Advantages and Limitations of Hydrogen Peroxide for Direct Oxidation of Methane to Methanol at Mono-Copper Active Sites in Cu-Exchanged Zeolites

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Abstract: The performance of the direct oxidation of methane to methanol (DMTM) is significantly influenced by the oxidant. It is still incredibly challenging to realize one-pot DMTM using dioxygen. So far, hydrogen peroxide is still the most frequently reported green oxidant for DMTM with a high selectivity for methanol. To achieve insights into the influence of oxidants on the DMTM performance, we computationally investigated the reaction mechanisms of DMTM using hydrogen peroxide at mono-copper sites in three kinds of Cu-exchanged zeolites with different sizes of the micropores. We identified the common advantages and limitations of hydrogen peroxide as the oxidant. In contrast to dioxygen, the O-O bond of hydrogen peroxide could be easily broken to produce reactive surface oxygen species, which enables the facile C-H bond activation of methane at a lower temperature. However, because of the radical-like process for C-H bond activation at mono-copper sites, it is kinetically challenging to actualize the preferential C-H bond activation of methane as compared to that of methanol. Moreover, the lower O-H bonding energy of hydrogen peroxide would result in the self-decomposition of hydrogen peroxide. Despite the bottlenecks, the kinetic analysis shows that it is still promising to improve catalysts to boost the performance of DMTM using hydrogen peroxide.

Keywords: Density Functional Theory, Cu-Exchanged Zeolites, Hydrogen Peroxide, Methane Partial Oxidation, Methanol
1. Introduction

As the most rapidly growing fossil fuel to 2035\(^1\), natural gas plays an increasingly important role in power generation and chemicals manufacturing.\(^2\) Considering its high transportation cost, it is always desirable to upgrade its main component, methane (CH\(_4\)), to liquid fuels such as methanol (CH\(_3\)OH). Ideally, the direct catalytic oxidation of methane to methanol (DMTM) could realize CH\(_4\) upgrading, which is a green chemistry reaction and thermodynamically favorable at ambient temperature. However, it is incredibly challenging due to the low affinity for electrons and protons, the low polarizability, the strongest C-H bond among alkanes (439 kJ·mol\(^{-1}\)), and the high ionization energy of CH\(_4\).\(^5\) Although many materials can catalyze methane activation and oxidation, the weaker C-H bonds of produced oxygenates readily lead to the deep oxidation and the production of a large amount of carbon dioxide (CO\(_2\)).\(^6\)-\(^9\) It is almost formidable to simultaneously achieve high activity and selectivity for CH\(_4\) partial oxidation, although the researchers have been studying DMTM in modern science for decades.\(^10\)-\(^17\) Interestingly, however, DMTM could occur efficiently in nature using soluble or particulate methane monooxygenases (MMO) under aerobic conditions at room temperature.\(^18\)

Inspired by pMMO with copper sites which can activate methane by decomposing molecular oxygen,\(^19\)-\(^22\) the pMMO-like catalysts such as the copper 0molecular sieve are considered as a kind of promising DMTM catalysts.\(^23\)-\(^28\) Leshkov and colleagues reported the first demonstration of DMTM using molecular oxygen (O\(_2\)) on the copper-
exchanged zeolite. However, the reaction must consist of two alternating steps: (1) O$_2$ activation at a high temperature and (2) CH$_4$ oxidation at a low temperature. Recently, Li and colleagues showed that a high selectivity of 91% CH$_3$OH over Cu-CHA with a yield of 543 mmol/mol$_{Cu}$/h at 573 K could be achieved using O$_2$ with the assistance of water. However, the activity and selectivity of one-pot DMTM reaction using O$_2$ at a low temperature are limited by the trade-off between C-H bond activation and deep oxidation of CH$_3$OH.

Identification of the active site of copper zeolites is of paramount significance for catalysts improvement. Despite numerous characterization methods to clarify the structure of the active site, it remains controversial. Many characterization data have indicated that the dinuclear copper center is an effective active site in the two-step reaction. Bokhoven and coworkers proposed that high methanol yields require highly dispersed copper oxide species. They further showed that mononuclear copper was the active center for DMTM in Cu-MOR as confirmed by in situ NMR and IR spectroscopy. Kulkarni et al. computationally identified the mononuclear [Cu$_{II}$OH]$^+$ as the active center of copper-exchanged SSZ-13 for methane partial oxidation reaction. Yashnik et al. suggested that the isolated mononuclear Cu site in Cu-ZSM-5 is one of the possible active sites for DMTM. In particular, Meyet et al. found that synthesized monomeric copper sites could selectively convert methane to methanol and also achieve good catalytic activity. Mono-copper may be the active site for DMTM.

The oxidant is also a critical factor for the performance of DMTM. In contrast to
O₂, another green oxidant, hydrogen peroxide (H₂O₂), can upgrade CH₄ more efficiently with high selectivity to CH₃OH at a lower temperature. Fan’s group found that the high H₂O₂ utilization could promote the DMTM at a low temperature. Hutchings and his colleagues found that copper addition in Cu-ZSM-5 can provide up to 97% CH₃OH selectivity in the presence of H₂O₂ at 50°C. Tang et al. reported that Cu₁-O₄/ZSM-5 single atom catalyst exhibits a 99% selectivity of C1 oxide with high conversion of CH₄ at 50°C. However, H₂O₂ is likely to readily generate the free radicals of ·OH and ·OOH as well, which may trigger a Fenton reaction and reduce the CH₃OH selectivity.

Inspired by previous work, we were dedicated to computationally explore the features of H₂O₂ as an oxidant for DMTM at mono-copper sites in Cu-exchanged zeolites to provide the guidelines for improving the catalysts and optimizing reaction conditions.

First, the most stable mononuclear-copper species at Cu-ZSM-5, Cu-MOR, and Cu-SSZ-13 were computationally studied. Then, the performances for the activation of O-O bond and methane were computationally compared between O₂ and H₂O₂ as oxidants under the reaction conditions. Further, the complete catalytic cycle from CH₄ to CH₃OH and competitive reaction pathways were studied. Finally, the competition among CH₄, CH₃OH, and H₂O₂ oxidation was discussed in detail upon both energetic and kinetic analysis to understand the limitation of using H₂O₂ as an oxidant.
2. Methods

2.1 Computational Details

The periodic density functional theory (DFT) calculations were applied using Vienna Ab-initio Simulation Package (VASP)\textsuperscript{52, 53} in simulating the heterogeneous reactions in the zeolite.\textsuperscript{54, 55} The electronic exchange-correlation energy was processed by the Perdew, Burke, and Ernzerhof (PBE) functional in the framework of generalized gradient approximation (GGA).\textsuperscript{56} The van der Waals interaction in the zeolite systems was described by the semi-empirical DFT-D3(BJ) method.\textsuperscript{57, 58} The plane-wave basis set was employed with a cutoff energy of 400 eV. The geometry optimization of intermediates was performed based on the conjugate gradient method, while the transition state was searched using the constrained optimization method based on the L-BFGS algorithm.\textsuperscript{59} The convergence criteria were set as 0.05 eV/Å for the maximal force of all the relaxed atoms. Heyd-Scuseria-Ernzerhoff functional (HSE06) was used to optimize the key elementary reactions and correct the relative energy.\textsuperscript{60}

The free energy was calculated with the total energy from DFT calculations corrected by statistical mechanics based on Boltzmann distribution under the reaction condition, including the influence from the zero-point energy, internal energy variation, and entropy.\textsuperscript{61, 62} The standard free energy of the solute (1M) in the aqueous solution was calculated with its standard gaseous free energy (1 bar) corrected by its solvation energy and the chemical potential variation corresponding to the unit change from 1 bar to 1M. The SMD model was employed to simulate the solvation energy.\textsuperscript{63, 64} For the
chemisorbed adsorbates, only the vibrational contribution was considered. Due to the restricted translation and rotation of the gaseous molecules in the micropores of zeolites, the lost translational and rotational entropies in different zeolites were corrected following the values from Dauenhauer et al.’s work,\textsuperscript{65} which was verified by Mikkel et al..\textsuperscript{66}

**Figure 1.** The optimized structure of (a) H-ZSM-5 with the unit cell of 20.517 Å × 20.293 Å × 13.627 Å, (b) H-MOR with the unit cell of 18.279 Å × 20.463 Å × 7.546 Å, and (c) H-SSZ-13 with the unit cell of 13.686 Å × 13.686 Å × 14.771 Å from the view of Z axis. The most stable substituted single Al cations are respectively located on the γ-8MR at the intersection of the straight channel and the sine channel of ZSM-5 zeolite, the 6MR of SSZ-13 zeolite, the 12MR of the straight channel of MOR zeolite. The H, C, O, Si, Al and Cu atoms are displayed in white, gray, red, yellow, magenta, and orange, respectively.

The DFT simulations for the ZSM-5, MOR, and SSZ-13 used 1×1×1(Γ-point), 1×1×2, and 2×2×2 k-point integration of the Brillouin zone, respectively. The used periodic slab of H-ZSM-5, H-MOR, and H-SSZ-13 are displayed in **Figure 1.** The optimized lattice parameters are consistent with previous experimental data.\textsuperscript{67-69} Since a high Si/Al ratio is conducive to improving the yield and selectivity of methanol,\textsuperscript{70, 71} the model with single Al cation was utilized. Comparing the possible sites for Al
placement (Fig. S1-S3), the energetically most stable site for the single Al substitution was adopted as the active site where the copper species would be anchored. The results are consistent with the previous studies. 72-75

2.2 Ab initio thermodynamic analysis

The stabilities of mono-copper species in the zeolites were studied using ab initio thermodynamic analysis. According to the general preparation process, the different copper species (Z[Cu\text{x}O\text{y}H\text{z}]) are produced from the copper(II) cations in the aqueous solution, H-zeolite (Z[H\text{z}]), gaseous O\text{2}, and water:

\[ x\text{Cu}^{2+}(\text{aq}) + Z[H\text{z}] + \frac{2y-z+1}{4}\text{O}_2 + \frac{z-1}{2}\text{H}_2\text{O} \rightleftharpoons Z[\text{Cu}_x\text{O}_y\text{H}_z] \] (2)

Hence, the stabilities of copper species would be evaluated according to the corresponding Gibbs free energy variation as follows:

\[ \Delta G(T, p) = G_{Z[\text{Cu}_x\text{O}_y\text{H}_z]} - xG_{\text{Cu}^{2+}(\text{aq})} - G_{Z[H\text{z}]} - \frac{2y-z+1}{4}\mu_{\text{O}_2} - \frac{z-1}{2}\mu_{\text{H}_2\text{O}} \] (3)

where the Gibbs free energy of \text{Cu}^{2+}(\text{aq}), \( G_{\text{Cu}^{2+}(\text{aq})} \), was calculated according to the Gibbs free energy of bulk Cu from DFT calculations with the correction by the difference of the formation free energies between bulk Cu and \text{Cu}^{2+}(\text{aq}) from the CRC Handbook of Chemistry and Physics, 76 namely,

\[ G_{\text{Cu}^{2+}(\text{aq})} = G_{\text{Cu} \text{--bulk}} + (\Delta_f G^\circ_{\text{Cu}^{2+}(\text{aq})} - \Delta_f G^\circ_{\text{Cu(s)}}) \] (4)
3. Results and discussions

3.1 Structures, stabilities and electronic properties of mono-copper species

Figure 2. (a) The Gibbs free energies of different mononuclear copper species against $\Delta \mu_{O_2}$ at the reaction temperature of 323 K with $10^{-2}$ mbar H$_2$O; (b) the phase diagram of Z[CuO$_x$H$_y$] before the catalysis, at which the dotted line is the most stable copper species before DMTM at 323 K with $10^{-2}$ mbar H$_2$O, and the optimized structure of the most stable mono-copper species at 323 K of (c) [Cu]$^+/ZSM-5$, (d) [Cu]$^+/MOR$, (e) [Cu]$^+/SSZ-13$.

We computationally simulated the stabilities of mono-copper species under different conditions. Taking Cu-ZSM-5 as an example, it is clear from Figure 2a that Z[CuO]$^+$ and Z[Cu(OH)$_2$]$^+$ are less stable, which could be owing to the formation of...
less stable Cu\(^{3+}\) or \(\cdot\text{OH}\) to match the valence of Z[CuO]\(^+\) and Z[Cu(OH)\(_2\)]\(^+\) (Table S1). As displayed in Figure 2b, Z[Cu]\(^+\) is the most stable mononuclear species for Cu-ZSM-5 before DMTM at 323 K. Likewise, Z[Cu]\(^+\) is also the most stable mononuclear copper species for Cu-MOR and Cu-SSZ-13 before DMTM (Figure S4).

3.2 Reaction mechanisms of methane partial oxidation towards methanol

3.2.1 O-O bond activation

Notably, H\(_2\)O\(_2\)/O\(_2\) would preferentially occupy Z[Cu]\(^+\) due to the weak adsorption of methane, as evidenced by Figure 3a. Accordingly, the methane oxidation would be triggered by O-O bond activation first. Taking Cu-ZSM-5 as the example to elucidate the mechanism for the O-O activation of H\(_2\)O\(_2\) at Z[Cu]\(^+\) site, as displayed in Figure 3c, the H\(_2\)O\(_2\) would chemisorb atop Z[Cu]\(^+\) via monodentate adsorption mode with the free energy of adsorption of -0.54 eV. Its O-O bond could be directly scissored to generate Z[Cu(OH)\(_2\)]\(^+\) after climbing over a free energy barrier of 0.63 eV, releasing the free energy of 1.04 eV. In comparison to the O-O bond breaking, the O-H bond dissociation of H\(_2\)O\(_2\) is more difficult at Z[Cu(H\(_2\)O\(_2\))]\(^+\) site (IM1), which needs to climb over a free energy barrier of 1.27 eV (Figure S7). The free energy barriers of this step are similar in Cu-MOR and Cu-SSZ-13. Hence, the O-O bond of H\(_2\)O\(_2\) is easy activated in mononuclear copper zeolites.

Intriguingly, water could make this process easier (Figure 3c). Despite the preferential adsorption of H\(_2\)O at Z[Cu\(^{2+}\)], Z[Cu\(^{2+}\)] site prefers the co-adsorption of H\(_2\)O\(_2\) with H\(_2\)O to the coadsorption of two H\(_2\)O molecules (Figure S8). At the TS of O-
O bond breaking (TS2), one H$_2$O molecule could provide a hydrogen atom to assist the O-O bond breaking of H$_2$O$_2$. The O-H bond at H$_2$O and the O-O bond in H$_2$O$_2$ are respectively elongated to 1.225 Å and 2.246 Å at TS2. Hence, two OH$^*$ (the asterisk denotes the species adsorbed at Cu site) at Z[Cu(OH)$_2$]$^+$ respectively come from the H$_2$O and H$_2$O$_2$ molecules, while the other OH from H$_2$O$_2$ regenerates H$_2$O. It can explain the reason why $^{18}$O from H$_2$O$^{18}$ could be found in CH$_3$OH in the isotopes labelling experiments$^{77,78}$. This water-mediated process lowers the free energy barrier of O-O activation to only 0.16 eV. Likewise, the DFT calculation results (Figure 3d) show that water-mediated process could readily activate the O-O bond of H$_2$O$_2$ to generate Z[Cu(OH)$_2$]$^+$ in Cu-MOR and Cu-SSZ-13 as well (Figure S9 and Figure S10). Hence, the O-O bond activation of H$_2$O$_2$ is almost effortless at mono-copper sites and is not very sensitive to the pore sizes of zeolites.

On the contrary, the O-O bond breaking of O$_2$ is formidable at Z[Cu]$^+$ despite the strong free energy of adsorption for O$_2$ (Figure 3a). The Bader charge analysis (Table S2) shows that O$_2$ could obtain one electron from Z[Cu]$^+$ to form ·O$_2^-$. The O-O bond of O$_2$ is thereby strengthened to 1.316 Å, implying the formation of superoxide as well$^{79}$. However, it is formidable for O$_2$ to capture more electrons to boost O-O bond activation to generate O$_2^{2-*}$ or assist the O-O bond breaking towards the generation of O$^{2-*}$. It is also similar in Cu-MOR and Cu-SSZ-13. It should be attributed to the stronger O-O bond (498 kJ/mol) of O$_2$ compared with hydrogen peroxide (210 kJ/mol)$^{80}$. Therefore, only the O-O bond of H$_2$O$_2$ could be cleaved at Z[Cu]$^+$. 

3.2.2 C-H bond activation

We further investigated the C-H bond activation of methane. As aforementioned, Z[Cu(OH)₂]⁺ could readily be formed in all these copper-exchanged zeolites using H₂O₂ as the oxidant. Geometrically, depending on whether the methyl group at TS chemisorbs over the surface, the mechanisms of C-H bond activation could be
categorized as the radical-like or the surface-stabilized ones\textsuperscript{81,82}. The first C-H bond of methane is broken at Z[Cu(OH)\textsubscript{2}]\textsuperscript{+} through a radical-like mechanism, which is in good agreement with the founding of \textcdot CH\textsubscript{3} in the previous experimental work\textsuperscript{83-86}. Among these copper-exchange zeolites, the lowest free energy barrier of the C-H bond activation is 0.75 eV in Cu-ZSM-5 (\textbf{Figure 3b}). Hence, the Z[Cu(OH)\textsubscript{2}]\textsuperscript{+} is likely to activate methane at a lower temperature. The Bader charge analysis indicates the formation of one adsorbed radical of \textcdot OH\textsuperscript{*} at Z[Cu(OH)\textsubscript{2}]\textsuperscript{+} (\textbf{Table S2}). The \textcdot OH\textsuperscript{*} could easily abstract hydrogen from methane, which may account for the lower free energy barrier of the C-H bond breaking.

On the contrary, methane activation is rather intractable at Z[CuO\textsubscript{2}]\textsuperscript{+} site. The free energy barriers in these copper-exchange zeolites are all beyond 1.52 eV (\textbf{Figure 3b}), indicating that the superoxide in the copper-exchange zeolites is difficult to activate methane at a lower temperature.

Hence, we could find that the facile O-O bond breaking of H\textsubscript{2}O\textsubscript{2} at mono-copper sites to produce reactive oxygen species is of paramount importance for the mild C-H bond activation at a lower temperature. Consequently, hydrogen peroxide could significantly promote methane activation at a lower temperature compared with molecular oxygen.

3.3 Methane direct conversion towards methanol

3.3.1 Methane oxidation

Based on the lowest barrier of the C-H bond activation, we further explored the
complete catalytic cycle of DMTM using H₂O₂ in Cu₁-ZSM-5.

Since the activation of methane proceeds through a radical-like mechanism, the ·CH₃ in the 10-membered ring and Z[CuOH(H₂O)]⁺ are produced. The Z[CuOH]⁺ is subsequentially produced after the facile H₂O desorption (0.23 eV). The reaction pathways would be bifurcated into two branches from Z[CuOH]⁺. Z[CuOH]⁺ could either capture ·CH₃ (blue pathway) or activate another CH₄ molecule (orange pathway). As shown in the blue branch of Figure 4, the ·CH₃ is energetically easy to be captured by the OH* at Z[CuOH]⁺ to produce CH₃OH* (-2.01 eV). After the facile desorption of methanol (0.77 eV), the Z[Cu]⁺ site could be regenerated.

In the orange pathway, the free energy barrier for the first C-H bond breaking of methane at Z[CuOH]⁺ to form CH₃* and Z[Cu(H₂O)]⁺ is 1.05 eV. It is higher than that at Z[Cu(OH)₂]⁺ due to the absence of the adsorbed radical ·OH* at Z[CuOH]⁺ (Table S2). The subsequent desorption of water (0.39 eV) enables the weak coadsorption of hydrogen peroxide with CH₃*, which triggers the facile O-O bond activation (ΔG° = 0.27 eV) to produce two ·OH* (Table S2). Then, one ·OH* only needs to overcome a free energy barrier of 0.10 eV to couple with CH₃* to produce CH₃OH*. Thus, the Z[CuOH]⁺ is regenerated after the swift desorption of methanol (-0.22 eV).

Comparing these two pathways, all the elementary steps in both mechanisms for methane oxidation are not difficult for Cu₁-ZSM-5 using DMTM using hydrogen peroxide as the oxidant. Nevertheless, due to the lower barrier of the key first C-H bond breaking, the catalytic cycle enclosing Z[Cu(OH)₂]⁺ (blue and black pathways) is energetically more favorable for DMTM.
Figure 4. The reaction network of methane conversion towards methanol in Cu-ZSM-5. The reaction network starts with the black pathway. The blue and the orange arrows are the reaction cycles of regenerating Z[Cu(OH)\_2]^+ and Z[CuOH]^+ sites, respectively. The black and red numbers respectively represent the free energy variation and the free energy of activation for each elementary step with the unit of eV. The geometry structures of some key transition states are also shown.

3.3.2 H\_2O\_2 decomposition

Although the conversion of methane is facile in mononuclear Cu zeolites, it is possible for Z[Cu(OH)\_2]^+ and Z[CuOH]^+ sites to launch the competition process of the hydrogen peroxide decomposition as well because of the weaker H-O bond of H\_2O\_2 (366 kJ/mol)\textsuperscript{80}. As depicted in Figure 5, the hydrogen bonding enables the H\_2O\_2 molecule to be stuck to Z[Cu(OH)\_2]^+ (IM1) with the adsorption energy of -0.33 eV. The hydrogen atom could be readily abstracted from H\_2O\_2 by the ·OH* at Z[Cu(OH)\_2]^+ to generate ·OOH and Z[CuOH(H\_2O)]^+ (IM2) via a radical-like mechanism, which only
needs to overcome a free energy barrier of 0.24 eV (TS1). It requires a free energy barrier of 0.55 eV (TS2) for the subsequent oxidative dehydrogenation of $\cdot$OOH to produce $\text{O}_2$. It also occurs via the radical mechanism. Finally, the $\text{Z[Cu]}^+$ is regenerated after the desorption of $\text{H}_2\text{O}$.

3.4 Competition among methane, methanol and hydrogen peroxide oxidation

Although methane could be intrinsically activated at active sites $\text{Z[Cu(OH)\_2]}^+$ and $\text{Z[CuOH]}^+$, regarding the limited number of active sites, the competition among methane, methanol, and hydrogen peroxide oxidation must exist. Importantly, the selectivity depends on the competition of C-H bond activation between methane and
methanol. The conversion of methane and the consumption of hydrogen peroxide are associated with the O-H bond activation of H$_2$O$_2$ and the C-H bond activation of CH$_4$. Hence, we computationally compared the free energy barriers of these bond activation, analyzed the different components contribution, and understood the resultant kinetic influence.

3.4.1 Oxidative dehydrogenation

The enthalpy, entropy, solvation, and concentration/partial pressure would have a combined effect on the priority of the bond activation. The cumulative bar graphs at Figure 6 have illustrated their respective contributions for the first C-H bond breakings of methane and methanol, and the first O-H bond breaking for H$_2$O$_2$ at the Z[Cu(OH)$_2$]$^+$ and the Z[CuOH]$^+$ sites of ZSM-5.

Figure 6. The cumulative bar graph for the activation free energies $\Delta G^\neq$ of the first C-H bond breaking of methane and methanol and the first O-H bond breaking of hydrogen peroxide at (a) [Cu(OH)$_2$]$^+/ZSM-5$ site, and (b) [CuOH]$^+/ZSM-5$ site. For each activation free energy, $\Delta H^\neq$, $TAS^\neq$, $\Delta G^\neq_{\text{sol}}$ represent the contribution of enthalpy, entropy, and free energy of solvation to the free energy.
barrier. $\Delta G^\neq_{\text{sol}}$ was calculated with reference to 1 mol/L CH$_3$OH solution, which corresponds to a gaseous CH$_3$OH partial pressure of 0.01 bar. $\Delta \mu$ corresponds to the influence of pressure and concentration on the free energy barrier at 323 K: 30 bar CH$_4$, 100 $\mu$mol CH$_3$OH/10 mL H$_2$O, and 0.51 M H$_2$O$_2$.

First, the enthalpy is found to play a leading role in oxidative dehydrogenation. In Figure 6, the free energy of activation $\Delta G^\neq$ for methane dehydrogenation is higher than those of methanol and hydrogen peroxide. It indicates that methane is the most difficult to be activated among three molecules at these two sites. It is mainly owing to the intrinsic bond strengths of the molecules. The C-H bond strength of methane (439 kJ/mol) is greater than that of methanol (402 kJ/mol), let alone the O-H bond of H$_2$O$_2$ (366 kJ/mol). The first O-H bond activation of hydrogen peroxide even has almost zero enthalpy changes at the two sites. What’s more, the hydrogen atom abstract from these molecules all occur via the radical-like mechanism at more active Z[Cu(OH)$_2$]$^+$. Since the radical mechanism indicates the similar formed O-H bonds (between the OH$^*$ at Z[Cu(OH)$_2$]$^+$ and the H of the reactant molecule) and the eliminated M-C/O bonds (between the surface and the reactant among reactants), the intrinsic strength of the C/O-H bond must play the dominant role in the preferential bond activation. In addition to subsequent C-H activation in methanol, the methanol formed could react with the Z[Cu(OH)$_2$]$^+$ or Z[CuOH]$^+$ site to release water and form a surface methoxy species.

We calculated the adsorption energy of methanol at the active site. The calculation results showed that there was no chemical adsorption between methanol and copper at the Z[Cu(OH)$_2$]$^+$ or Z[CuOH]$^+$ site. In addition, the C-H bond activation of methanol
is prior to its O-H bond activation (Figure S11).

Second, the entropic effect has an inverse trend against the enthalpy effect, which possibly narrows down the gap of the bond activation. Compared with methanol and hydrogen peroxide, the smaller entropy of methane results in a lower entropy loss during its activation. Thus, the entropic effect would promote the methane conversion and its selectivity for DMTM. Nonetheless, the entropic advantage of methane is trivial in the confined micropores at a low temperature.

Last but not least, the activity and the selectivity would be affected by the chemical potential variation due to the concentration/partial pressure of these molecules. The high partial pressure of methane would boost the probability of the C-H bond activation, promoting both activity and selectivity towards methanol. The resultant low concentration of methanol due to the low conversion of methane would limit the deep oxidation of methanol.

Hence, on the one hand, the generation of active sites of [CuOH]$^+$ and [Cu(OH)$_2$]$^-$ relies on hydrogen peroxide. On the other hand, the active sites would preferentially catalyze the self-decomposition of hydrogen peroxide. Accordingly, the oxidation of hydrogen peroxide would suppress the methane activation and its deep oxidation.

3.4.2 Kinetic analysis

We further understand the impact of the active sites and the oxidant hydrogen peroxide on the activity and selectivity for methane partial oxidation based on kinetic analysis.
Regarding the prior C-H bond activation of methanol to the O-H bond activation of methanol, we also employed the simplified kinetic model of a simple two-step mechanism proposed by Nørskov to simulate the limitation between selectivity and activity of DMTM.\textsuperscript{87} Except for the rate-determining and selectivity-determining first C-H bond cleavages of methane and methanol, all the other steps were assumed to reach the quasi-equilibrium.

\[ \text{CH}_4 \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CO}_2 \quad (5) \]

where the desired product methanol is thereby a transition intermediate. The selectivity towards methanol (\(S_{\text{CH}_3\text{OH}}\)) can be expressed as a function of methane conversion rate (\(X\)) and the difference of the free energies of activation (\(\Delta G_1^\neq\)) between the first C-H bond breaking of methane (\(\Delta G_{\text{CH}_4}^\neq\)) and methanol (\(\Delta G_{\text{CH}_3\text{OH}}^\neq\)) as follows:

\[
S_{\text{CH}_3\text{OH}} = \frac{1 - X - (1 - X) e^{\Delta G_1^\neq/RT}}{X \cdot e^{\Delta G_1^\neq/RT} - 1} \quad (6)
\]

where \(\Delta G_1^\neq = \Delta G_{\text{CH}_4}^\neq - \Delta G_{\text{CH}_3\text{OH}}^\neq\)  \( (7)\)
Figure 7. The relationship between the conversion rate and methanol selectivity at different times was investigated. The red line corresponds to the real situation of the $Z[\text{CuOH}]^+$ site; The blue line corresponds to the real situation of the $Z[\text{Cu(OH)}_2]^+$ site. Reaction conditions: 28 mg catalysts dispersed in 10 ml of 0.51 M $\text{H}_2\text{O}_2$ aqueous solution, 30 bar $\text{CH}_4$ for 30 min at 323K.

Since the C-H bond activations all occur via the radical-like mechanism at $Z[\text{Cu(OH)}_2]^+$ in Cu-exchanged zeolites, methanol is always easier to be activated, i.e., $\Delta G_1^\neq > 0$, the selectivity of methanol and the activity of methane oxidation is always mutually inhibited. The smaller $\Delta G_1^\neq$ is significantly beneficial to DMTM. Among the investigated zeolites, the minimum gaps of the free energies of activation between methane and methanol dehydrogenation are achieved at the $Z[\text{Cu(OH)}_2]^+$ and the
Z[CuOH]$^+$ sites in ZSM-5, respectively 0.26 eV and 0.33 eV. As seen from Figure 7, the conversion rate of methane is rather low at these sites when the desired selectivity towards methanol is higher than 90%. If the conversion rate of methane is expected to arrive at 10% with a selectivity of 90% towards methanol, then $\Delta G_1^\neq$ must be lower than 0.10 eV to achieve the same selectivity. Hence, the high selectivity towards methanol with high conversion must face the tremendous challenge of using H$_2$O$_2$ as the oxidant. On the other hand, since the 10% conversion in 24 h corresponds to the turnover frequency (TOF) of 2340 h$^{-1}$, which is significantly higher than the previously reported results$^{49, 88-90}$, it is still promising to improve DMTM catalysts using H$_2$O$_2$ as the oxidant in the future despite the existence of the bottleneck in the long term due to the activity-selectivity trade-off.

In addition, the active Z[Cu(OH)$_2$]$^+$ and Z[CuOH]$^+$ sites are energetically more favorable to activate hydrogen peroxide. Competition exists between the conversion of methane and hydrogen peroxide. The ratio of reaction rates between methane and hydrogen peroxide conversion could be expressed as follows:

$$\frac{k_{CH_4}}{k_{H_2O_2}} = e^{-\frac{(\Delta G_2^\neq)}{RT}} \quad (9)$$

$$\Delta G_2^\neq = \Delta G_{CH_4}^\neq - \Delta G_{H_2O_2}^\neq \quad (10)$$

where $\Delta G_2^\neq$ is the difference of the free energies of activation between the first methane C-H bond cleavage and the second hydrogen peroxide O-H bond cleavage, which are the rate-determining steps for methane and hydrogen peroxide oxidation, respectively.

As displayed in Figure 8, the highest methane conversion is obtained at [Cu(OH)$_2$]$^+/ZSM-5$ among the investigated mono-copper active sites. However, the
self-decomposition of hydrogen peroxide is still overwhelming. It is consistent with the experimental observation of Yashnik et al. Nevertheless, since the $\text{Z[Cu(OH)\textsubscript{2}]^{+}}$ and $\text{Z[CuOH]^{+}}$ sites would mainly catalyze the self-decomposition of hydrogen peroxide, the rate of methanol oxidation would be significantly suppressed, preventing methane from the deep oxidation. Hence, the reported high selectivity toward methanol for DMTM using hydrogen peroxide at copper-zeolites may be related to the low methane conversion.

**Figure 8.** The ratio of the conversion rate of methane and hydrogen peroxide oxidation against the difference of the free energy of activation between the first C-H bond breaking of methane and the second O-H bond breaking of hydrogen peroxide and temperature.

It might be a common problem for DMTM using hydrogen peroxide as the oxidant.
that the active site prefers catalyzing self-decomposition of hydrogen peroxide. Pidko and his colleagues also found that hydrogen peroxide is not suitable for methane oxidation catalyzed by iron-based materials.\textsuperscript{92, 93} Although Xiao’s group reported that the addition of Brönsted acid could inhibit the self-decomposition of hydrogen peroxide, it might also hinder the C-H bond breaking.\textsuperscript{94} The inhibited self-decomposition mainly results from Le Chatelier's principle whereby the higher concentration of Brönsted acid prevents the equilibrium from offsetting towards the dehydrogenation. Likewise, it could obstruct the C-H bond breaking as well. Still, the self-decomposition of hydrogen peroxide would be energetically superior to methane conversion. Therefore, the use of hydrogen peroxide as an oxidant in DMTM would often result in excessive consumption of hydrogen peroxide.

4. Conclusion

Our theoretical calculation unravels that the O-O bond could be readily broken to form surface reactive hydroxyl through a water-mediated mechanism in mononuclear copper zeolites using hydrogen peroxide as the oxidant to form reactive Z[Cu(OH)$_2$]$^+$. It enables the mild C-H bond activation of methane at a low temperature. On the contrary, the O-O bond of dioxygen is formidable to be scissored to produce reactive surface oxygen species at mono-copper sites, resulting in the formidable C-H bond activation of methane at the low temperature. Hydrogen peroxide exhibits a higher reactivity for methane activation compared with molecular oxygen.

Although methane and hydrogen peroxide can easily react to form methanol at the
active site, we find that the $Z[\text{Cu(OH)}_2]^+$ could preferentially catalyze the deep oxidation of methanol and the self-decomposition of hydrogen peroxide. The C-H bond and O-H bond activation occur via the radical-like mechanism at $Z[\text{Cu(OH)}_2]^+$. The further kinetic analysis discloses that the radical-like mechanism would result in the trade-off between the selectivity and activity for DMTM using hydrogen peroxide. Moreover, it also suffers from the self-decomposition of hydrogen peroxide. Nevertheless, the kinetic analysis unravels that it is still promising to improve DMTM catalysts using hydrogen peroxide to achieve the higher TOF of DMTM with a high selectivity.

Conflicts of Interest

There are no conflicts to declare.

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