Synergistic Effect of Neighboring Fe and Cu Cation Sites Boosts Fe$_n$Cu$_m$-BEA Activity for the Continuous Direct Oxidation of Methane to Methanol

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Abstract: Direct oxidation of methane to methanol (DMTM), constituting a major challenge for C$_1$ chemistry, has aroused significant interest. The present work reports the synergistic effect of neighboring [Fe]–[Cu] cations, which can significantly boost the CH$_3$OH productivity (100.9 and 41.9 → 259.1 µmol g$^{-1}$ cat h$^{-1}$) and selectivity (0.28 and 17.6% → 71.7%) of the best performing Fe$_{0.6}$Cu$_{0.68}$-BEA (relative to monomeric Fe$_{1.28}$– and Cu$_{1.28}$-BEA) during the continuous H$_2$O-mediated N$_2$O DMTM. The combined experimental (in situ FTIR, D$_2$O isotopic tracer technique) and theoretical (DFT, ab initio molecular dynamics (AIMD)) studies reveal deeper mechanistic insights that the synergistic effect of [Fe]–[Cu] can not only significantly favor active O production ($\Delta G = 0.18$ eV), but also efficiently motivate the reaction following a H$_2$O proton-transfer route ($\Delta G = 0.07$ eV), eventually strikingly promoting CH$_3$OH productivity/selectivity. Generally, the proposed strategy by employing the synergistic effect of bimetallic cations to modify DMTM activity would substantially favor other highly efficient catalyst designs.

Keywords: methane direct oxidation to methanol (DMTM); N$_2$O; [Fe-O-Cu]$^{2+}$ active site; mechanism; ab initio molecular dynamics (AIMD)

1. Introduction

Methane, being a primary component of natural gas, constitutes the main feedstock during methanol production, which traditionally follows the syngas route, needing high temperature and pressure [1]. By contrast, the direct oxidation of methane to methanol (DMTM) operated under mild conditions is greatly appealing for CH$_3$OH production; however, this process suffers from low selectivity and productivity, due to the extremely high C-H bond energy (413 kJ mol$^{-1}$) of CH$_4$ but relatively low thermostability of CH$_3$OH [2–4]. Although it is still a major challenge to make breakthroughs for the DMTM, the development of suitable catalysts and reaction systems to promote CH$_3$OH selectivity and productivity has never ceased.

Methane monoxygenases (MMOs), as a type of methanotrophic bacteria, can readily transform CH$_4$ into CH$_3$OH at room temperature, the active site of which consists of iron or copper [5]. To mimic its catalytic behavior, the Fe- and Cu-exchanged zeolites have been extensively investigated for the DMTM [6–16], wherein the specific active site motifs significantly affect the DMTM activity. For example, Jeong et al. [7] recently reported a continuous DMTM by passing O$_2$ over Cu-MOR, finding that the binuclear [Cu-O-Cu]$^{2+}$ site possessed much higher activity than that of the mononuclear [Cu]$^{+}$ site. To further
improve the DMTM activity, the strategy of introducing another transition metal into the Cu- or Fe-exchanged zeolite to modify the active motif has also been proposed [8–14]. The group of Hutchings [8–10] performed pioneering works finding that the Cu species can dramatically promote the CH$_3$OH selectivity (>92%) and productivity of the Fe/Cu-ZSM-5 zeolite catalyst through efficiently inhibiting the overoxidation of CH$_3$OH (into formic acid and CO$_2$) during the H$_2$O$_2$ DMTM. Recently, Yu et al. [11] further found that the Cu species of Fe/Cu-ZSM can also facilitate the generation of OH- radicals which thereby can quickly react with -CH$_3$ to produce CH$_3$OH. Meanwhile, some theoretical simulations have also been conducted for the DMTM over a series of zeolitic bimetal active centers of [Cu-O-M]$^{2+}$ and [Cu-O$_2$-M]$^{2+}$ (M = Pd, Pt, Fe, Co, Ni, Zn, Au and Ag) [12–14], aiming at favoring the rational design of highly efficient bimetallic ion-exchanged zeolite catalysts.

In addition to the active site motifs, the utilized oxidant as well as H$_2$O also significantly affect the zeolitic DMTM activity and efficiency. In comparison to O$_2$ and H$_2$O$_2$, N$_2$O is a promising oxidant for the DMTM due to the much more ready formation of highly active oxygen species (named aO, T < 250 °C) after the in situ interaction with the metal modified zeolite (M-Z) catalyst [17]. Additionally, the in situ generation of active oxygen (aO) at low temperatures demonstrates N$_2$O as being a promising oxidant for the continuous DMTM, which can strikingly promote DMTM efficiency relative to that of the widely reported stepwise DMTM. Moreover, differing from H$_2$O$_2$, which is a type of expensive oxidant, N$_2$O can be largely released from the tail gas of the adipic acid industry (effluent N$_2$O content > 35 vol%) [18], which can effectively solve the source problem of N$_2$O for the N$_2$O DMTM. In light of these advantages, several studies on N$_2$O DMTM operated under moderate temperatures have recently been reported, achieving the superior DMTM activity relative to that of O$_2$ DMTM [19–25]. As for H$_2$O$_2$, it has long been recognized as a solvent to sweep out CH$_3$OH during the DMTM [6,26] until recently, when Bokhoven et al. [27,28] and Liu et al. [29] discovered that H$_2$O could directly participate in the DMTM, working as an oxidant and directing the reaction pathway. Inspired by these literature reports, a proton-transfer reaction of H$_2$O can be found in our previous work [24], pronouncedly the enhancing of CH$_3$OH production (16.8 (absence of H$_2$O) → 242.9 μmol·g$^{-1}$·cat·h$^{-1}$) and the selectivity (3.1 → 71.6%) of Cu$_{0.6%}$-BETA (BEA) zeolite during the continuous N$_2$O DMTM.

In the present work, to further improve the catalytic behavior of Cu$_{0.6%}$-BEA, a series of bimetallic Fe$_x$Cu$_m$-BEA zeolites with different Fe/Cu ratios (see Table S1) was prepared and evaluated for the H$_2$O-mediated continuous N$_2$O DMTM, based on the acknowledgement that the Fe-modified zeolite is much more favorable for N$_2$O dissociation [17], as well as the assumption that the bimetallic Fe and Cu can provide some unique activity through the synergetic effect. In particular, a strikingly promoted activity can be observed for the best-performing sample of Fe$_{0.6%}$Cu$_{0.68%}$-BEA. Specifically, higher CH$_3$OH productivity (259.1 μmol·g$^{-1}$·cat·h$^{-1}$) can be achieved at a much lower reaction temperature (T = 270 °C) relative to that of Cu$_{0.6%}$-BEA (242.9 μmol·g$^{-1}$·cat·h$^{-1}$, T = 320 °C), while in comparison to the monomeric Fe$_{1.28%}$ or Cu$_{1.28%}$-BEA with the same metal loadings, Fe$_{0.6%}$Cu$_{0.68%}$-BEA also exhibits overwhelming superiority in both CH$_3$OH productivity (259.1 versus 100.9 and 41.9 μmol·g$^{-1}$·cat·h$^{-1}$) and CH$_3$OH selectivity (71.7% versus 0.28 and 17.6%). These can be closely correlated with the synergetic effect of the neighboring [Fe]–[Cu] cations, which can efficiently favor the active O generation as well as the H$_2$O$_2$-mediated proton-transfer reaction. This specific mechanistic insight was illustrated based on the combined experimental (in situ DRIFTS and TPD-MS) and theoretical (DFT and ab initio dynamics (AIMD)) investigations. Overall, the present work systematically investigated the synergistic effect of the neighboring [Fe]–[Cu] cations over the Fe$_x$Cu$_m$-BEA zeolite, eventually leading to boosted H$_2$O$_2$-mediated N$_2$O DMTM activity, the study of which would substantially contribute to other highly efficient zeolite catalyst designs for the continuous DMTM.
2. Result and Discussion
2.1. Physicochemical Property Characterizations

Table S1 lists the physiochemical properties of the investigated Fe$_n$Cu$_m$-BEA samples (n and m represent the metal loadings), which were prepared by the tradition ion-exchange method. Briefly, the H-BEA (5g) was mixed with certain amounts (see Table S2) of Fe(NO$_3$)$_3$·9H$_2$O and Cu(NO$_3$)$_2$·5H$_2$O and thereby solved by 200 mL deionized water under stirring for 4 h at 100 °C. After being washed, dried (100 °C, 24 h) and calcined (550 °C, 4 h), the final product can be obtained. As noted, for the purpose of comparison the physiochemical properties of the monomeric Fe$_{1.28}$%- and Cu$_{1.28}$%-BEA, being prepared by the incipient-wetness impregnation method and with a metal loading amount of 1.28 wt.% (see details in Supplementary Materials), was also listed in Table S1. The small crystal-size (~17–18 mm) associated with a high Brunner–Emmet–Teller (BET) surface area (>500 m$^2$·g$^{-1}$) indicates the nano-zeolite catalysts of the prepared Fe$_n$Cu$_m$-BEA and H-BEA. The related XRD patterns confirm the characteristic BEA crystal structures of the prepared samples, with no CuO or Fe$_3$O$_4$ diffraction patterns being observed (see Figure S2a). However, the coexistence of well-dispersed metal oxides cannot be totally ruled out due to their minor amounts, being below the XRD detection limit.

To further identify the chemical states of the loaded Fe and Cu species over the Fe$_n$Cu$_m$-BEA samples, the H$_2$ temperature program reduction (H$_2$-TPR) was thereby conducted, with the results being profiled in Figure 1a. As can be seen, there are four types of reduction peak in total, as marked by orange, purple, dark green and blue, which can be assigned to the reduction of CuO, Fe$^{3+}$ ion, Cu$^{2+}$ ions and Fe$_2$O$_3$, respectively [18,24,30]. The species occupations are further depicted in Figure 1b (see details in Table S3), indicating that the Cu$^{2+}$ cations constitute the major species over Fe$_{0.38}$Cu$_{0.74}$%-BEA, while both the Cu$^{2+}$ and Fe$^{3+}$ cations can be observed for Fe$_{0.6}$Cu$_{0.68}$%-BEA (0.56 and 0.40%) and Fe$_{1.0}$Cu$_{0.5}$%-BEA (0.37 and 0.28%), although large amounts of Fe$_3$O$_4$ species (0.74%, Figure 1b) can also coexist with metal cations over Fe$_{1.0}$Cu$_{0.5}$%-BEA. Noteworthily, the Cu$^{2+}$ species' contents (green columns) were higher than those of the Fe$^{3+}$ cations (purple columns), even for the sample of Fe$_{1.0}$Cu$_{0.5}$%-BEA (0.37 versus 0.28%, Figure 1b) with much higher Fe loadings than those of Cu. This finding reveals that the Cu$^{2+}$ cations prefer to occupy the Brønsted acid ion-exchange site compared to Fe$^{3+}$ cations, eventually resulting in Fe$_3$O$_4$ as the major Fe species, especially for the sample of Fe$_{1.0}$Cu$_{0.5}$%-BEA with the highest Fe loadings. The valance states of the loaded Cu and Fe species of Fe$_n$Cu$_m$-BEA were further characterized by XPS, as shown in Figure 1c,d. The main peak located at 933.5 eV (Cu 2p$_{3/2}$), being associated with a shake-up peak at 944.5 eV (Figure 1c), indicates the characteristic Cu$^{2+}$ valance state of the surface Cu species [18], while the two main peaks located at 712.3 (Fe 2p$_{3/2}$) and 725.7 eV (Fe 2p$_{1/2}$), being associated with the satellite peaks at 718.2 and 732.9 eV (Figure 1d), indicate the 3+ valance state of the surface Fe species [31]. For comparison, H$_2$-TPR and XPS were also conducted on the monomeric Fe$_{1.28}$% and Cu$_{1.28}$%-BEA (see Figure 1a and Figure S3a,b), which indicate that both the CuO (0.52%) and Cu$^{2+}$ (0.76%) cations can be formed over Cu$_{1.28}$%-BEA. The large reduction domain of Fe$^{3+}$ species over Fe-BEA-1.28% (250–600 °C of Figure 1a) can be related to the reduction of Fe$^{3+}$ cations or oxo-cations into Fe$^{2+}$, which can be further confirmed by the H$_2$ consumption quantitatation (see Table S3). As noted, in comparison to that of Fe-BEA-1.28%, the Fe$^{3+}$ cation reduction peaks became narrower for the scenario of Fe$_n$Cu$_m$-BEA samples, which can be related to the much lower Fe$^{3+}$ cation amounts resulting from the much stronger ion-exchange ability of Cu$^{2+}$ cations at the Brønsted acid site (as stated above).
Figure 1. (a) H2-TPR profiles of the investigated Fe$_n$Cu$_m$-BEA samples; (b) Fe, Cu species quantification based on the H$_2$ consumption of H2-TPR; XPS of Cu 2p; (c) and Fe 2p; (d) of the Fe$_n$Cu$_m$-BEA samples.

2.2. Activity Measurement
2.2.1. Activity Comparison with Monomeric Fe- and Cu-BEA

With a basic understanding of the loaded metallic species, the continuous N$_2$O DMTM activity measurements were further conducted over the Fe$_n$Cu$_m$-BEA and Fe$_{1.28\%}$-Cu$_{1.28\%}$-BEA samples, as shown in Figure 2a–d and Figure S4, being associated with the CH$_4$ conversion and product selectivities being listed in Table S4. As can be seen, much higher CH$_3$OH productivities (259.1 µmol·g$^{-1}·$cat·h$^{-1}$, Figure 2a), being respectively of 2.6 and 6.2 times high than those of Fe$_{1.28\%}$- and Cu$_{1.28\%}$-BEA. Especially for the best-performed sample of Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA, it displays a boosted CH$_3$OH productivity (259.1 µmol·g$^{-1}·$cat·h$^{-1}$, Figure 2a), being respectively of 2.6 and 6.2 times high than those of Fe$_{1.28\%}$- and Cu$_{1.28\%}$-BEA (100.9 and 41.9 µmol·g$^{-1}·$cat·h$^{-1}$) with the similar total metal loadings. This finding implies that there probably exists some synergetic effect between the loaded Fe and Cu species, which can efficiently promote the H$_2$O-mediated N$_2$O DMTM activity of Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA. This will be further discussed later based on the combined experimental and theoretical studies. As for the monomeric Fe$_{1.28\%}$-BEA, large amounts of CO$_2$ (selectivity of 97.2%, see Figure 2b) can be formed, being accompanied with the N$_2$O conversion of 99.1% and CH$_4$ conversion of 47.8%.
which indicates the overoxidation of CH₄ probably due to the strong oxidation property of the generated αO over the Fe cation site; additionally, the Cu₁.₂₈%−BEA displays the lowest CH₃OH productivity (41.9 µmol·g⁻¹·cat⁻¹·h⁻¹), which can be related to the lower reaction efficiency to generate αO of the Cu cations relative to that of Fe as well as the coexistence of large amounts of CuOₓ species (0.52%, see Table S3) that can readily lead to the overoxidation of CH₃OH into CO₂ (22.6%, Figure 2b).

Figure 2. Activity measurement results of H₂O-mediated continuous N₂O DMTM over Fe₀.₆%Cu₀.₆₈%−BEA and Cu₁.₂₈%−BEA zeolite catalyst [24], eventually.

In addition to that, it can be found that the simultaneous introduction of 10 vol% H₂O into the reaction system can pronouncedly promote the CH₃OH productivity (134.8 µmol·g⁻¹·cat⁻¹·h⁻¹ → 259.1 µmol·g⁻¹·cat⁻¹·h⁻¹, Figure 2a) and CH₃OH selectivity (14.4 → 71.7%, Figure 2b) as well as the long-term stability (passing through 25 h’s test, Figure 2d) of the best-performed Fe₀.₆%Cu₀.₆₈%−BEA. This finding gives us a clue that there probably also exits the proton-transfer reaction over the Fe₀.₆%Cu₀.₆₈%−BEA, wherein the H₂O molecule could directly participate in the reaction through a proton-transfer route, as proposed in our previous work over the Cu₀.₆%−BEA zeolite catalyst [24], eventually...
pronouncedly promoting the CH$_3$OH productivity & selectivity. On the contrary, a large amount of coke can be generated during H$_2$O-absence N$_2$O DMTM over Fe$_{0.6}$Cu$_{0.68}$-BEA (67.3%, see Figure 2b), which can be closely related to the undesired side reaction of the accumulated CH$_3^-$ radicals being generated during CH$_4$ activation over the active site. Meanwhile, it is also worth noting that the Fe$_{0.6}$Cu$_{0.68}$-BEA can achieve higher CH$_3$OH productivity under a much lower reaction temperature (259.1 µmol·g$^{-1}$·cat·h$^{-1}$, T = 270 $^\circ$C) than that of Cu$_{0.6}$-BEA (242.5 µmol·g$^{-1}$·cat·h$^{-1}$, T = 320 $^\circ$C) of our previous report [24], which can well verify the viability of the proposed strategy by modifying active site motifs to improve the N$_2$O DMTM activity of Cu-BEA.

2.2.2. Activity Comparison among Fe$_n$Cu$_m$-BEA

The diverse catalytic activities of the Fe$_n$Cu$_m$-BEA samples can be closely correlated with the chemical states as well as the correlated synergetic effect of the loaded Fe and Cu species. As is well known, the metal cations constitute the active sites for N$_2$O dissociation [17], which are responsible for the production of αO for the scenario of the present reaction system, while the metal oxides readily lead to the overoxidation of CH$_3$OH into CO$_2$ [24]. In this regard, we can deduce that the highest CH$_3$OH productivity of Fe$_{0.6}$Cu$_{0.68}$-BEA can be closely correlated with its higher Fe and Cu metal cation amounts (0.56 and 0.40%, Figure 1b), which greatly favor the active O production as well as the reaction synergies between these bimetal cations. Similar findings can also be derived for the sample of Fe$_{1.0}$Cu$_{0.5}$-BEA; however, the relatively lower metal cation amounts (0.37 and 0.28%, Figure 1b) combined with the larger amounts of coexisting Fe$_x$O$_y$ (0.74%, Figure 1b) constitute two major factors leading to the relatively lower CH$_3$OH productivity compared to that of Fe$_{0.6}$Cu$_{0.68}$-BEA (223.6 versus 259.1 µmol·g$^{-1}$·cat·h$^{-1}$, Figure 2a). As for the sample of Fe$_{0.38}$Cu$_{0.74}$-BEA, possessing the highest Cu cation amount (0.73%, Figure 1b), it exhibits the lowest CH$_3$OH productivity (108.6 µmol·g$^{-1}$·cat·h$^{-1}$) among the Fe$_n$Cu$_m$-BEA samples; this can be closely related to it having the lowest amount of Fe cations (0.08%, Figure 1b), which significantly limits the reaction synergies between the loaded Cu and Fe cations. This finding can also support the proposed assumption that the synergetic effect of the loaded Fe and Cu species (the metal cations) play a vital role in the H$_2$O-mediated N$_2$O DMTM.

2.3. Evolution of the Bimetal Active Center of [Fe-O-Cu] and Thermodynamics Stability Analysis

2.3.1. NO In Situ FTIR

The in situ FTIR utilizing NO as the probe molecule (NO in situ FTIR) was employed to explore the active-site structure evolutions under the reaction condition of the present work over the best-performed Fe$_{0.6}$Cu$_{0.68}$-BEA. As shown in Figure 3a, after the He (>99.999 vol%, T = 500 $^\circ$C for 1 h) pretreatment (wine line), two broad ν(NO) bands centered at 1873 and 1864 cm$^{-1}$, being associated with characteristic ν(NO) bands belonging to the monomeric metal cation sites including 1962, 1937 and 1913 cm$^{-1}$ of [Cu]$^{2+}$ and 1840, 1818, and 1805 cm$^{-1}$ of reduced-cation sites ([Cu]$^{+}$ or [Fe]$^{2+}$) [32–34], can be clearly observed. Interestingly, after the further N$_2$O (30 vol% in He, T = 250 $^\circ$C for 1 h) treatment, an obvious enhancement for the bands at 1873 and 1864 cm$^{-1}$ (green line), which can be clearly observed, where the band of 1864 cm$^{-1}$ was merged as a shoulder of 1873 cm$^{-1}$, being accompanied with the evident decreasing of ν(NO) over the monomeric cation sites, especially for the 1840, 1818, and 1805 cm$^{-1}$ of reduced metal cation sites.
After carefully analyzing this experimental phenomenon as well as scanning the literature reports [32–34], we would assign the major bands at 1873 and 1864 cm$^{-1}$ to be $\nu$(NO) over the evolved bimetal [Fe-O-Cu] site, being in the form of [NO-Fe-O-Cu] and [Fe-O-Cu-NO]. Specifically, after the He pretreatment, part of the monomeric Fe$^{3+}$ and Cu$^{2+}$ cations would be auto-reduced by displaying the characteristic $\nu$(NO) bands at 1840, 1818 and 1805 cm$^{-1}$; concurrently, parts of the neighboring Fe$^{3+}$ and Cu$^{2+}$ cations would prefer forming the bimetallic [Fe-O-Cu] through the dihydroxylation by displaying two obvious NO adsorption bands at 1873 and 1864 cm$^{-1}$ (see Figure 3a). The subsequent N$_2$O treatment would further favor [Fe-O-Cu] formation through the interaction with reduced neighboring Fe and Cu cations. The free energy barrier of this step was simulated to be only 0.18 eV at T = 270 °C (as will be further discussed later). In this regard, the further enhancements of $\nu$(NO) at 1873 and 1864 cm$^{-1}$ ([Fe-O-Cu] site) being accompanied with the simultaneous decreasing of $\nu$(NO), especially at the reduced metal cation sites of (1840, 1818, 1805 cm$^{-1}$), can be observed in Figure 3a. To exclude the possibility of generations of large amounts of [Cu-O-Cu] or [Fe-O-Fe] species, the UV-vis and ab initio thermodynamics analyses have also been conducted (See Figure S5a,b); (i) no obvious characteristic UV-vis band belonging to [Cu-O-Cu] (~440 nm) can be observed in Figure S5a, although the same
formation Gibbs free energy ($\Delta G = -7.62$ eV) can be achieved for the [Cu-O-Cu] and [Fe-O-Fe] site (see Figure S5b); (ii) the [Fe-O-Cu] exhibits much lower formation Gibbs free energy than that of [Fe-O-Fe] ($-7.62$ versus $7.15$ eV, see Figure S5b), which indicates that it would be much more preferable to form [Fe-O-Cu] under the reaction condition of the present work due to the higher thermodynamic stabilities; (iii) the split two obvious $v$(NO) bands at 1873 and 1864 cm$^{-1}$ (see Figure 3a of He pretreatment) can also give good evidence of the formation of [Fe-O-Cu]$^{2+}$ species due to the fact that the [Fe-O-Fe] can only show up one type of characteristic $v$(NO) band around 1875 cm$^{-1}$ [32].

In light of the above statement, we can deduce that the [Fe-O-Cu] would constitute the major active site during the $N_2O$ DMTM over $\text{Fe}_{0.6\%}\text{Cu}_{0.68\%}$-$\text{BEA}$ by displaying much more extensive band intensities at 1873 and 1864 cm$^{-1}$ than those of 1840, 1818 and 1805 cm$^{-1}$ after the $N_2O$ pretreatment (see Figure 3a). To make comparisons, the NO in situ FTIR was also conducted over $\text{Fe}_{0.38\%}\text{Cu}_{0.74\%}$- and $\text{Fe}_{1.0\%}\text{Cu}_{0.5\%}$-$\text{BEA}$ (being after in situ $N_2O$ pretreatment), as shown in Figure 3b. The characteristic $v$(NO) bands over the bimetallic [Fe-O-Cu] site (1873 and 1864 cm$^{-1}$) can also be clearly observed for these two samples, the band area of which were however much lower than that of $\text{Fe}_{0.6\%}\text{Cu}_{0.68\%}$-BEA, as quantified in Figure 3c. This finding gives us a clue that the much higher $N_2O$ DMTM activity of $\text{Fe}_{0.6\%}\text{Cu}_{0.68\%}$-$\text{BEA}$ (Figure 2a) can be closely correlated with its higher amounts of evolved [Fe-O-Cu] active species in comparison to other samples.

### 2.3.2. $H_2$-TPR after $N_2O$ and $O_2$ Pretreatment

The $H_2$-TPR was further conducted over the $N_2O$ and $O_2$ (taken as a reference) pretreated $\text{Fe}_{0.6\%}\text{Cu}_{0.68\%}$-$\text{BEA}$ to confirm the evolved [Fe-O-Cu] site. Similarly, a pretreatment strategy to that of NO in situ FTIR was applied, wherein the sample were initially pretreated by He at $T = 500\,\degree\text{C}$ for 1 h before the subsequent $N_2O$ (30 vol% in He, $T = 250\,\degree\text{C}$ for 1 h) and $O_2$ (15 vol% in He, $T = 500\,\degree\text{C}$ for 1 h) pretreatments; and to obtain the better signals, the mass spectrometer (MS) was utilized to monitor the $H_2$ ($m/e = 2$) consumptions. As noted, the $O_2$ pretreatment temperature of $500\,\degree\text{C}$ was chosen according to literature reports [26] that it commonly needs a high temperature ($T > 500\,\degree\text{C}$) to generate active $O$ species during DMTM over the zeolitic catalyst. As shown in Figure 3d, three types of $H_2$ reduction peaks can be clearly observed, which can be respectively corresponding to the reduction of Fe, $O_2$ ($\sim 500\,\degree\text{C}$, blue), [Fe-O-Cu] (650 $\degree\text{C}$, purple) and the $Fe^{2+}/Cu^{+}$ cations ($900\,\degree\text{C}$, dark green). Obviously, in comparison with the $O_2$-pretreated $\text{Fe}_{0.6\%}\text{Cu}_{0.68\%}$-$\text{BEA}$, much higher amounts of [Fe-O-Cu] species (purple peak) can be formed over the $N_2O$-pretreated $\text{Fe}_{0.6\%}\text{Cu}_{0.68\%}$-$\text{BEA}$, which also constitute the major active species being in good agreement with the NO in situ FTIR result of Figure 3a. On the contrary, only trace [Fe-O-Cu] can be formed over the $\text{Fe}_{0.6\%}\text{Cu}_{0.68\%}$-$\text{BEA}$ due to the extremely low dissociation activity of $O_2$. This finding is in good agreement with the significantly lower $O_2$ DMTM activity (~1 $\mu$mol $\cdot$ g$^{-1}$ $\cdot$ cat $\cdot$ h$^{-1}$ of CH$_3$OH, see Figure S6) relative to that of $N_2O$ DMTM. Therefore, the evolution of the [Fe-O-Cu] site through the in situ interaction with $N_2O$ at low temperature ($T = 250\,\degree\text{C}$) can be safely confirmed based on the $H_2$-TPR of Figure 3d over the $\text{Fe}_{0.6\%}\text{Cu}_{0.68\%}$-$\text{BEA}$, which also constitutes the major active sites during $N_2O$ DMTM over $\text{Fe}_{0.6\%}\text{Cu}_{0.68\%}$-$\text{BEA}$.

### 2.3.3. Ab Initio Thermodynamics (AIT) Analysis

In this section, DFT-based ab initio thermodynamics (AIT) analysis was further conducted to evaluate the thermostability of the [Fe-O-Cu] site under the reaction conditions of the present work (10 vol% $H_2$O, 30 vol% $N_2$O and 1atm), as shown in Figure 4b, c, wherein the other active-site motifs, including the monomeric [Cu], [Cu-O], [CuOH] and neighboring bimetallic [Fe]-[Cu] sites, were also taken into account. Obviously, the [Fe-O-Cu] site exhibited dramatically lower $\Delta G$ values than the other active sites, indicating the stronger thermodynamic stability of the evolved [Fe-O-Cu] site. As noted, the much higher thermodynamic stability of [Fe-O-Cu] relative to that of [Fe]-[Cu] indicates that it is also
thermodynamically favorable to evolve into [Fe-O-Cu] through the in situ interaction of [Fe]-[Cu] with N₂O under the reaction conditions of the present work.

Figure 4. (a) Optimized structure models with diverse active-site motifs on the BEA zeolite; Z represents the BEA zeolite framework; the Al atom was located at the T5 site for the monomeric active site [18]; the T2 and T5 sites were chosen as the neighboring framework Al site based on previous studies [24]; (b) Gibbs-free energy of formation (ΔG) as a function of ΔH_N₂O and ΔH_H₂O (chemical potentials) for different active motifs at T = 270 °C; (c) ΔG as a function of temperature under N₂O DMTM reaction condition of 10 vol% H₂O, 30 vol% N₂O and 1 atm pressure.

2.4. Mechanistic Insight into Synergetic Effect of Neighboring Fe and Cu Cations during H₂O-Mediated N₂O DMTM

2.4.1. Experimental Mechanism Study

Based on the above studies, the active-site motif evolutions have been clarified. In this section, the H₂O-mediated N₂O DMTM reaction mechanism was further investigated by in situ FTIR and D₂O isotopic tracer techniques to explore the reaction synergy of the loaded neighboring Cu and Fe cations over the best-performing Fe₀.₆%Cu₀.₆₄%-BEA.

(a) In situ FTIR

As shown in Figure 5a, three types of ν(CH₃) vibration frequencies can be clearly observed after introducing the reactant mixtures (N₂O, CH₄ and H₂O) into the system at T = 270 °C, corresponding to the ν(CH) of CH₄ (3015 cm⁻¹), the ν(CH₃) of generated CH₃OH (2963, 2853 cm⁻¹) and the ν(CH₃) of the metal cation site (2926 cm⁻¹, [M-CH₃]), respectively [24]. As noted, except for the band at 2926 cm⁻¹ belonging to the ν(CH₃) of [M-CH₃], no obvious bands related to the ν(CH₃) of methoxy groups (CH₃O, 2980, 2869 and 2823 cm⁻¹) [27] can be observed, which implies that the H₂O-mediated N₂O DMTM follows the radical mechanism in which the CH₄ is activated into the radical of CH₃⁻ and OH⁻ at the evolved active site of [Fe-O-Cu] of Fe₀.₆%Cu₀.₆₄%-BEA. To further verify this assumption, in situ FTIR by introducing the CH₄ (2 vol% in He) into the N₂O-pretreated Fe₀.₆%Cu₀.₆₄%-BEA was further conducted, wherein the H₂O was not fed into the system to avoid its influence on ν(OH). As shown in Figure 5c, the band at 3675, being
related to the $v$(OH) at metal cations site ($\alpha$-site), can be clearly observed, which can solidly verify the deduction that the CH$_4$ activation would follow the radical mechanism over Fe$_{0.6\%}$Cu$_{0.64\%}$-BEA, as illustrated by Equations (1) and (2), wherein the M$_a$ and M$_b$ in Equation (2) represent the metal cations of Cu or Fe, respectively (the specific states will be determined by the DFT, as will be further discussed later).

$$\text{N}_2\text{O} + [\text{Cu}] - [\text{Fe}] - Z \rightarrow [\text{Cu} - \text{O} - \text{Fe}] - Z + \text{N}_2$$  \hspace{1cm} (1)

$$\text{CH}_4 + [\text{Cu} - \text{O} - \text{Fe}] - Z \rightarrow [\text{M}_a - \text{CH}_3] - [\text{M}_b - \text{OH}] - Z$$  \hspace{1cm} (2)

Figure 5. In situ FTIR spectra derived under different conditions over the Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA: (a,b) co-feeding experiment of N$_2$O (2 vol%, in He), CH$_4$ (2 vol%, in He) and H$_2$O (bubbled by the mixed flow of 40 mL·min$^{-1}$) at a time interval of 0.5 min ($T = 270 ^\circ C$), wherein the sample was pretreated in situ for 1 h at $T = 500 ^\circ C$ under vacuum conditions; (c,d) after the vacuum ($T = 500 ^\circ C$, 1 h) and subsequent N$_2$O (2 vol% in He, $T = 270 ^\circ C$ of 1 h) pretreatment, the IR signal begins to be monitored along with the interaction with CH$_4$ (2 vol%, in He).

Therefore, based on the in situ FTIR, we can deduce that the neighboring [Fe]-[Cu] would initially interact with N$_2$O, generating [Fe-O-Cu] ($\alpha$-site), which thereby favors CH$_4$ activation following a radical mechanism.
(b) D$_2$O isotopic tracer experiment

According to our previous study [24], the H$_2$O molecules could directly participate in N$_2$O DMTM through a proton-transfer route after the activation of CH$_4$ at the evolved [Cu-O-Cu] site of Cu$_{0.6\%}$-BEA. In light of that, the temperature-programmed surface reaction (TPSR-) MS-based D$_2$O isotopic tracer technique was also employed in the present work to explore whether the proton-transfer reaction of H$_2$O also occurs during the H$_2$O-mediated N$_2$O DMTM over the Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA. As shown in Figure 6a, the obviously emerged peaks of CH$_3$OD (33) and D$_3$O$^+$ (33), accompanied by the simultaneous increase/decline in the signals of HOD (19)/[D$_2$O (20)], respectively, provide us with solid evidence that the D$_2$O can also participate in the N$_2$O DMTM through a proton-transfer route after CH$_4$ activation over the evolved [Fe-O-Cu] site of Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA (see Equation (3)).

$$[M_a - CH_3] - [M_b - OH] - Z + 2D_2O \xrightarrow{\text{Proton transfer}} CH_3OD + HOD + D_2O + [M_a] - [M_b] \quad (3)$$

**Figure 6.** D$_2$O isotopic tracer study based on temperature-programmed surface reaction (TPSR) over the Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA. (a) D$_2$O-mediated N$_2$O DMTM and (b) N$_2$O DMTM in the absence of D$_2$O; as noted, the signal contributions of CH$_3$OD (33), D$_3$O$^+$ (22), HOD (19) and D$_2$O (22) from panel (b) (N$_2$O DMTM without D$_2$O) have been subtracted from panel (a); (c) peak area comparisons of CH$_3$OH (31) and CH$_3$OD (33) derived in panels (a,b).

To make comparisons, the TPSR-MS without D$_2$O addition was also conducted over Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA, as shown in Figure 6b. It is observed that the signals of CH$_3$OD (33), D$_3$O$^+$ (22), HOD (19) and D$_2$O (22) can also be detected, especially for D$_2$O (22), emerging as a small peak. In fact, this can be related to the overoxidation of CH$_4$ (99.999%), which contains small isotopic abundance of the atomic D, to produce minor D$_2$O that can further participate in the N$_2$O DMTM reaction following the proton-transfer route, eventually generating the detected signals of CH$_3$OD (33), HOD (19) and D$_3$O$^+$ (22) in Figure 6b. Therefore, this finding can also support the H$_2$O proton reaction during N$_2$O DMTM over Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA.
Figure 3c further compares the peak areas of the signals of CH$_3$OH (31) and CH$_3$OD (33) derived from Figure 3a,b, which demonstrates that the addition of D$_2$O would lead to N$_2$O DMTM following the proton-transfer route by producing much higher amounts of CH$_3$OD (33) relative to that of CH$_3$OH (31). Small amounts of CH$_3$OH can also be generated during the D$_2$O-mediated N$_2$O DMTM, which may be related to the N$_2$O DMTM over the monomeric cation sites, where no proton-transfer reactions can occur [24]. In addition to that, herein, we suggest that the D$_2$O direct-reaction route may also exist during the D$_2$O-mediated N$_2$O DMTM, wherein one D$_2$O molecule can dissociatively react with the [CuCH$_3$]–[FeOH] to generate [CuCH$_3$OD]–[FeOHD] (see Equation (4)). This reaction route will be discussed later based on the DFT and with the results being further compared with that of the H$_2$O proton-transfer route.

\[
D - O^3D + [CuCH_3] - - [FeOH] \rightarrow [CuCH_3O^3D] - - [FeOHD]
\] (4)

2.4.2. Theoretical Mechanism Simulations by DFT and AIMD

To shed deeper mechanistic insight into reaction synergy of the neighboring Fe and Cu cations of Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA, both the DFT and AIMD were employed in this part to simulate the reaction mechanism based on the constructed FeCu-BEA model with the neighboring [Fe]–[Cu] as the active site (auto-reduced form after He pretreatment, see Figure S7). In total, three types of reaction mechanisms were proposed, including the H$_2$O absence mechanism (taken for comparison) and the H$_2$O proton-transfer mechanism as well as the H$_2$O direct-reaction mechanism, as illustrated in detail in in Scheme 1. The derived reaction energy diagrams are depicted in Figure 7a and Figure S8a,b, as stated in detail below.

Scheme 1. Schematic diagram of proposed N$_2$O DMTM reaction mechanism over the best-performing sample of Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA in the presence and absence of H$_2$O; specifically, after the initial N$_2$O dissociation and CH$_4$ activation steps (black line), three types of routes were proposed, namely: (i) in the absence of H$_2$O (blue line); (ii) the H$_2$O proton-transfer route (red line); and (iii) the H$_2$O direct-reaction route. The chemical structure was labeled according to constructed models depicted in the energy diagrams of Figure 7 and Figure S8a,b.
in a (b) 2D and (c) 3D view based on the AIMD, wherein the minimal free energy route is shown by gray balls in panel (b).

(a) N₂O dissociation and CH₄ activation steps

As shown in Scheme 1, the same reaction routes are followed during the initial N₂O dissociation and CH₄ activation steps (marked by black arrow) for the three proposed types of mechanisms. Specifically, the N₂O molecule readily interacts with the neighboring [Fe]–[Cu] site to generate the α-site of [Fe-O-Cu] by overcoming an extremely low Gibbs free energy barrier of ∆G = 0.18 eV (see TS-I of Figure 7a), which is much lower than those derived from Cu-BEA of our previous work (ΔG = 0.91 and 1.31 eV of di-copper [Cu]–[Cu] site and monomeric [Cu] site, respectively) [24]. This finding demonstrates that the synergistic effect of the neighboring [Fe]–[Cu] could significantly promote N₂O dissociation to generate the active O, which constitutes the major reason leading to the much higher CH₃OH productivity and lower operation temperature of Fe₀.₆%Cu₀.₆₈%-BEA relative to that of Cu₀.₆%-BEA of our previous work. After that, the CH₄ can be subsequently activated into CH₃- and OH- (III→IV, Figure 7a); a similar reaction route of III→TSII has also been reported by the literature [35,36], following a radical mechanism as revealed by the in situ FTIR (Figure 5a–d), the free energy barrier of which is calculated to be 0.92 eV (TS-II of Figure 7a). Noteworthily, according to the DFT calculations (Figure S9a,b), the CH₄ is both kinetically and thermodynamically much more favorable to be activated into the [Fe-OH]–[Cu-CH₃] state relative to the scenario of the [Fe-CH₃]–[Cu-OH] state.

(b) Further reaction of [Fe-OH]–[Cu-CH₃] in the absence and presence of H₂O

H₂O absence mechanistic. Three types of routes were proposed for the further reaction of [Fe-OH]–[Cu-CH₃]. As shown in Scheme 1 and Figure S8a, the H₂O absence route would follow the widely reported rebound mechanism, wherein the radical of CH₃- could migrate from the [Cu]²⁺ site to interact with OH-, producing [Fe(CH₃OH)] (IV→V) by overcoming a relatively high free energy barrier of 1.21 eV (TS-III). After crossing another energy barrier of 1.12 eV (VI), the CH₃OH can be eventually desorbed.
H$_2$O proton-transfer mechanism. Based on the above in situ FTIR (Figure 5a–d) and D$_2$O isotopic transfer (Figure 6a,b) studies, the AIMD-based metadynamic simulations were employed to explore the H$_2$O proton-transfer mechanism (see Movie S1, $T = 270$ ºC, $P = 1$ atm). As shown in Figure 7a, two H$_2$O molecules can be initially inserted between the generated radicals of [FeOH]–[CuCH$_3$] (model V), which is much more thermodynamically favorable than the scenario of the H$_2$O direct-reaction mechanism with one H$_2$O molecule being adsorbed on the [Cu]$^{2+}$ site (as will be further discussed later). After that, one H$_2$O molecule would dissociatively interact with the neighboring [CuCH$_3$] and H$_2$O molecule to produce [CuCH$_3$OH]$^+$ and H$_2$O$^+$, respectively (as detected by means of the D$_2$O isotopic transfer technique in Figure 6a). Subsequently, one H$^+$ could quickly migrate from the H$_3$O$^+$ to [FeOH], generating [FeOH$_3$]$^+$ (adsorbed H$_2$O), and the H$_3$O$^+$ would be restored to H$_2$O. Finally, the adsorbed CH$_3$OH and H$_2$O ([CuCH$_3$OH]–[FeOH$_2$]) could be barrierlessly desorbed to regenerate the [Fe]–[Cu] active site. Noteworthily, an extremely low energy barrier of 0.07 eV can be observed during the H$_2$O proton-transfer process, which is comparable to the value of 0.03 and 0.05 eV for the scenario of Cu$_{0.6\%}$-BEA presented in our previous work [24]. This finding validates the suggestion that the synergistic effect of the neighboring [Fe]–[Cu] site can also favor the H$_2$O proton-transfer reaction to pronouncedly promote CH$_3$OH productivity over Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA, as observed in Figure 2a. The Gibbs free energy surface is further depicted in Figure 7b,c as a function of the coordinate number of CN$^\circ$ (O-H) and CN$^b$ (O-H) (see Figure S1a), which clearly displays the reaction energy variations from one energy minimum to another minimum.

H$_2$O direct-reaction mechanism. As stated above, the H$_2$O direct-reaction route may also occur during the H$_2$O-mediated DMTM over Fe$_{0.6\%}$Cu$_{0.68\%}$-BEA. In this regard, the H$_2$O direct-reaction mechanism was further simulated by DFT. As shown in Figure S8b, initially, one H$_2$O site forms [H$_2$OCuCH$_3$]$^+$ (VII). Thereby, the H$_2$O can be readily dissociated from (H=$^-$O$^+$H) to react with the [FeOH] and [Cu–CH$_3$], producing [FeOH$_3$]–[H$^+$OCuCH$_3$] ($\Delta G = 0.24$ eV, TS-III). After the rebounding of CH$_3$– and $^-$O$^+$H– by crossing a free energy barrier of $\Delta G = 1.14$ eV (TS-V), [CuCH$_3$OH$^+$H] can be formed. With the assistance of H$_2$O (being desorbed from [FeOH$_2$]), the CH$_3$OH$^+$H can be barrierlessly released from the [Cu]$^{2+}$ site.

(c) Reaction mechanism comparisons

In comparison to the H$_2$O absence mechanism, the slightly lower barrier of the radical rebound step (1.14 (TSIV, marked blue) versus 1.21 eV (TSIII, marked green) (see inserted energy diagram of Figure 7a) combined with the barrierless desorption of CH$_3$OH indicates that H$_2$O could also favor CH$_3$OH production through the direct-reaction route. However, the H$_2$O-mediated N$_2$O DMTM would generally follow the H$_2$O proton-transfer route due to the extremely low energy barrier of 0.07 eV. To make quantitative comparisons, microkinetic modeling was further conducted for these three types of mechanisms, with the results being profiled in Figure S10a–d. As can be seen (Figure S10a), the overall reaction rates were predicted to be $3.64 \times 10^9$ s$^{-1}$ (H$_2$O proton-transfer route), $1.05 \times 10^4$ s$^{-1}$ (H$_2$O direct-reaction route) and $7.64 \times 10^{-10}$ s$^{-1}$ (H$_2$O absence route), respectively, which quantitatively verified that the significant promotion effect of H$_2$O during N$_2$O DMTM is generally through the H$_2$O proton-transfer route, being favored by the synergistic effect of the neighboring [Fe]–[Cu] site. It is worth noting that the DFT-calculated reaction rate of the H$_2$O-mediated N$_2$O DMTM was several orders of magnitude higher than that of the H$_2$O-absence N$_2$O DMTM; however, it was only two times higher for the scenario of the experimental result of Figure 2a (CH$_3$OH productivity). This discrepancy is related to the utilized DFT calculation method during the microkinetic modeling, especially for the pre-exponential factor calculations derived by the frequency calculations. However, it does not affect the parallel comparisons of the DFT-based microkinetic modeling results.

2.4.3. Illustration of the Synergistic Effect of Neighboring Fe and Cu Cations

Based on the above experimental and the theoretical mechanism studies, we can obtain a comprehensive understanding of the synergistic effect of the neighboring [Fe]–[Cu] cations...
during the \( \text{H}_2\text{O} \)-mediated \( \text{N}_2\text{O} \) DMTM. On the one hand, it can efficiently promote \( \text{N}_2\text{O} \) dissociation to generate active O ([Fe-O-Cu]) by extensively reducing the \( \text{N}_2\text{O} \) dissociation barrier from 0.91 eV (the neighboring [Cu–[Cu] site [24]) to 0.18 eV. On the other hand, it can also motivate the reaction following the \( \text{H}_2\text{O} \) proton-transfer route by crossing an extremely low free energy barrier of 0.07 eV, thereby pronouncedly enhancing \( \text{CH}_3\text{OH} \) productivity/selectivity, as well as long-term stability (reducing carbon depositions). To provide deeper insights, from the electronic structure point of view, into the synergistic effect of neighboring [Fe–[Cu] on \( \text{N}_2\text{O} \) dissociation to generate active O, the theoretical simulations including electronic density difference, the Bader charge analysis and density of state (DOS) were further conducted (see Figure 8a–d) based on the optimized \( \text{N}_2\text{O} \)-adsorption model and DFT, wherein the neighboring [Cu–[Cu] was also taken into account for comparison.

As can be seen (Figure 8a,b), much higher amounts of charge transfers occur after the adsorption of \( \text{N}_2\text{O} \) onto the the [Fe–[Cu] site, wherein the bimetal cations of [Fe–[Cu], especially for the cationic [Fe], acting as the charge donors, donate much greater charges (0.2 and 0.44) to the \( \text{N}_2\text{O} \) molecule relative to that of the neighboring [Cu–[Cu] cations.

![Figure 8. (a,b) Electronic density difference upon adsorption of \( \text{N}_2\text{O} \) onto FeCu-BEA and Cu-BEA, respectively, with neighboring [Fe–[Cu] and [Cu–[Cu] as the active site; the yellow and blue colors represent electron density increases and decreases, respectively; the metal cations are labeled by the subscript characters a and b to mark differences; (c) comparisons of transferred charges after adsorption of \( \text{N}_2\text{O} \) for the neighboring metal cations based on the Bader charge analysis; (d) total DOS comparisons for the models depicted in panels (a,b); Si (yellow), O (red), N (blue), Al (pink), Cu (orange) and Fe (purple).](image-url)
This finding indicates that the neighboring [Fe]–[Cu] site can exert much a stronger electric field effect on the adsorbed N₂O, which is greatly favorable for the pre-activation of N₂O and subsequent O-N₂ bond fracture to produce active O. As observed (Figure S11a,b), much more extensive structure distortion can be clearly observed for the adsorbed N₂O molecule onto the [Fe]–[Cu] site: ∠N-N-O bending from 180° to 129.7° versus (180° → 175°) of the [Cu]–[Cu] site. The stronger charge transfer effect (or electric filed effect) of the [Fe]–[Cu] site can be explained by the total DOS (Figure 8d) as well as partial DOS (PDOS) results (Figure S12a–h), which indicates that the [Fe]–[Cu] site not only possesses much lower electron-transfer band gaps but also can reduce the band gaps of the N and O atoms, N₂O (0.77 versus 1.83 eV), eventually significantly promoting the charge transfers between the [Fe]–[Cu] active site and the N₂O molecule. In light of the above studies, we can conclude that the much more efficient synergistic effect of the [Fe]–[Cu] active site (relative to that of [Cu]–[Cu] site) during the N₂O dissociation step can be interpreted by its stronger electric field effect, leading to the significantly enhanced electron transfer between the bimetal active site and the N₂O molecule due to the lowered band gaps of bimetal cations as well as the N and O atoms of the N₂O molecule.

3. Materials and Methods

3.1. Experimental Methods

3.1.1. Catalyst Preparation

The commercial H-BEA with the Si/Al of 12.5 (mole ratio) was purchased from Tianjin Nankai University Catalyst Co., Ltd. of China, based on which a series of FeₙCuₘ-BEA zeolites (Table S1) were prepared by means of the traditional wet ion-exchange method. For the purpose of comparison, the monomeric Fe₁.28%- and Cu₁.28%-BEA, with the total metal loading amounts being the same as those of Fe₀.6%-Cu₀.68%-BEA (1.28 wt.%), were prepared by means of an incipient-wetness impregnation method. More details regarding the catalytic preparations are stated in the Supplementary Materials.

3.1.2. Catalyst Characterizations

The characterizations of X-ray diffraction (XRD), element content (determined by inductively coupled plasma (ICP), X-ray photoelectron spectroscopy (XPS), N₂ adsorption/desorption, H₂-temperature programmed reduction (H₂-TPR), UV-vis diffuse-reflectance, in situ FTIR and D₂O isotopic tracer were conducted as described in detail in our previous work [24]—alternatively, please see details in the Supplementary Materials.

3.1.3. Activity Measurement

The continuous N₂O DMTM in both scenarios of the presence and absence of H₂O (10 vol%) was conducted over a fixed bed reactor (O.D. 11 mm, I.D. 8 mm, L485 mm) under a total flow rate of 100 mL·min⁻¹ [GHSV (gas hourly space velocity) = 12,000 h⁻¹]. The reaction products were analyzed by a gas chromatograph (SHIMADZU GC-2014) being equipped with the thermal conductivity detector (TCD) and flame ionization detector (FID). To prevent condensation, the gas line from the point of liquid injection to then GC unit was heated (T = 200 °C) by resistive heating tape. More details regarding activity measurement can be found in the Supplementary Materials or our previous work [24].

3.2. Computational Methods

3.2.1. Constructed Model

The model of FeₙCuₘ-BEA with the neighboring [Fe]–[Cu] bimetal active site was constructed based on the BEA structure (a = 12.632, b = 12.632 and c = 9.421 Å) from the database of IZA [37], wherein the framework Al was located at the T2 and T5 site according to our previous work [24], and the Si atoms were set to be fixed during the structure optimization and transition state (TS) calculations to keep the structure of BEA.
3.2.2. Computational Method

The periodic density functional theory (DFT) analysis was performed based on the Vienna ab-initio simulation package (VASP) [38], which was employed in the present work to simulate the N₂O DMTM mechanism (in the presence and absence of H₂O) and conduct microkinetic analysis, electronic structure analysis (including electronic density difference, Bader charge and density of state (DOS)) and ab initio thermodynamics analysis (evaluating the thermostabilities of active-site motif and generating radical intermediate). The ab initio molecular dynamics (AIMD) analysis was conducted based on CP2K code [39] to explore the H₂O proton-transfer mechanism, wherein the AIMD-based metadynamic simulations were conducted utilizing two types of collective variables, the coordination numbers (CN) of [CN⁰O-H] and [CN²O-H] (as illustrated in Figure S1a). The detailed method descriptions of DFT and CP2K can be found in the Supplementary Materials or our previous work [24].

4. Conclusions

The present work systematically investigated the H₂O-mediated continuous N₂O DMTM over a series of FeₙCuₙ₋ₘ-BEA zeolites based on combined experimental and theoretical approaches. The strikingly promoted CH₃OH productivity (259.1 µmol g⁻¹ cat⁻¹ h⁻¹) and selectivity (71.7%), as well as long-term reaction stability, can be achieved over the best-performed sample of Fe₀.6%Cu₀.6%-BEA, which is closely correlated with the synergistic effect of the loaded neighboring Fe and Cu cations. On the one hand, it is much more favorable for N₂O dissociation to generate the αO (bridge O of [Fe-O-Cu]²⁺, ΔG = 0.18 eV at T = 270 °C) due to the exerted strong electric field effect. On the other hand, it can motivate the N₂O DMTM reaction following a H₂O-mediated proton-transfer route to produce CH₃OH by crossing a much lower energy barrier (ΔG = 0.07 eV), eventually pronouncedly enhancing CH₃OH production and desorption as well as the catalytic reaction’s long-term stability (through efficiently reducing carbon depositions). Generally, the present work reported the synergistic effect of neighboring Fe and Cu cations over the FeₙCₘ⁻BEA zeolite, which can efficiently promote its CH₃OH productivity/selectivity during H₂O-mediated N₂O DMTM. Thereby, employing the synergistic effect of bimetallic cations to modify zeolitic activity constitutes a promising strategy for a highly efficient catalyst design for the DMTM.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11121444/s1: Figure S1: (a) Illustration of selected coordination number (CN) during which can efficiently promote its CH work to simulate the N Vienna ab-initio simulation package (VASP) [38], which was employed in the present Activity measurement results of N (evaluating the thermostabilities of active-site motif and generating radical intermediate). ◦ T = 270 The ab initio molecular dynamics (AIMD) analysis was conducted based on CP2K code [39] ported the synergistic effect of neighboring Fe and Cu cations over the Fe (a) CH (b) variations of derived CN numbers indicating (O-H) bond factures the H (a) CH (b) UV-vis spectra of Fe (c) TEM-EDX mapping results of Fe (d) N (m) TEM-EDX mapping results of Fe (d) TEM-EDX mapping results of Fe (c) TEM-EDX mapping results of Fe (b) TEM-EDX mapping results of Fe (a) X-ray diffraction patters and (b) isothermal adsorption/desorption (derived by N₂ adsorption/desorption) of FeₙCuₙ₋ₘ-BEA and monomeric Fe₁₂₈%-BEA; (c) TEM-EDX mapping results of Fe₀.6%-Cu₀.6%-BEA-0.6% (the Fe and Cu species are uniformly distributed on the catalyst), Figure S3: XPS characterization results of (a) Fe₁₂₈%- and (b) Cu₁₁₂₄%-BEA (the metal cations constitute major metallic species). Figure S4: Activity measurement results of N₂O-DMTM in both presence and absence of H₂O over the prepared bimetallic FeₙCuₙ₋ₘ-BEA and monomeric Fe₁₂₈%- and Cu₁₁₂₄%-BEA samples after 5 h’s reactions: (a) CH₃OH productivity; (b) product selectivity; (c) CH₄ conversion; (d) N₂O conversion; reaction condition N₂O:CH₄:H₂O:He = 30:15:10:45 (presence of H₂O); and O₂:CH₄:He = 30:15:55 (absence of H₂O); GHSV = 12,000 h⁻¹ and T = 270 °C, Figure S5: (a) UV-vis spectra of Fe₀.6%-Cu₀.6%-BEA being respectively pretreated by N₂ and at T = 200, 250 and 300 °C; no obvious band emerged at 440 nm belong to the characteristic peak of [Cu-O-Cu]; (b) thermodynamic stabilities comparisons of diverse bimetallic active sites, including [Cu-O-Cu], [Fe-O-Cu] and [Fe-O-Fe] based on the DFT-based ab initio thermodynamic analysis by taking the reaction condition of present work into account: 10 vol% H₂O, 30 vol% N₂O, and total pressure of 1 atm; obviously, the [Fe-O-Cu] & [Cu-O-Cu] possessed much lower formation Gibbs free energy than that of [Fe-O-Fe]²⁺ site, indicating higher thermodynamic
stability; as noted, the data of ΔG for [Cu-O-Cu]-Z was covered by those of [Fe-O-Cu]-Z, Figure S6: O2-DMTM activity measurement result over Fe0.6%Cu0.68%-BEA with the reaction condition being similar to that of N2O-DMTM:O2:CH4:H2O:He = 30:15:10:45, GHSV = 12,000 h⁻¹ and T = 270 °C, Figure S7: Optimized periodic FeCu-BEA model with neighboring [Fe]–[Cu] as the active site, Figure S8: (a) DFT simulated H2O absence mechanism during N2O-DMTM over construed Fe0.6%Cu0.68%-BEA model with neighboring [Fe]–[Cu] as the active site, (b) DFT simulated H2O direct reaction mechanism during N2O-DMTM over construed Fe0.6%Cu0.68%-BEA model with the neighboring [Fe]–[Cu] as active site with the derived Gibbs free energy being compared with that of H2O absence mechanism (see inserted energy diagram), Figure S9: (a) kinetic comparisons of radical evolutions during CH4 activation step; (b) thermostability comparisons of generated intermediate radicals in [FeCH3]–[CuOH] and [FeOH]–[CuCH3] state based on ab initio thermodynamics taking the reaction conditions of 10 vol% H2O, 30 vol% N2O and 1 atm into account, Figure S10: Microkinetic modeling results based on DFT at T = 270 °C: (a) overall reaction rate of different reaction mechanisms; surface coverage variations as a function of reaction time t of (b) H2O absence route; (c) H2O direct reaction route; and (d) H2O proton transfer reaction route. Figure S11: Optimized N2O-adsorption model of with (a) neighboring [Fe]–[Cu] site and (b) neighboring [Cu]–[Cu] site; Si (yellow), O (red), N (blue), Al (pink), Cu (orange) and Fe (purple), Figure S12: Partial density of sate (PDOS) of bimetal cations and N, O atoms of N2O based on N2O-adsorption models; (a–d) [Fe0.6%], [Cu0.68%], atomic O and end N of N2O over neighboring [Fe]–[Cu] model; (e–h) [Cu0.68%], [Cu0.68%], atomic O and end N of N2O over neighboring [Cu]–[Cu] model, Figure S13: Reaction condition determination based on the N2O-DMTM measurement over Fe0.6%Cu0.68%-BEA: (a) reaction temperature (T); (b) introduced H2O content, Figure S14: N2O-DMTM activity measurement result over Fe0.6%Cu0.68%-BEA and monomeric Fe1.28%-Cu1.28%-BEA in presence (a–b) and absence (c–d) of H2O for 5 h: (a,c) CH3OH productivity; (b,d) N2O conversion, Figure S15: Thermogravimetry (TG) and differential thermogravimetric analysis (DTG) curves of the Fe0.6%Cu0.68%-BEA-0.6% samples being after 25 h’s long-term test in absence (a) and presence (b) of 10vol% H2O, Figure S16: 29Si MAS NMR of Fe0.6%Cu0.68%-BEA being respectively before and after the 5 h’s reaction (H2O-mediated N2O-DMTM), Table S1: Physicochemical property of investigated samples, Table S2: Consumption of metal salts for catalysts preparation, Table S3: Loaded Fe and Cu species quantifications based on H2-TPR, Table S4: Methane conversion and products selectivity of investigated samples, Table S5: (a) Elementary steps and kinetic parameters involved in microkinetic modeling for the H2O absence mechanism, (b) Elementary steps and kinetic parameters involved in microkinetic modeling for the H2O direct reaction mechanism, (c) Elementary steps and kinetic parameters involved in microkinetic modeling for the H2O-proton-transfer mechanism.

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