂]⁺ [Figure 4E], the primary reaction pathway was identified: CH₄(g) → CH₃OH (•CH₃) + (•OH or •OOH) → CH₃OOH/CH₂OH• + (•OH or •OOH) → (•CH₃O)/HOCH₂OH•/HOCH₂OOH → HCOOH, forming four C1 oxygenated products including CH₃OH, CH₃OOH, HOCH₂OOH, and HCOOH. They also investigated the reaction pathway of methane to oxygenate on the active binuclear [H₂O(OH)–Fe^{III}–(μ-OH)₂–Fe^V=O(OH)]²⁺. The calculated Gibbs activation barrier for the rate-limiting step in the methane conversion over the binuclear Fe site is 34.4 kJ/mol, which is higher than that over the mononuclear Fe

(21.5 kJ/mol). This indicates that the mononuclear Fe^{3+} site confined in ZSM-5 zeolite possesses higher activity compared to binuclear Fe^{3+} , which is consistent with the experimental results.

Gas phase methane conversion over Fe-containing zeolites

Fe-containing zeolite catalysts applied in methane oxidation in H_2O_2 aqueous solution have several shortcomings, such as over-oxidation of methanol, high oxidant costs, and low yields of oxygenates^[99]. Due to these limitations in the aqueous-phase catalytic system, one promising option is the gas-phase oxidation of methane. Fe-containing zeolites have shown great potential in gas-phase methane oxidation using N_2O or O_2 as oxidants, offering a more efficient route for methane conversion^[56,100].

N_2O as oxidant

Catalytic conversion of CH_4 with N_2O to value-added chemicals can effectively reduce greenhouse gas emissions while addressing the growing demand for chemicals^[101]. In Fe-containing zeolite catalysts, the mechanism for breaking C–H bonds in the Fe- N_2O system typically involves two steps. Initially, N_2O decomposes at the active Fe center (α -site or α -Fe), generating surface oxygen species (α -O), which can subsequently oxidize inert C–H bonds. Xiao *et al.* utilized the interzeolite conversion method to rapidly synthesize Fe-containing AEI zeolites with varying Si/Fe ratios in a one-pot process^[102]. The reaction mechanism involves N_2O dissociation at the active Fe site, producing highly reactive oxygen species (e.g., $[\text{Fe}=\text{O}]$ or $[\text{Fe}(\mu\text{-O})]^{2+}$) while releasing N_2 . These oxygen species activate the C–H bond of CH_4 to generate methoxy intermediates, which convert to methanol upon interaction with water [Figure 5A]. Specifically, water can facilitate the regeneration of α -Fe active sites through redox interactions, thereby prolonging the catalyst's lifespan and enabling catalytic cycling. Moreover, methane oxidation to methanol can be achieved by loading Fe species in small-pore CHA zeolite, either with or without sodium [Figure 5B and C]^[103]. Fe-containing zeolites show good selectivity and stability under N_2O conditions, but excessive activation of oxygen species may lead to further oxidation of methanol.

O_2 as oxidant

Fe-containing zeolite catalysts also demonstrated activity in the production of methanol from methane using O_2 as the oxidant^[104]. O_2 is abundant, inexpensive, and environmentally friendly, making it preferable over other oxidants such as N_2O and H_2O_2 . Utilizing O_2 streamlines the reaction process by eliminating the need for additional oxidant treatment steps. The unique structure of Fe-containing zeolites enhances O_2 activation and stabilizes high-activity oxygen species, such as $[\text{Fe}=\text{O}]$ and dioxygen bridge $[\text{Fe}(\mu\text{-O})]$, facilitating methane oxidation. Mlekodaj *et al.* systematically investigated the spectral characteristics of the Fe(II) center in FER during an oxidation-reduction cycle at 220 °C using FTIR, Mossbauer, and X-ray absorption spectroscopy (XAS) techniques^[56]. Their studies confirmed the dissociation of O_2 on the cooperating Fe(II) sites [Figure 5D]. With the time reaching 60 min, all Fe(II) in β sites were oxidized and the highest intensity of the band typical for α -O was obtained [Figure 5E]. The interaction between α -O and methane at 220 °C produced methanol in three cycles. Notably, the stability of α -O at elevated temperatures promises the application of Fe-FER catalysts in methane oxidation upon a wide range of temperatures. Table 2 summarizes the catalytic performance of reported Fe- and Cu-containing zeolite catalysts in methane oxidation under the gas phase.

Cu-containing zeolite catalysts

Cu-containing zeolites have demonstrated the ability to convert methane to methanol with high selectivity using O_2 or N_2O as oxidants. Groothaert *et al.* first reported that O_2 -activated Cu-containing MFI and MOR zeolites exhibit activity for methane oxidation to methanol^[52]. Subsequently, it was discovered that Cu-containing CHA zeolite also works on methane oxidation to methanol^[105,106,114]. Two distinct processes for

Table 2. Catalytic performance of reported Fe- and Cu-containing zeolite catalysts for methane oxidation in gas phase

Catalysts	Oxidant	Type	Conditions	Performance	Ref.
Fe/AEI-100	N ₂ O	Continuous	100 mg catalyst, 250 °C, CH ₄ /N ₂ O/H ₂ O/Ar = 10/10/2/3 (total: 25 mL/min)	CH ₃ OH rate: 4.0 μmol·g ⁻¹ ·min ⁻¹	[102]
Fe/AEI-400	N ₂ O	Continuous	100 mg catalyst, 350 °C, CH ₄ /N ₂ O/H ₂ O/Ar = 10/10/2/3 (total: 25 mL/min)	CH ₃ OH rate: 45.0 μmol·g ⁻¹ ·min ⁻¹	[102]
H-Cu-SSZ-13	N ₂ O	Step-wise	300 °C, 30.4 kPa CH ₄ , 30.4 kPa N ₂ O, 3.2 kPa H ₂ O, 37.3 kPa He, flow rate: 120 cm ³ ·min ⁻¹ , WHSV = 19,650 g _{feed} ·g _{cat} ⁻¹ ·h ⁻¹	CH ₃ OH rate: 55.0 μmol·g ⁻¹ ·min ⁻¹	[105]
Cu0.9-CHA13	O ₂	Continuous	300 °C, CH ₄ /O ₂ /H ₂ O/N ₂ = 48/2/10/50 mL·min ⁻¹	CH ₃ OH rate: 236.5 μmol·g ⁻¹ ·h ⁻¹	[106]
Fe-CHA	N ₂ O	Step-wise	Activation: 180 °C, 35% N ₂ O/He Reaction: room temperature pure CH ₄ Extraction: water/acetonitrile mixture	CH ₃ OH yield: 183 μmol·g ⁻¹	[107]
Cu-Na-MOR(0.28)	O ₂	Step-wise	Activation: 250 °C, O ₂ Reaction: 150 °C under CH ₄ Extraction: water/acetonitrile mixture	CH ₃ OH yield: 41.1 μmol·g ⁻¹	[108]
1.1%Cu-H-MOR (15)	O ₂	Continuous	400 °C, 33 mol% methane, 85 ppm O ₂ , and 67 mol% steam	CH ₃ OH rate: 143 ± 1.9 mmol·mol _{Cu} ⁻¹ ·h ⁻¹	[109]
5Cu/AEI(Na)-850	N ₂ O	Continuous	350 °C, N ₂ O/CH ₄ /H ₂ O/Ar = 10/10/2/3 mL·min ⁻¹ , WHSV = 15,000 mL·g ⁻¹ ·h ⁻¹	CH ₃ OH rate: 27.3 μmol·g ⁻¹ ·min ⁻¹	[110]
Cu(0.31)MFI(12)	O ₂	Step-wise	Activation: 450 °C under O ₂ Reaction: 180 °C, 8 bar CH ₄ Extraction: 75 °C, wet Helium	CH ₃ OH yield: 22.8 μmol·g ⁻¹	[111]
Cu/AEI	N ₂ O	Continuous	100 mg catalyst, 350 °C, CH ₄ /N ₂ O/H ₂ O/Ar = 10/10/2/3 (total: 25 mL/min)	CH ₃ OH rate: 41.0 μmol·g ⁻¹ ·min ⁻¹	[112]
Cu-MOR	O ₂	Step-wise	Activation: 450 °C under O ₂ Reaction: 200 °C, 1 bar CH ₄ Extraction: 200 °C, H ₂ O	CH ₃ OH yield: 155.0 μmol·g ⁻¹	[113]

WHSV: Weight hourly space velocity.

the methane conversion to methanol over Cu-containing zeolite catalysts have been proposed: a stepwise method involving successive activation-reaction cycles (referred to as “chemical looping”)^[54,115,116] and a catalytic system utilizing continuous gas flow with either O₂^[117,118] or N₂O^[105] as the oxidant. As the synthesis methods of Cu-containing zeolite are similar to those of Fe-containing zeolite catalysts, this section focuses on the active metallic sites and reaction mechanisms, together with influences of zeolite descriptors on the catalytic performance.

Modulating zeolite descriptors to promote methane oxidation

Cu/Al and Si/Al ratios

Modulating the Cu/Al ratio is effective in promoting the catalytic performance of Cu-containing zeolite for methane oxidation^[108,109]. An optimal Cu/Al ratio strikes a balance between methane conversion rate and methanol selectivity. Dinh *et al.* asserted that low copper loading (Cu/cage < 0.3) combined with high aluminum content (Si/Al > 30) is essential for facilitating methane oxidation by the enhanced amount of [Cu–O–Cu]²⁺ species^[117]. This approach mitigates the formation of other copper structures and Cu_xO_y nanoclusters that favor the over-oxidation of methane to CO₂. Similar to Fe-containing zeolite catalysts, the

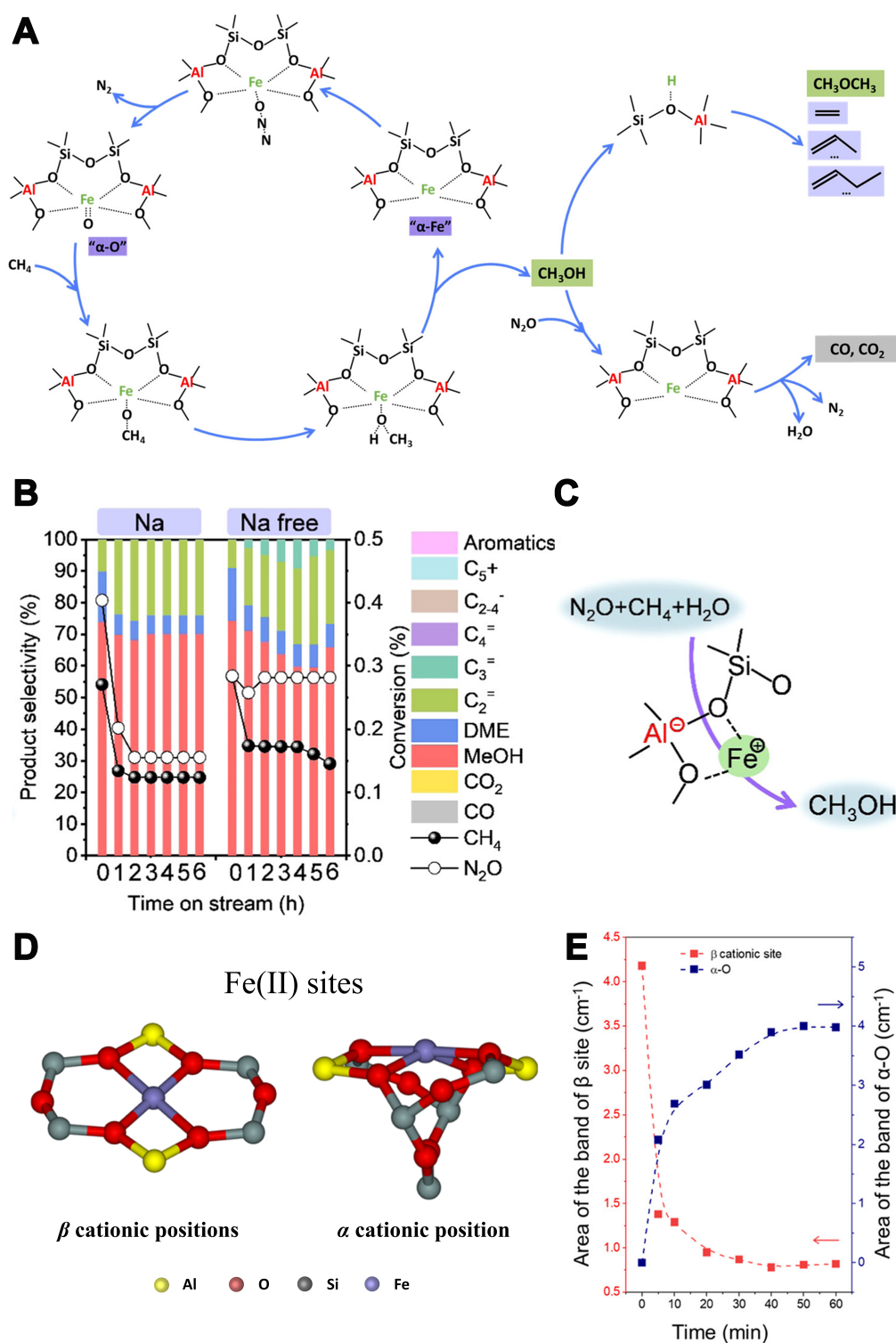


Figure 5. (A) Possible reaction pathway of the direct oxidation of methane with N_2O on the Fe-AEI zeolite catalyst. Reprinted with permission from ref^[102]. Copyright 2023. American Chemical Society; (B) Comparing conversion and selectivity of H-type Fe-CHA(Na)-100 and Fe-CHA(Na free)-100 at 250 °C; (C) Direct oxidation of methane to methanol on active Fe sites over Fe-containing zeolites. Reprinted with permission from ref^[103]. Copyright 2024. American Chemical Society; (D) Schematic representation of Fe(II) located in the β cationic position and the α cationic position; (E) Time dependence of the evolution of the bands characteristic for α -O and Fe(II) in β sites. Reprinted with permission from ref^[56]. Copyright 2023. American Chemical Society.

reactivity of Cu-containing zeolite for methane oxidation is influenced by the Si/Al molar ratio and zeolite topology. Research on methane conversion over Fe-containing zeolite has demonstrated that iron-based α -oxygen active sites can be stabilized at the IE sites that derive from framework Al atoms^[97]. This stabilization principle applies equally to Cu-containing zeolites^[110,119,120]. Artsiusheuski *et al.* provided a clear understanding of the impact of the Cu/Al and Si/Al ratios on the catalytic performance^[111]. They found that, when the Cu/Al ratio was below 0.3, binuclear Cu species with a Cu–Cu of 2.9 Å dipoles and a UV-vis absorption band at 27,200 cm⁻¹ were observed in Cu-containing MFI zeolites. This configuration facilitates the selective methane oxidation to methanol at 450–550 K. In contrast, a higher Cu/Al ratio results in mono- μ -oxo dicopper sites (Cu–Cu = 3.2 Å), which display a characteristic band at 21,900 cm⁻¹ and react with methane at lower temperatures (< 450 K) to produce over-oxidized products [Figure 6A].

Pore window size of zeolites

The variations in size and shape of zeolite pore structures significantly influence the distribution, oxidation state, and stability of active Cu sites, thereby determining their reactivity and selectivity in chemical reactions. Calculations of dimer exchange probabilities across all unique 2Al configurations within various zeolite topologies indicated that binuclear Cu species are preferentially formed at the sites with an Al–Al distance of 5–9 Å^[122–124]. This requirement fosters the formation of dimers in 8- and 10-membered rings (8- and 10-MR) across various zeolite topologies. In contrast, 6-membered rings (6-MR) favor monomer formation, while 4- and 5-membered rings (4- and 5-MR) are generally less favorable for copper exchange due to steric repulsions. Wijerathne *et al.* recently employed spectroscopic characterization, DFT calculations, and machine learning classification models to elucidate the influence of zeolite topologies on copper active sites^[125]. Their study found that MFI-type zeolites, characterized by medium pores and intersecting channels, preferentially form binuclear copper sites. In comparison, CHA and AEI zeolites with small pores are more effective for stabilizing mononuclear copper sites. Furthermore, by employing machine learning models to analyze the formation preferences of mononuclear versus binuclear Cu sites across 200 zeolite types from the International Zeolite Database under varying aluminum configurations, the relationship between the metal nuclearity and zeolite topologies was established, which is of great significance to prepare efficient metal-zeolite catalysts by design. The study revealed that MOR zeolite exhibits a higher proportion of binuclear Cu species than CHA, AFX, BEA, and FER for two primary reasons. Firstly, MOR possesses more 2Al configurations that favor binuclear Cu exchange. Secondly, commercial MOR zeolite decreases the availability of 2Al sites for monomer exchange while increasing the number of 2Al sites that contribute to lowering binuclear Cu exchange free energies. Figure 6B illustrates the structures of Cu species in various zeolite topologies and their evolution during methane conversion^[121]. For Cu-containing MFI, mono- μ -oxo binuclear Cu(II) sites are the predominant species, whereas Cu-containing MOR exhibits a coexistence of mononuclear and binuclear Cu(II) sites, and Cu-containing FAU hosts Cu(II)-oxo clusters. Both mononuclear and binuclear Cu(II) sites transformed to isolated Cu(I) sites, while the Cu(II)-oxo clusters undergo restructuring during the reaction, resulting in the formation of Cu(I)-oxo clusters.

Al pairs in Cu-containing zeolites

Binuclear Cu species has been regarded as a highly active species, which is closely linked to the aluminum pairs (2Al) within the zeolite framework^[126]. In Al-rich zeolites, framework Al atoms predominantly exist in Al–Si–Si–Al and Al–Si–Al sequences, forming Al pairs. These Al pairs provide two adjacent negative charges to stabilize active Cu species, thereby enhancing their reactivity and overall catalytic performance. For instance, using interzeolite conversion method, Xiao *et al.* synthesized AEI-type zeolite with an enhanced amount of Al pairs^[112]. These Al pairs facilitated the formation of abundant binuclear Cu sites in Cu-containing AEI zeolite and therefore enhanced the methane selective oxidation efficiency. This resulted in a

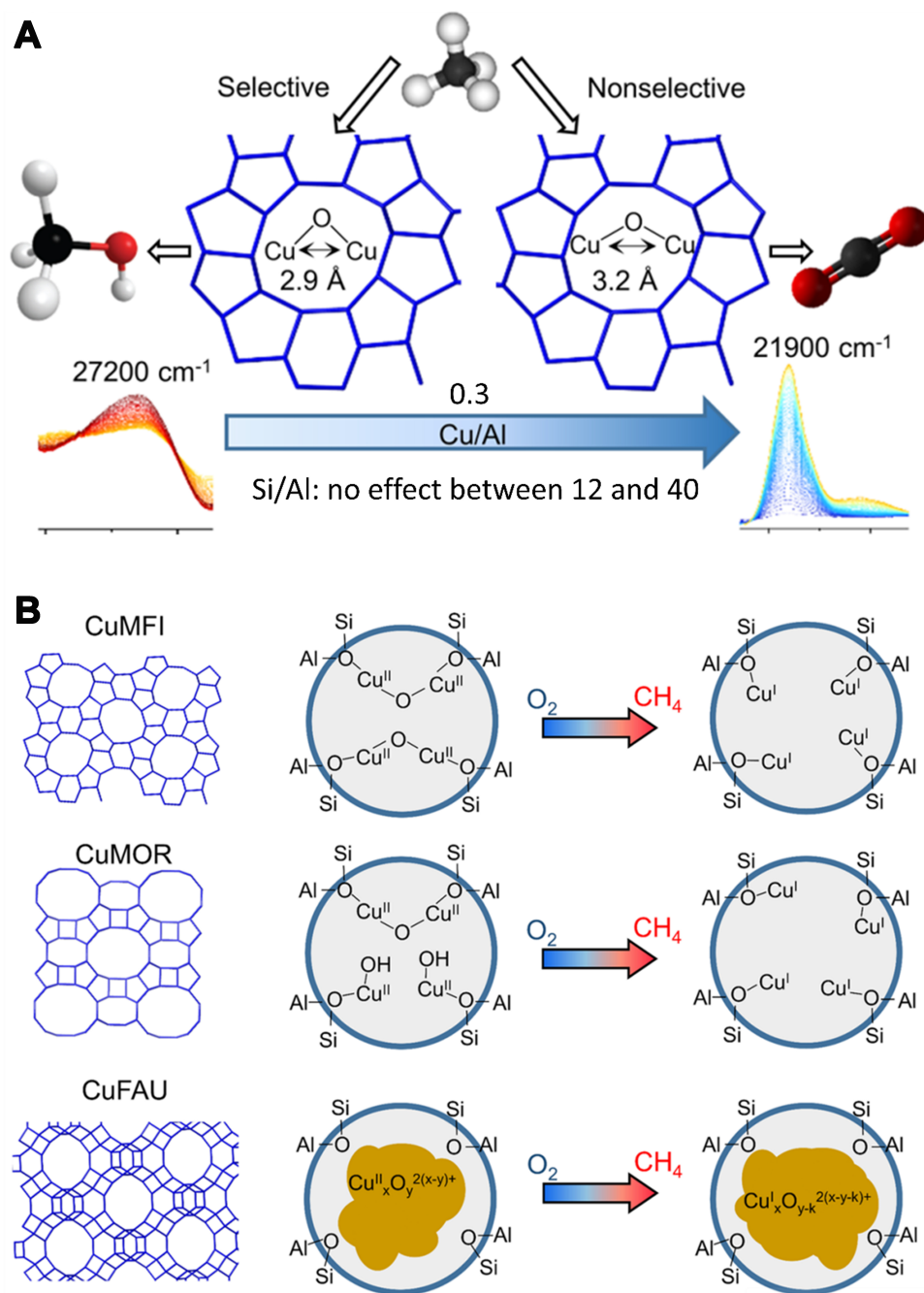


Figure 6. (A) Characteristics of mono- μ -oxo dimeric copper sites formed in oxygen-activated Cu-MFI materials at different Cu/Al ratios. Reprinted with permission from ref^[111]. Copyright 2022. American Chemical Society; (B) Structures of different copper sites hosted in zeolites with different topologies and their evolution during the reaction with methane. Reprinted with permission from ref^[121]. Copyright 2023. American Chemical Society.

methanol productivity of $40.8 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$, a methanol selectivity of 45%, and long-term stability in reactions at 350°C using N_2O as an oxidant.

Active sites in Cu-containing zeolites

It has been widely accepted that multinuclear Cu species are active sites in pMMO^[106,127]. However, the precise structure of Cu species in pMMO remains debatable^[128,129]. The design of Cu-containing zeolite catalysts for methane conversion processes is inspired by these naturally occurring enzymes. UV-vis spectroscopy is generally employed to analyze the configurations of active sites in Cu-containing zeolites, as the UV-vis spectrum varies with the copper composition^[130-133]. The proposed active Cu sites in zeolites primarily involve mono-, bi- and trinuclear Cu species, which will be discussed in this section.

Binuclear Cu species

The high activity of Cu/ZSM-5 zeolite catalyst for CH₄ oxidation to CH₃OH has been demonstrated, which is ascribed to the extra-framework binuclear Cu species in zeolites^[134]. Initially, a bis(μ -oxo) binuclear Cu(II) complex was proposed, denoted as [Cu(μ -O)₂Cu]²⁺, with a UV-vis absorption peak at 22,700 cm⁻¹. Woertink *et al.* highlighted the significance of a (μ -oxo) binuclear Cu(II) complex, namely [Cu(μ -O)Cu]²⁺ sites^[75]. The resonance Raman (rR) vibrations at 237, 456, and 870 cm⁻¹ were assigned to the Cu–O–Cu bending mode of the mono(μ -oxygen bridge) binuclear Cu site (Cu–O–Cu bond angle of 140°), the symmetric Cu-oxygen stretching vibration (ν_s), and the asymmetric Cu-oxygen stretching vibration (ν_{as}), respectively. Recently, utilizing the variable-field magnetic circular dichroism (VTVH MCD) technology, Heyer *et al.* effectively explored the magnetism of these active sites in the mixtures, thereby minimizing interference from other Cu species^[135]. They characterized the magnetic exchange coupling of the [Cu₂O]²⁺ species within CHA and MFI and demonstrated that in binuclear Cu sites, the ground-state magnetism is primarily determined by the relative orientation of the bidentate aluminosilicate zeolite linking the two Cu atoms, rather than the Cu–O–Cu angle [Figure 7A]. Plessers *et al.* identified a new active species for direct methane oxidation to methanol, termed MOR₃, in high copper-loaded Cu-MOR^[108]. Characterized by the UV-vis DR absorption and rR spectroscopy, the MOR₃ was identified as a [CuOCu]²⁺ species with a Cu–O–Cu bond angle of 127°. The location of MOR₃ sites in Cu-K-MOR (0.25) was probed using the bulky substrate tetrahydrofuran which can only react with Cu species exposed to the 12-membered ring (12-MR) channels of MOR. The results indicated that MOR₃ is located inside the 8-MR side pocket or the compressed 8-MR channel. Such MOR₃ species showed higher activity than previously characterized [CuOH]⁺ site, as observed in other [CuOCu]²⁺ sites (a Cu–O–Cu bond angle of 137° and 141°).

Trinuclear Cu species

Recent research highlighted the significance of trinuclear Cu species in methane conversion^[137]. It has been revealed that such a motif promotes oxygen transfer during alkane hydroxylation and enables regeneration of the active site in the presence of O₂. Grundner *et al.* reported the successful modification of H-MOR zeolites with copper (Cu/MOR) featuring uniform extra-framework trinuclear species, which mimic the active metal species in enzyme^[138]. *In situ* XAS results demonstrated the structure of trinuclear Cu-oxo species in activated Cu-MOR, namely [Cu₃(μ -O)₃]²⁺, stabilized by two framework aluminum atoms at the mouth of the 8-MR side pockets. The [Cu₃(μ -O)₃]²⁺ showed remarkable stability under dry conditions, consistent with *ab initio* thermodynamic analyses derived from DFT results. Although methanol extraction by steam treatment leads to the hydrolysis of the cluster, it can be reconstituted without a loss of activity upon reactivation in O₂. Li *et al.* studied the structure of active sites and reaction mechanisms in Cu-containing ZSM-5 zeolite^[136]. The periodic DFT calculations and thermodynamic analyses indicated that, at relatively low O₂ partial pressures, the formation of binuclear [Cu(μ -O)Cu]²⁺ site is favored [Figure 7B], while the trinuclear Cu-oxygen species emerges as the most thermodynamically stable sites in the Cu/ZSM-5 activated at high temperatures in an O₂-rich environment. Both structures can activate methane; however, only the trinuclear complex provides a favorable energy reaction pathway for methanol production, following a direct free radical rebound mechanism.

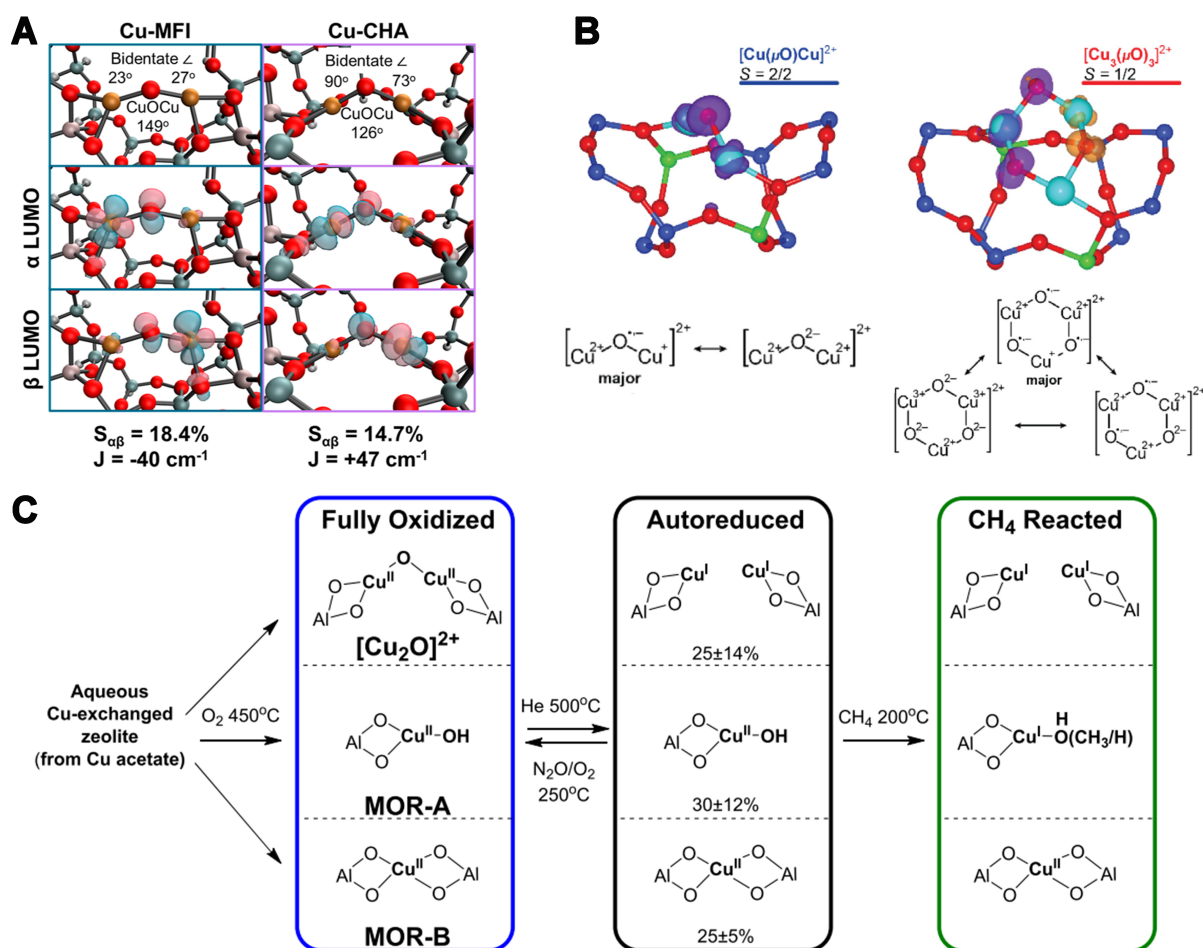


Figure 7. (A) DFT models for Cu-MFI Site 7 (left) and Cu-CHA (right). The orbital contours for the α LUMO and β LUMO for the BS singlet are given for each model along with the calculated J and orbital overlap term (Color scheme: red = O, pink = Al, light gray = Si, white = hydrogen, and mustard = Cu). Reprinted with permission from ref^[135]. Copyright 2024. American Chemical Society; (B) Spin density distributions for bi- and trinuclear Cu-oxo complexes and the respective possible resonance structures that could be proposed to describe the formal charge configuration in the extra-framework species. Reprinted with permission from ref^[136]. Copyright 2016. Elsevier; (C) Composition of species in Cu-MOR under various conditions. Reprinted with permission from ref^[6]. Copyright 2022. American Chemical Society. DFT: Density functional theory; LUMO: lowest unoccupied molecular orbital; BS: broken symmetry.

Mononuclear Cu species

The mononuclear $[\text{CuOH}]^+$ active sites in zeolites provide complementary pathways for methane oxidation, alongside the established $[\text{Cu-O-Cu}]^{2+}$ and Cu_3O_3 structures^[139]. Kulkarni *et al.* prepared low aluminum-content CHA zeolite catalysts as a model system through copper ion exchange and systematically examined the methane partial oxidation reaction in the Cu-containing zeolite using DFT calculations^[140]. Their findings indicated that the $[\text{CuOH}]^+$ located in the 8-MR serves as the active species, whereas 6-MR structures are detrimental to the catalytic reaction. The 8-MR is desired for increasing the amount of $[\text{CuOH}]^+$ species. Sushkevich *et al.* revealed that, in Cu-containing MOR, besides the known mono- μ -oxo binuclear copper sites, the mononuclear $[\text{CuOH}]^+$ site was identified as an active species^[141]. Both sites can react with methane at moderate temperatures to produce methoxy, methanol, and several over-oxidation products (e.g., formate and carbon monoxide). They proposed that reactions at $[\text{CuOH}]^+$ sites require lower activation energy but proceed more slowly than those at the mono- μ -oxo binuclear copper species within the relevant temperature range. Furthermore, Heyer *et al.* employed a range of characterization techniques,

including DR UV-vis spectroscopy and magnetic circular dichroism, to definitively identify the mononuclear $[\text{CuOH}]^+$ as the active site in the self-reduced Cu-MOR zeolite catalyst for methane oxidation^[6]. They proposed the structure of active species evolution in zeolite under different conditions [Figure 7C]. Kinetic experiments comparing the reactivities of the $[\text{CuOH}]^+$ and $[\text{Cu}_2\text{O}]^{2+}$ sites revealed that the binuclear species exhibit higher reactivity, which is due to the stabilization of the $[\text{Cu}_2\text{OH}]^{2+}$ H-atom abstraction product over the two Cu cations.

Reaction mechanisms over Cu-containing zeolite

O₂ as oxidant

In Cu-containing zeolite catalysts, the methane oxidation mechanism using O₂ as the oxidant involves the activation of the copper sites with O₂ to form highly reactive Cu–O species or double oxide-bridged binuclear copper species (e.g., $[\text{Cu}_2(\mu\text{-O})]^{2+}$). These active species interact with methane at moderate temperatures, activating the C–H bond and generating methoxy intermediates. Subsequently, these generated methoxy intermediates are hydrolyzed to produce methanol. Throughout the reaction, the active copper sites are continuously regenerated by oxidation, maintaining the catalytic cycle. Due to the strong oxidizing ability of O₂, a key challenge lies in controlling the activity of oxygen species to prevent excessive methanol oxidation. Dinh *et al.* elucidated the reaction pathway and active sites for CH₄ conversion to methanol on Cu-SSZ-13 zeolite through dynamic experiments and spectroscopic techniques^[117]. CH₄ activation entails critical cleavage of C–H bonds on the surface to generate a surface-bound C1 intermediate, which can desorb to form methanol in the presence of H₂O/H⁺ or be fully oxidized to CO₂ in the presence of O₂. The $[\text{Cu-O-Cu}]^{2+}$ structure is thought to be formed through the diffusion of hydrated copper ions along a proton-assisted pathway [Figure 8A].

N₂O as oxidant

The methane oxidation mechanism over Cu-containing zeolite catalyst using N₂O as an oxidant begins with the dissociation of N₂O at the copper site, generating active oxygen species (e.g., Cu–O or $[\text{Cu}_2\text{O}]^{2+}$) and releasing N₂^[73]. These activated oxygen species promote C–H bond cleavage in methane, generating methoxy intermediates. These intermediates can further react with water to produce methanol, while the copper site regenerates its activity through reaction with N₂O. The binuclear copper site demonstrated superior efficiency and selectivity for methane oxidation [Figure 8B]^[112].

Other catalysts

Non-noble metal in zeolites

Besides Fe and Cu species, other transition metals have also attracted significant interest from researchers. For instance, cobalt (Co) and nickel (Ni) are anticipated to exhibit methane partial oxidation activities comparable to Fe^[139]. Mahyuddin *et al.* conducted theoretical studies on MO⁺-ZSM-5 zeolites (M = Fe, Co, Ni, Cu) using DFT to investigate the influence of various metals on methane oxidation reactions [Figure 9A and B]^[142]. Their calculations revealed the following predicted activity order for the cleavage of the C–H bond of methane: CoO⁺-ZSM-5 < NiO⁺-ZSM-5 < FeO⁺-ZSM-5 < CuO⁺-ZSM-5. In contrast, the predicted methanol selectivity follows the order of FeO⁺-ZSM-5 < CoO⁺-ZSM-5 < NiO⁺-ZSM-5 < CuO⁺-ZSM-5. In Co-containing ZSM-5 zeolites, at least two distinct Co species may be present: Co²⁺ ions located at IE sites and Co oxide species, each with differing catalytic and magnetic properties^[143]. Beznis *et al.* found that Co-containing ZSM-5 prepared through ion exchange with cobalt acetate primarily contains highly dispersed Co species within zeolite channels, demonstrating selectivity towards formaldehyde at 150 °C in O₂^[57]. In contrast, impregnated Co-containing ZSM-5 samples that mainly contain cobalt oxide species on zeolite particle surfaces showed higher selectivity towards methanol. Shan *et al.* anchored a bent mono(μ -oxo)dinickel complex within ZSM-5 micropores using a WI method^[58]. The yield of CH₃OH, HCOOH, and HOCH₂CH₂OH over ZSM-5 catalyst at 175 °C in 1 bar of CH₄ is 14.9 μmol per gram. In another work,

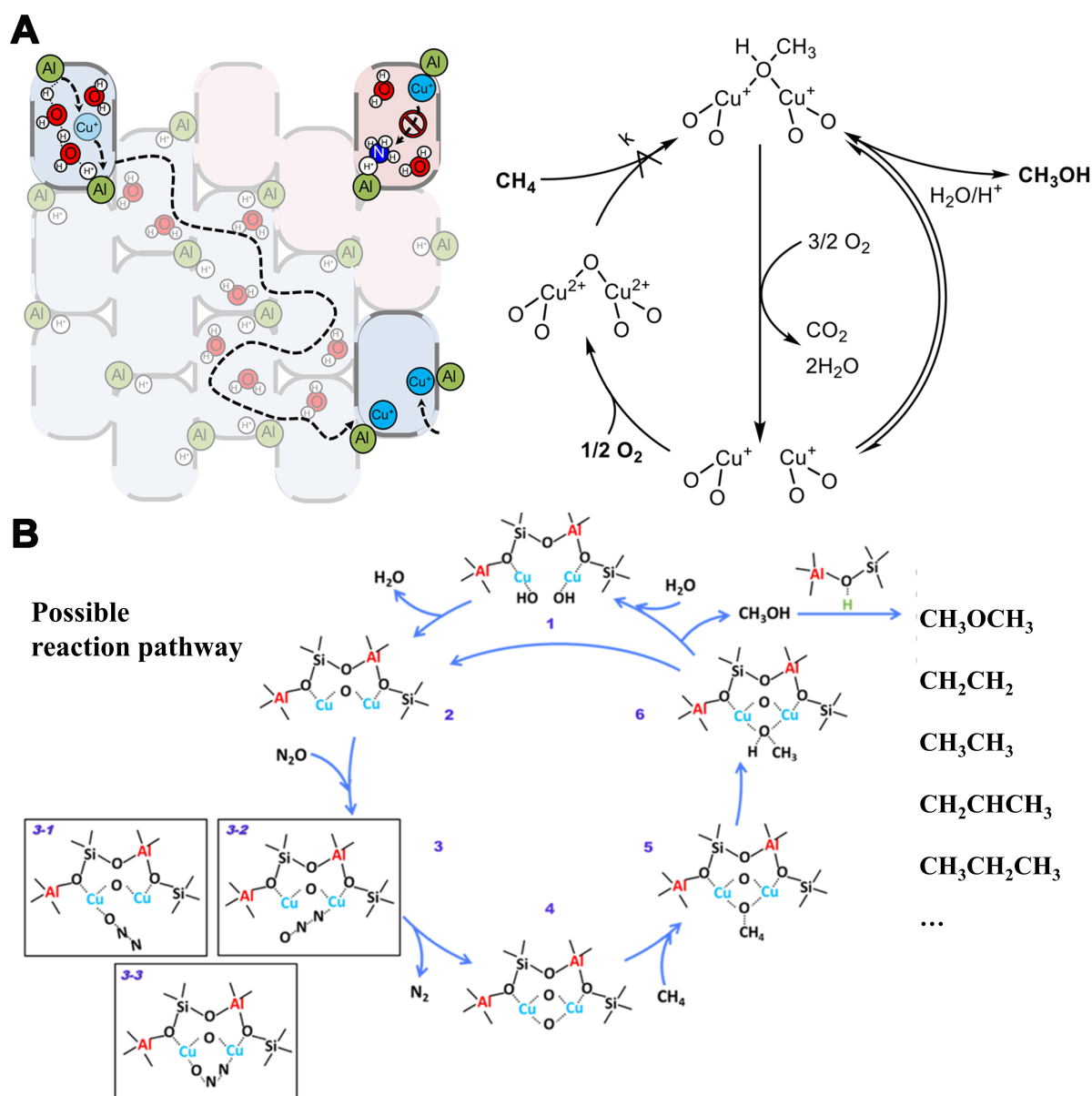


Figure 8. (A) Depiction of hypothesized $\text{H}^+/\text{H}_2\text{O}$ -aided diffusion of Cu^+ and NH_3 inhibition within SSZ-13 to form Cu dimers relevant to the proposed catalytic methane oxidation cycle. Single O atoms may correspond to framework zeolite O atoms or coordinating H_2O molecules. Reprinted with permission from ref^[117]. Copyright 2019. American Chemical Society; (B) The possible reaction pathway of the direct conversion of methane with N_2O on the Cu/AEI zeolite catalyst. Reprinted with permission from ref^[112]. Copyright 2023. American Chemical Society.

theoretical studies proposed an alternative candidate for the active site, a bis(μ -O) bimetallic nickel structure [Figure 9C]^[144,145]. In 2012, Xu *et al.* reported that Zn-loaded H-ZSM-5 zeolite exhibits activity for methane activation^[59]. Isolated Zn^{2+} ion facilitated the heterolytic cleavage of the C–H bond and led to the formation of zinc methyl species, while the dizinc cluster preferentially generated surface methoxy species through the homolytic cleavage of a C–H bond. Recently, Xiao *et al.* demonstrated that FER zeolite exhibited high reactivity in converting methane to methanol in the presence of nitrous oxide, in which a high methanol rate of $305 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ and a high methanol selectivity of 89% were steadily achieved^[146]. As indicated by ^{27}Al magic-angle spinning nuclear magnetic resonance (^{27}Al MAS NMR) spectra, distorted tetracoordinated

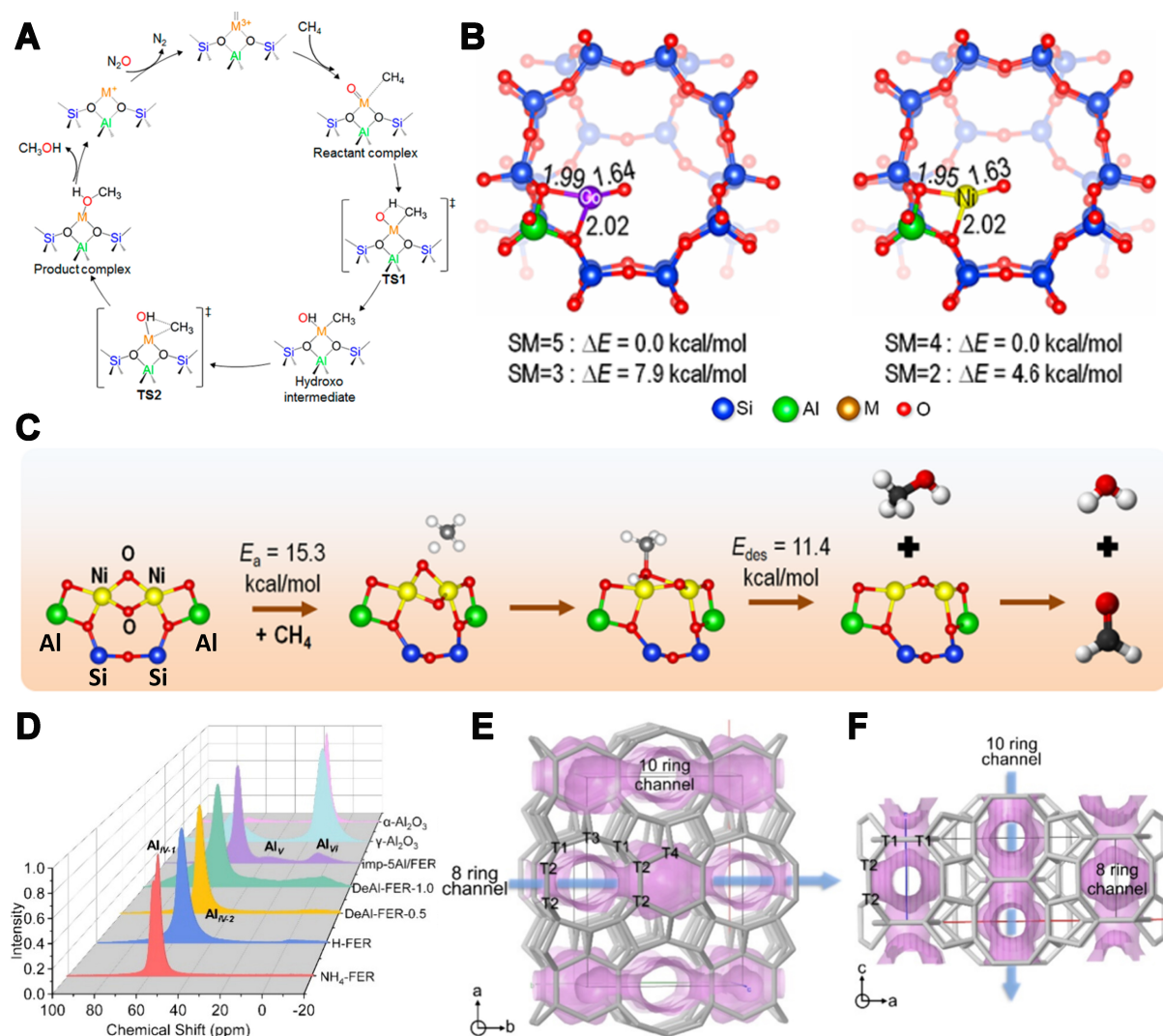


Figure 9. (A) Possible catalytic cycle for the methane to methanol conversion by MO^+ -ZSM-5; (B) Optimized structures of CoO^+ - and NiO^+ -ZSM-5 in the corresponding high-spin state. Reprinted with permission from ref^[142]. Copyright 2016. American Chemical Society; (C) Probable scenarios of the reaction pathway for methane overoxidation to formaldehyde (CH_2O) and dimethyl ether ($\text{C}_2\text{H}_6\text{O}$) over Ni-ZSM-5 zeolites. Reprinted with permission from ref^[144]. Copyright 2021. American Chemical Society; (D) ^{27}Al MAS NMR spectra of FER zeolites after dealumination and supplement Al by impregnation; Positions of four crystallographically independent T sites and the two perpendicular intersecting channels accessible via (E) 001 and (F) 010 faces. Reprinted with permission from ref^[146]. Copyright 2024. American Chemical Society. ^{27}Al MAS NMR: ^{27}Al magic-angle spinning nuclear magnetic resonance.

Al species in the framework and pentacoordinated Al species at the extra framework were confirmed as the active sites [Figure 9D]. The sustained high efficiency of methanol production in FER zeolite is attributed to its bidirectional microporous structure, where 8- and 10-MR channels intersect at the FER cage, along with the unique distribution of aluminum in FER zeolite [Figure 9E and F].

Noble metal in zeolites

Noble metal atoms^[39,147-150], clusters^[151], and nanoparticles^[152-156] also work for C-H activation. AuPd-based catalysts are particularly effective for the catalytic synthesis of H_2O_2 using O_2 and H_2 , which readily decomposes into highly active hydroperoxyl and hydroxyl species^[157-161]. These species participate in various selective oxidation reactions, providing a robust strategy for enhancing catalytic activity and selectivity

toward oxygenates compared to O_2 as the oxidant^[162,163]. A notable study by Jin *et al.* involved embedding AuPd alloy nanoparticles within ZSM-5 zeolite and subsequently coating the external surface of zeolite with a hydrophobic organosilane to impart hydrophobicity (AuPd@ZSM-5- C_{16})^[31] [Figure 10A-C]. This hydrophobic shell prevented the diffusion of hydrophilic H_2O_2 , formed from hydrogen and oxygen, away from the interior AuPd nanoparticles. It increases H_2O_2 concentration within the zeolite crystals. Meanwhile, hydrophobic methane molecules effectively interact with the AuPd nanoparticles in concentrated hydrogen peroxide due to the hydrophobic shell. The resulting AuPd@ZSM-5- C_{16} demonstrated a 17.3% methane conversion rate, 92% methanol selectivity, and 91.6 millimoles of methanol per gram of AuPd per hour [Figure 10D].

Recent studies have shown that methane oxidation can occur solely in the presence of oxygen^[164]. Qi *et al.* demonstrated this using Au nanoparticles supported on ZSM-5 zeolite to convert CH_4 to CH_3OH and CH_3COOH in water at temperatures ranging from 120 to 240 °C^[29]. The Au-ZSM-5 catalyst exhibited higher oxygenate productivity compared to Cu-containing zeolite catalysts, with C_2 oxygenates being the primary products. It was established that oxygen activation occurred on the Au nanoparticles, while the acidity of the zeolite facilitated the activation of methane into reactive $\bullet CH_3$ species for further transformations. Meanwhile, Wu *et al.* reported a ZSM-5 (Z-5) loaded with a bimetallic PdCu catalyst (PdCu/Z-5), which catalyzes the reaction of methane with oxygen in the presence of H_2 at 120 °C to produce oxygenated products^[165]. In this system, PdO nanoparticles facilitated the *in situ* production of H_2O_2 , while Cu single atoms enhanced the decomposition of H_2O_2 to generate a substantial amount of hydroxyl radicals ($\bullet OH$). These radicals subsequently promoted the homolysis of CH_4 to produce $\bullet CH_3$, which reacts with $\bullet OH$ to generate CH_3OH with high selectivity [Figure 10E].

CATALYTIC COUPLING OXIDATION OF CH_4 WITH CO OVER METAL-ZEOLITE CATALYSTS

CO is a common carbonylation substrate that shows promise in coupling oxidation reactions with methane, providing a new strategy for low-temperature methane conversion to C_2 oxygenated products, namely acetic acid^[166]. Metal-zeolite catalysts, such as Rh-ZSM-5^[167], Cu-ZSM-5^[168] and Zn-ZSM-5^[169], have demonstrated potential due to their favorable pore structures, acidic properties, and synergistic effects between metallic species and zeolite frameworks. These metal-zeolite catalysts provide a mild and efficient pathway for coupling methane with CO, effectively activating methane to generate methyl and methoxy active intermediates. This section will introduce recent research advancements in metal-zeolite catalysts for the coupling reaction of methane with CO.

Previous studies utilizing metal-zeolite catalysts for methane and CO coupling have primarily focused on acetic acid formation via the carbonylation of methanol, following the conventional Koch carbonylation mechanism^[170]. In this process, methane undergoes partial oxidation to yield methanol, which subsequently reacts with CO on the catalyst surface to produce acetic acid (Pathway 1, Figure 11). However, this method necessitates high temperatures, elevated pressures, and acidic conditions, leading to substantial energy consumption and rapid catalyst deactivation^[171]. These challenges limit its scalability and industrial applicability. Recent advancements have introduced the “methane carbonylation” concept, where methane is directly activated through oxidation-reduction or chemical looping processes^[168]. This method generates active intermediates, such as methyl and methoxy species, which then couple with CO to form acetic acid and other oxygenated compounds under mild conditions (Pathway 2, Figure 11). This innovative pathway not only achieves high selectivity and efficiency, but also mitigates previous limitations by facilitating target conversions at significantly lower temperatures and pressures, presenting a promising route for the direct valorization of methane into high-value oxygenates.

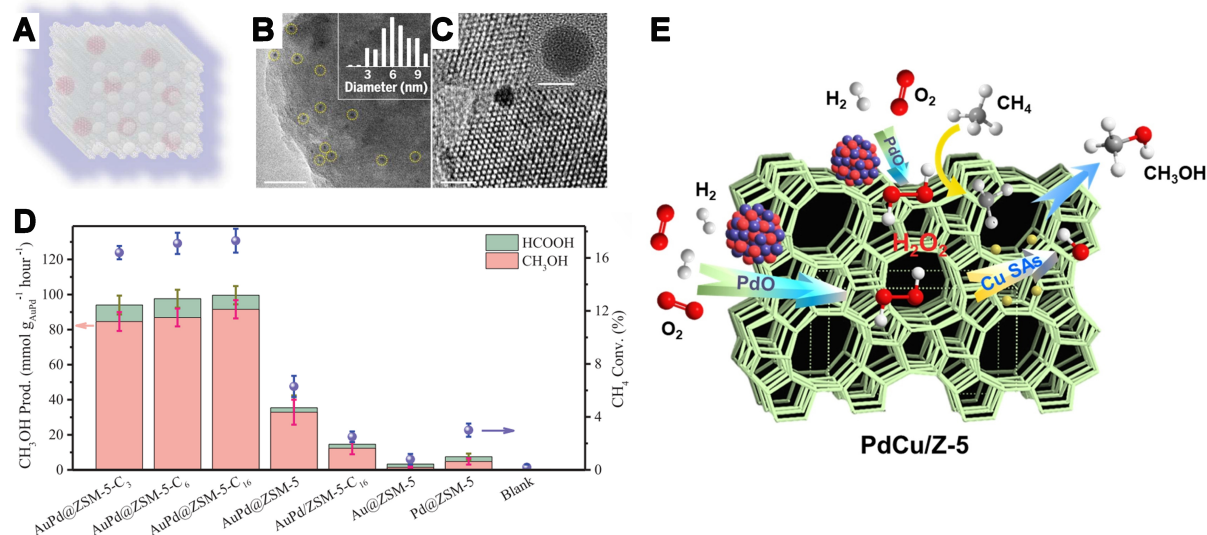


Figure 10. (A–C) Models and tomographic section TEM images of AuPd@ZSM-5-C₁₆; (D) Data characterizing the oxidation of methane with H₂ and O₂ over various catalysts. Reprinted with permission from ref^[31]. Copyright 2020, the American Association for the Advancement of Science; (E) Scheme of proposed reaction pathway for selective oxidation of CH₄ with O₂ and H₂ over PdCu/Z-5. Reprinted with permission from ref^[165]. Copyright 2022, Wiley-VCH GmbH. TEM: Transmission electron microscopy.

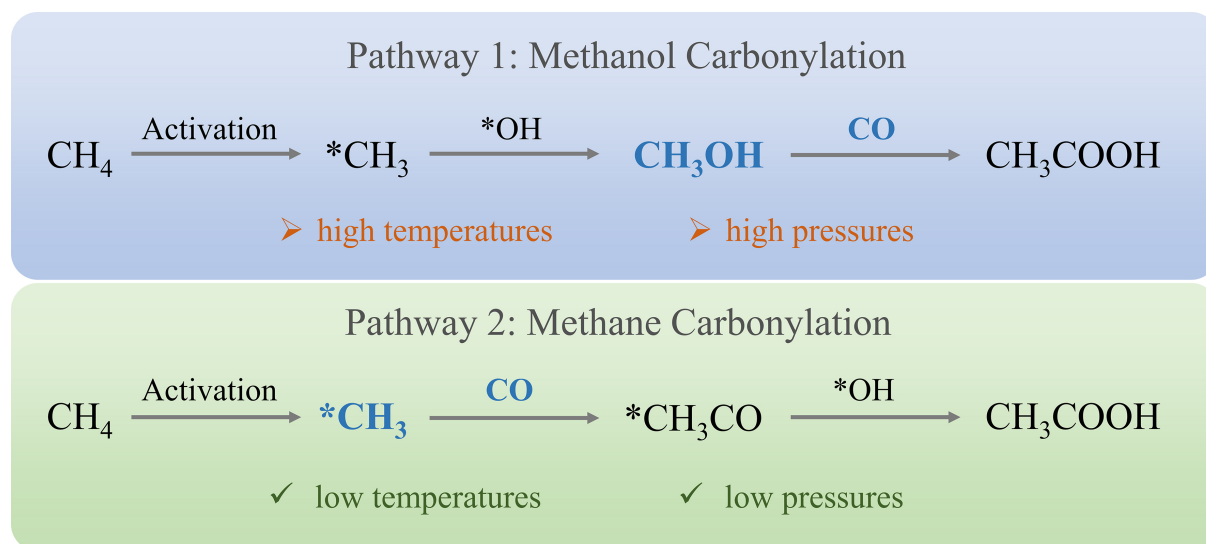


Figure 11. Schematic illustration of two reaction pathways of coupling oxidation of CH₄ with CO.

Monometallic species in zeolites

Moteki *et al.* discovered that transition metals (Fe, Co, Ni, Cu) and platinum group metals (Ru, Rh, Pd, Ir, Pt) loaded on ZSM-5 effectively catalyze the coupling oxidation of CO and CH₄^[172]. Recently, Wang *et al.* found that the Fe/ZSM-5 (0.25) zeolite catalyst, featuring mononuclear Fe³⁺ species located in the 5-MR units, exhibited high activity and selectivity for CH₄ coupling oxidation with CO using H₂O₂ as oxidant at 50 °C^[173]. A high acetic acid space-time yield (12.01 mmol·g_{cat}⁻¹·h⁻¹) and a high acetic acid selectivity (63.2%) were achieved. Platinum group metals, particularly Rh, exhibit significantly enhanced reactivity than transition metals. The partial oxidation of methane towards methanol or formic acid parallels the oxidative carbonylation of methane to acetic acid, with the researchers proposing that CO may act as a ligand,

reductant, and reactant in this system. In 2017, Shan *et al.* developed Rh-ZSM-5 catalyst with Rh contents of 0.5 wt% and 0.6 wt%^[38]. The as-prepared Rh-ZSM-5 catalyst was tested at 20 bar of CH₄, using 20 mg of catalyst suspended in 20 mL of water within a Parr reactor. O₂ and CO were introduced at the partial pressures of 0.5–5 bar (total 30 bar), with the temperature varied between 100–170 °C. Under conditions of 150 °C for six hours at 2 bar O₂, the acetic acid yield exceeds 13,000 μmol·g_{cat}⁻¹, with ~60% selectivity of acetic acid. The researchers proposed that methane is converted to Rh–CH₃ on isolated Rh⁺ cations. Rh–CH₃ then reacted with O₂ or CO to produce methanol or acetic acid. Tang *et al.* prepared Rh/ZSM-5 with Rh content of 0.10 wt%, featuring highly dispersed Rh₁O₅ single sites^[174]. Their results showed that the activity of Rh₁O₅ sites to produce oxygenates could reach approximately 0.10 acetic acid molecules per Rh₁O₅ site per second at 150 °C, with a ~70% selectivity for acetic acid. This activity is more than 1,000 times higher than that of Rh³⁺ in an aqueous solution. Isotope labeling experiments using ¹³CH₄ and ¹³CO suggested that the CH₃ in CH₃COOH arises from CH₄, while the C=O in CH₃COOH is formed through the insertion of CO into Rh–OH and then connected with Rh–CH₃ [Figure 12A].

Besides CO gas, carbonyl groups on carbon additives can also participate in the oxidation of CH₄^[175]. The incorporation of carbon additives into an Au/ZSM-5 catalyst significantly enhanced the performance of methane oxidation using O₂ as the oxidant, yielding both methanol and acetic acid as products together with CO₂. Notably, ¹³C labeling studies attributed the production of acetic acid to the carbon additive. X-ray photoelectron spectroscopy (XPS) results showed that the surface of the carbon additives was oxidized to –CO/–COH functionalities. It is proposed that CO group on the carbon additives exerts a similar influence as to CO gas, contributing to the oxidation of CH₄ [Figure 12B].

Bimetallic species in zeolites

The bimetallic catalyst design also provides a novel approach for the carbonylation of methane. Wu *et al.* demonstrated that Au–Fe/ZSM-5 catalysts achieve an acetic acid yield of 5.7 mmol·g_{cat}⁻¹ with a selectivity of 92% at 120 °C after three hours using O₂ as the oxidant^[176]. *In situ* DRIFTS results indicated that CO facilitates the dissociation of H₂O to form Au–H and Au–COOH species. The presence of O₂ promotes the reaction of Au–H species with O₂ to form [•]OOH, which subsequently converts to [•]OH. In the presence of CO (with H₂O₂ as the oxidant), Fe/ZSM-5 exhibited a higher yield (2.5 mmol·g_{cat}⁻¹) of liquid products compared to Au/ZSM-5 and Au–Fe/ZSM-5 (both yielding 0.81 mmol·g_{cat}⁻¹) and Fe-free ZSM-5 (yielding 0). Therefore, dispersed iron species on ZSM-5 are crucial for the hydroxyl-mediated coupling of CH₄ and CO to form acetic acid. Cheng *et al.* reported an efficient 0.1Cu/Fe–HZSM-5–TF catalyst synthesized via a template-free method, which features mononuclear Fe and Cu species within ZSM-5^[166]. This catalyst achieved a high acetic acid yield of 40.5 mmol·g_{cat}⁻¹·h⁻¹ at 50 °C, which is three times the previous record of 12.0 mmol·g_{cat}⁻¹·h⁻¹. The combination of various characterizations, isotope labeling experiments, and DFT calculations indicated that mononuclear Fe species are responsible for methane conversion, while adjacent Cu species play a critical role in decelerating the oxidation process, thus enhancing the synthesis of acetic acid product. Furthermore, the methyl carbon of acetic acid was derived entirely from methane, and the carbonyl carbon was sourced solely from CO.

CONCLUSION AND OUTLOOK

In summary, metal-zeolite catalysts have demonstrated a pivotal role in the low-temperature oxidation of methane. This effectiveness stems from the unique features of zeolites, including their regular microporous structure, high specific surface area, adjustable Si/Al ratio, large IE capacity, confinement effect, and robust thermal and hydrothermal stabilities. This review summarizes recent advancements of metal-zeolite catalyst processing low-temperature methane oxidation to oxygenates, providing deeper insights into the synthesis methods, reaction mechanisms, metallic active sites, and catalytic performance. Currently, the low-

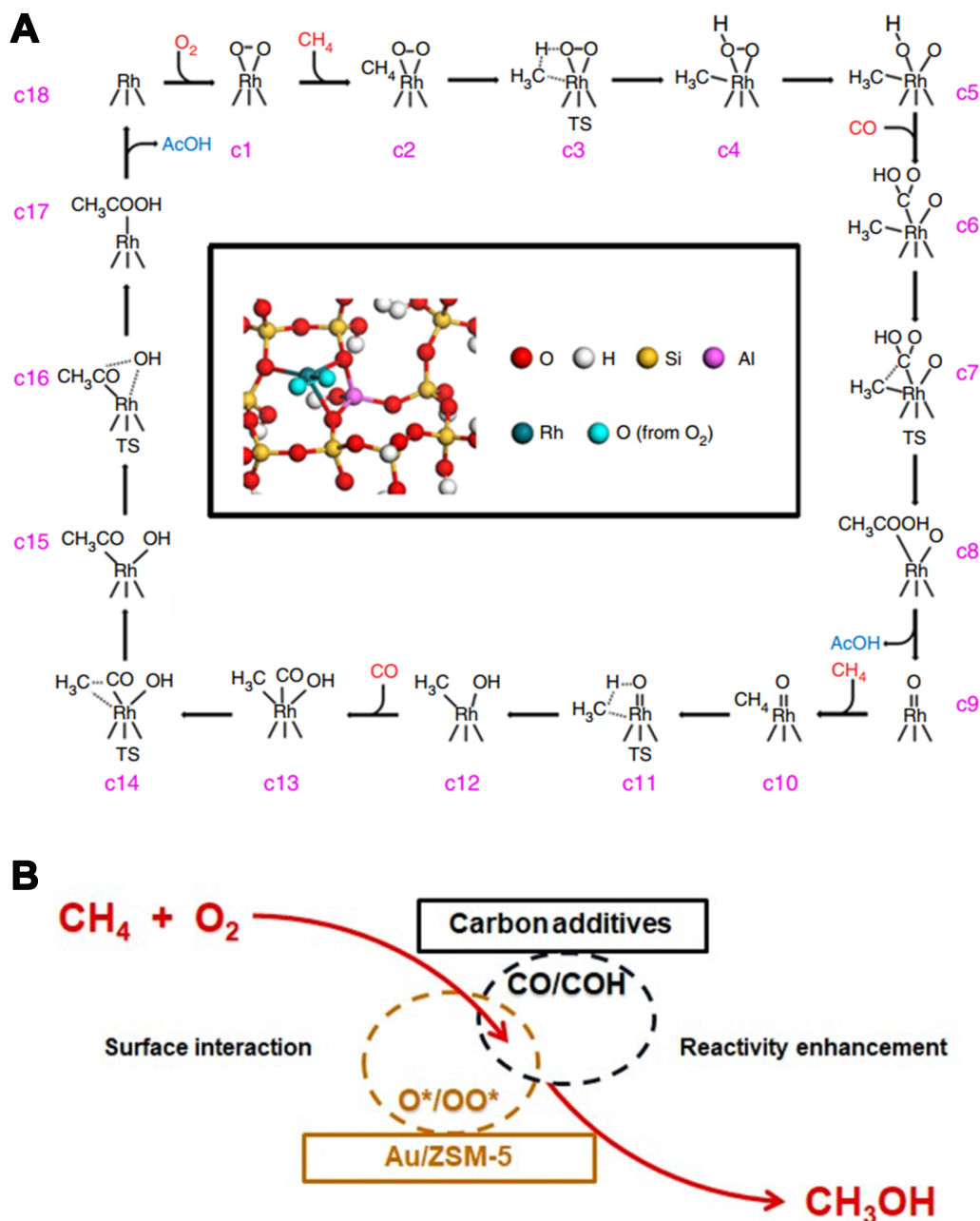


Figure 12. (A) The optimized catalytic sites, Rh_1O_5 anchored on Brønsted site in microspore of ZSM-5, and intermediates and transition states for a complete catalytic cycle, starting with Rh_1O_5 . Reprinted with permission from ref^[174]. Copyright 2018. Springer Nature; (B) Schematic illustration on the promotive effect of carbon additives on the methane oxidation catalyzed by Au/ZSM-5. Reprinted with permission from ref^[175]. Copyright 2023. the American Chemical Society.

temperature oxidation of methane using metal-zeolite catalysts still faces several challenges yet accompanied by opportunities. Future research directions in the field of low-temperature methane oxidation could focus on the following points.

Developing high activity and selectivity metal-zeolite catalysts

While metal-zeolite catalysts promote the low-temperature oxidation of methane to oxygenates with high TOF value and product selectivity, the low-temperature methane oxidation still suffers from low methane conversion efficiency (generally below 5%) and oxygenate productivity. This limits the commercial viability of low-temperature methane conversion processes. It is crucial to explore novel high-performance catalysts or develop new catalytic systems to facilitate the industrial application of metal-zeolite for low-temperature conversion. Based on existing mature metal-zeolite systems, fine tailoring zeolite framework, type of extra-framework metal species, metal dispersion, coordination environment of metallic species, and proximity between active sites are desirable to achieve enhanced catalytic performance. Moreover, to date, only several types of zeolites have been utilized as matrices for low-temperature methane oxidation, such as MFI, CHA, AEI, FER, and MOR. Other types of zeolite topologies with varied nanoconfinements should be employed in this field.

Breaking the loading amount limit of highly active metal species

Increasing the loading amount of highly active metallic sites, such as mono-, bi- and trinuclear metal species, is a straightforward method to achieve a substantially enhanced catalytic performance. For instance, the maximum Fe loading of Fe-containing zeolites that primarily contain mononuclear Fe species is approximately 0.5 wt%. With increasing metal loading, large metal clusters/particles are generally formed inside/outside zeolite crystals. Up till now, the synthesis of metal-zeolite catalysts with high metal loading and good metal dispersion remains a big challenge. From both academic and industrial perspectives, it is of great importance to develop novel synthetic approaches to break the loading amount limit of mono-, bi- and trinuclear metallic species. This will be an escalating significant research direction for the synthesis of metal-zeolite catalysts.

Green catalytic system over metal-zeolite catalysts

H₂O₂ and N₂O are frequently used as oxidants in the low-temperature oxidation of methane; however, they present several limitations, such as high costs, stringent storage requirements, etc. Using O₂ as an oxidant for continuous methane conversion is highly desired but remains a big challenge due to the poor productivity, selectivity, and security issue with mixing O₂ and combustible gas. Two approaches could be considered to achieve a green catalytic system in the future: (i) Developing highly active metal-zeolite catalysts that can be efficiently activated by using H₂O and CO₂ as weak oxidants; (ii) Constructing a photo-assisted thermocatalytic system in which the sunlight promotes the activation of methane.

Mechanism investigation and identification of active metal sites via *operando* or *in situ* characterization methods

In-depth understanding of the structural evolution and dynamics of metal sites during reaction and the reaction mechanisms of low-temperature methane oxidation is important to accelerate the rational design of metal-zeolite catalysts and optimize the reaction conditions. Current research on reaction mechanisms and active sites for low-temperature methane oxidation relies on DFT calculations. *Operando* or *in situ* spectroscopic and microscopic techniques, such as XAS, Mössbauer spectroscopy, and aberration-corrected STEM, are expected to be feasible to unravel the reaction mechanism, the structure of real active sites, and structural evolution of active sites in zeolites under catalytic conditions.

Screening and developing of high-performance metal-zeolite catalysts via artificial intelligence technology

Currently, the exploration of novel metal-zeolite catalysts strongly relies on labor-intensive work. The prediction of the synthesis–structure–property relationships of the metal-zeolite system based on available data in previously reported work is crucial to promote the discovery of new catalytic systems and efficient metal-zeolite catalysts. The rapid advancement of artificial intelligence (AI) technology offers exciting

prospects for catalyst design. Future research can leverage AI technology to predict new types of metal active sites, suitable catalytic conditions, and possible reaction pathways for direct methane conversion.

In conclusion, with the development of synthesis methods, powerful characterization techniques, and AI, metal-zeolite catalysts are expected to achieve more success and bring more new opportunities for efficient methane utilization under mild conditions.

DECLARATIONS

Authors' contributions

Wrote the draft manuscript: Xiang, B.; Li, J.; Chang, B.

Initiated, supervised, and revised the manuscript: Zhang, Q.

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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