

Article

Mechanistic Insight into the Propane Oxidation Dehydrogenation by N₂O over Cu-BEA Zeolite with Diverse Active Site Structures

Ruiqi Wu, Ning Liu , Chengna Dai, Ruinian Xu, Gangqiang Yu, Ning Wang  and Biaohua Chen

Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, China; b202265055@emails.bjut.edu.cn (R.W.); daicn@bjut.edu.cn (C.D.); xuruinian@bjut.edu.cn (R.X.); yugq@bjut.edu.cn (G.Y.); ning.wang.1@bjut.edu.cn (N.W.); chenbh@bjut.edu.cn (B.C.)

* Correspondence: liuning@bjut.edu.cn

Abstract: The present work theoretically investigated propane oxidation dehydrogenation by utilizing N₂O as an oxidant (N₂O-ODHP) over Cu-BEA with three different types of active site, including monomeric Cu ([Cu]⁺), dimeric Cu ([Cu—Cu]²⁺), and distant monomeric Cu sites ([Cu]⁺—[Cu]⁺). Energetically, we calculated that the monomeric [Cu]⁺ is favorable for the αH dehydrogenation step (ΔE = 0.05 eV), which, however, suffers from high barriers of N₂O dissociation and βH dehydrogenation steps of 1.40 and 1.94 eV, respectively. Although the dimeric [Cu—Cu]²⁺ site with a Cu—Cu distance of 4.91 Å is much more favorable for N₂O dissociation (0.95 eV), it still needs to overcome an extremely high barrier (ΔE = 2.15 eV) for βH dehydrogenation. Interestingly, the distant [Cu]⁺—[Cu]⁺ site with the Cu—Cu distance of 5.82 Å exhibits low energy barriers for N₂O dissociation (0.89 eV) and ODHP steps (0.01 and 0.33 eV) due to the synergistic effect of distant [Cu]⁺. The microkinetic analyses quantitatively verified the superior activity of the distant [Cu]⁺—[Cu]⁺ site with a reaction rate being eight to nine orders of magnitude higher than those of the monomeric and the dimeric Cu sites, and this is related to its ready charge-transfer ability, as shown by the partial Density of State (PDOS) analysis and the static charge differential density analysis in this study. Generally, the present work proposes that the distance between the [Cu]⁺ sites plays a significant and important role in N₂O-ODHP over the Cu-based zeolite catalyst and modulates Cu—Cu distance, and this constitutes a promising strategy for highly-efficient Cu-zeolite catalyst design for N₂O-ODHP.

Keywords: propane oxidation dehydrogenation (ODHP); N₂O; Cu-BEA; density functional theory (DFT); microkinetic modelling



Citation: Wu, R.; Liu, N.; Dai, C.; Xu, R.; Yu, G.; Wang, N.; Chen, B.

Mechanistic Insight into the Propane Oxidation Dehydrogenation by N₂O over Cu-BEA Zeolite with Diverse Active Site Structures. *Catalysts* **2023**, *13*, 1212. <https://doi.org/10.3390/catal13081212>

Academic Editors: De Fang and Yun Zheng

Received: 19 July 2023

Revised: 13 August 2023

Accepted: 14 August 2023

Published: 15 August 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Propylene is one of the most important organic raw materials, and it can be used to synthesize petrochemical products, such as polyurethane, polypropylene, acetone, acrylonitrile, polyacrylonitrile, and propylene oxide. The traditional commercial production of propylene is mainly through fluid catalytic cracking (FCC) and steam cracking (SC) of petroleum by-products, such as naphtha and light diesel oil [1,2]. However, relatively low selectivity as well as limited resources cannot meet the growing demand of propylene, thereby making it highly desirable to develop some efficient and economical methods to produce propylene [3–5]. The massive exploitation and use of shale gas has increased the production of low-carbon alkanes, and propane has thus become a cheap chemical raw material. Converting abundant propane into propylene is not only an important topic in the field of the petrochemical industry but is also a research hotspot in the field of heterogeneous catalysis [4,5], and it is a promising means of meeting the huge demand of the propylene market [2,6].

The catalytic dehydrogenation of propane techniques include the direct dehydrogenation of propane (PDH) and the oxidative dehydrogenation of propane (ODHP). The direct PDH has been industrialized: one example is the Catofin process using chromium

aluminum oxide as a catalyst by the Lummus Company [7,8], and another is the Oleflex process from UOP utilizing platinum-based catalysts [7,8]. However, the direct PDH is a reversible and strongly-endothermic reaction that is limited by thermodynamic equilibrium. Moreover, C–C bond breaking to produce methane/ethylene is much more likely to occur at high temperatures, which can further lower propylene selectivity [7,8]. Due to these shortcomings, researchers have conducted studies on the catalytic dehydrogenation of propane under aerobic conditions. Recently, it has been reported that utilizing N_2O as the oxidant is much more effective than O_2 for the ODHP [9–11]. For example, Bulanek et al. [9] have reported that the N_2O -ODHP is much more efficient relative to that of O_2 -ODHP by displaying its higher propane conversion rate and its propylene selectivity. Katerinas et al. [10] have also reported that the selectivity of propylene increased from 33.6% to 68% when using N_2O as the oxidant, which can also improve the conversion rate of propane [12].

At the current stage, researchers are still trying to find the suitable catalyst for the N_2O -ODHP, and the zeolite catalyst is notable here due to its excellent N_2O dissociation activity, which generates αO [13]. The BEA zeolite, with a unique twelve-ring structure, possesses better N_2O dissociation activity than those of Y, MFI, FAU, and MOR [14,15]. Sobalikseta al. [16] have reported that Cu (II) in BEA is the active site of N_2O decomposition. In our previous works, the catalytic dissociation of N_2O [17] as well as the N_2O oxidation of methane into methanol [18] were also investigated over the Cu-BEA, and it was found that both the monomeric and the dimeric Cu sites can function as the active sites for N_2O dissociation to generate αO . In the present work, the N_2O -ODHP was theoretically investigated over the Cu-BEA zeolite with diverse active site structures, including monomeric $[\text{Cu}]^+$, dimeric $[\text{Cu}-\text{Cu}]^{2+}$, and distant $[\text{Cu}]^+ \cdots [\text{Cu}]^+$ sites. The Mars van Krevelen mechanism is related to the reaction between the reactant and the lattice oxygen of the oxidation catalyst [19,20]. The first step is the oxidation of the reductant by the lattice oxygen of the catalyst that generates the product, with a simultaneous formation of oxygen vacancy. The second step is the regeneration of the catalytic active site through the dissociated oxygen in order to replenish oxygen vacancies. Being similar to such a mechanism, in the present work, the αO functions as the active site, and it is utilized to oxidize C_3H_8 into C_3H_6 and H_2O . The αO would thereby be further regenerated through the reoxidation by N_2O . The specific reaction mechanisms were well illustrated by DFT, and the microkinetic modeling was further conducted in order to quantitatively compare the reaction rates of the diverse active sites. Generally, the present work aims to shed a deeper mechanistic light on the active-site motif structural effect on N_2O -ODHP and, moreover, emphasize that modulating the Cu–Cu distance would constitute a promising method for a highly efficient Cu-based zeolite catalyst design for the N_2O -ODHP.

2. Result and Discussion

2.1. N_2O -ODHP Mechanism Simulation over Diverse ACTIVE Site

Three types of Cu-BEA models with different active centers (Figure S1a,c) were constructed for the N_2O -ODHP mechanism simulations, which comprised three steps: (i) N_2O dissociation to produce αO with the simultaneous release of N_2 , and the dehydrogenation of (ii) the αH and (ii) the βH of C_3H_8 . The derived energy diagrams along with a different reaction route (Routes A–C) over these active sites are depicted in Figure 1a–d, and based on this, we conducted an in-depth analysis of the specific reaction pathways and the evolution of the structures intermediately generated, and we then compared the derived energy barrier in order to determine the optimal active center for N_2O -ODHP.

2.1.1. N_2O -ODHP over Monomeric $[\text{Cu}]^+$ Site of Route A

(a) Dissociation of N_2O to form αO (Reaction Step A1). In this part, the N_2O -ODHP over the monomeric $[\text{Cu}]^+$ site of Cu-BEA (noted as $\text{Z}^{\text{a}}-\text{Cu}$) was simulated by DFT. Firstly, the N_2O molecule can be adsorbed over the $\text{Z}^{\text{a}}-\text{Cu}$ site through the O end with a bond length of 2.00 Å. After overcoming a relatively high energy barrier of 1.40 eV (TSA1; Figure 1a), the αO can be generated. As noted, compared with the structure of the N_2O -

adsorption state, the bond of $[\text{CuO}]-\text{N}$ was elongated from 1.22 to 1.89 Å, and the bond angle of $\text{Cu}-\text{O}-\text{N}_2$ bent from 121.4 to 124.0° (Figure 2a,b). Such structural distortion can be related to the pre-activation effects of the monomeric $[\text{Cu}]^+$. The αO of $[\text{Cu}-\text{O}]^+$ can be formed, as shown in Figure 2c, with a $[\text{CuO}]-\text{N}$ bond of 3.76 Å.

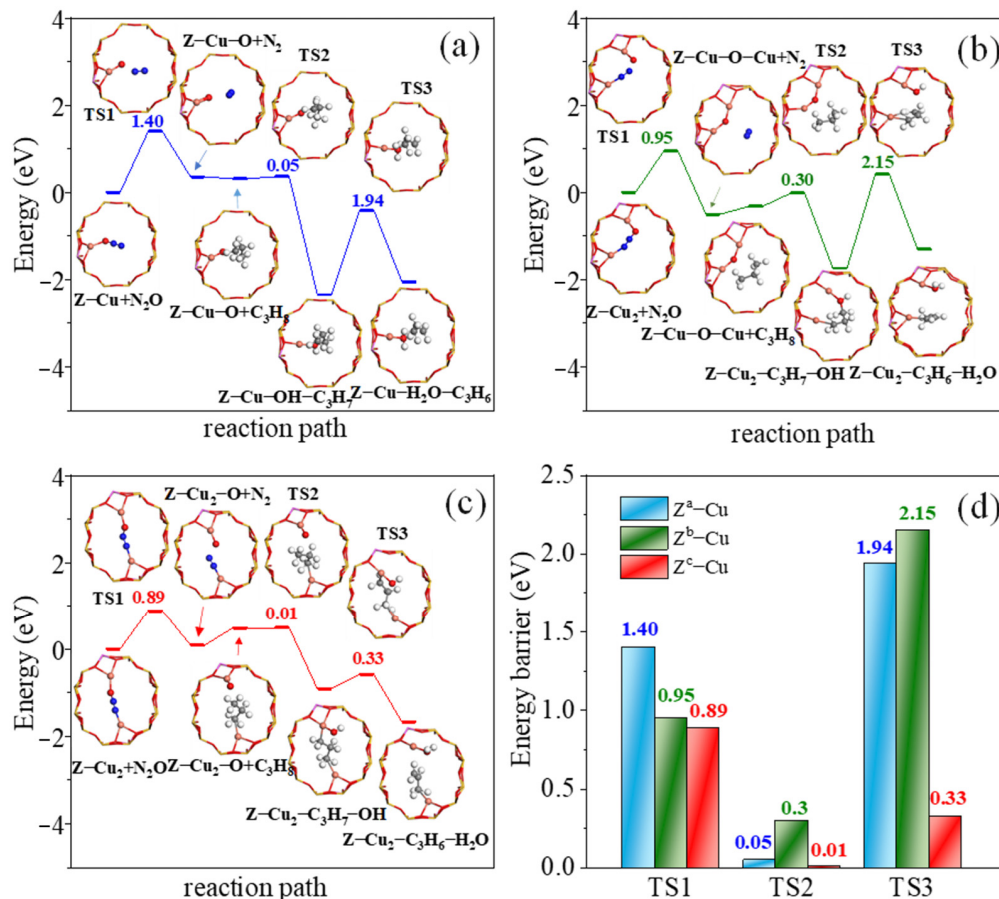


Figure 1. Energy diagram of N_2O -ODHP over Cu-BEA with different active sites of (a) $Z^a-\text{Cu}$ (reaction Route A); (b) $Z^b-\text{Cu}$ (reaction Route B); (c) $Z^c-\text{Cu}$ (reaction Route C); and (d) energy barrier comparisons. Si (yellow), O (red), N (blue), Al (pink), Cu (orange).

(b) Propane dehydrogenation of αH (Reaction Step A2). Reaction Route A2 describes the propane dehydrogenation of αH over $Z^a-\text{Cu}-\text{O}$, wherein there exists one bond fracture of $\text{H}-\text{C}_3\text{H}_7$ and two bond formations of $[\text{Cu}-\text{O}]-\text{H}$ and $[\text{Cu}-\text{O}]-\text{C}_3\text{H}_7$ (the αO being connected with the subtracted H and the radical of C_3H_7). As shown in Figure 2d,e, the distance of $\text{O}-\alpha\text{H}$ slightly shrunk from 2.26 to 1.84 Å, and the bond of $\text{C}-\alpha\text{H}$ extended from 1.11 to 1.13 Å after the adsorption of C_3H_8 ($\Delta E = -0.06$ eV, Figure 1a). The αH dehydrogenation occurred by crossing the energy barrier of 0.05 eV through the TSA2, which can be characterized by the $\text{Cu}-\text{O}-\text{C}$ bond angle of 100.6° and the $\text{Cu}-\text{O}-\text{H}$ bond angle of 97.5°. After that, the αH can be subtracted from C_3H_8 , forming $Z^a-\text{Cu}-\text{OH}$ with the OH bond of 0.97 Å (Figure 2e). In comparison to 1.49 eV of αH dehydrogenation over the $\text{CeO}_2(111)$ [21], it would be easier for αH dehydrogenation to occur over the monomeric $[\text{Cu}]^+$ site of Cu-BEA.

(c) Propane dehydrogenation of βH to form propylene (Reaction Step A3). The dehydrogenation of βH occurred in Route A3 through another transition state of TSA3 with a greatly higher energy barrier of 1.94 eV (Figure 1a), wherein the βH can migrate from C_3H_7 to $Z^a-\text{Cu}-\text{OH}$, finally generating the C_3H_6 and the H_2O . The distance of the $[\text{CuO}]-\beta\text{H}$ shrunk from 2.62 to 1.72 Å, and the bond of $\text{C}-\alpha\text{H}$ extended from 1.11 to 1.28 Å and formed the $Z^a-\text{Cu}-\text{H}_2\text{O}-\text{C}_3\text{H}_8$ that can be seen in Figure 2f,g. Therefore, according to

the above DFT energy calculations, we can derive that the monomeric $[\text{Cu}]^+$ site possessing a relatively high barrier for N_2O -ODHP, especially for the βH dehydrogenation step, is not potentially active for the N_2O -ODHP.

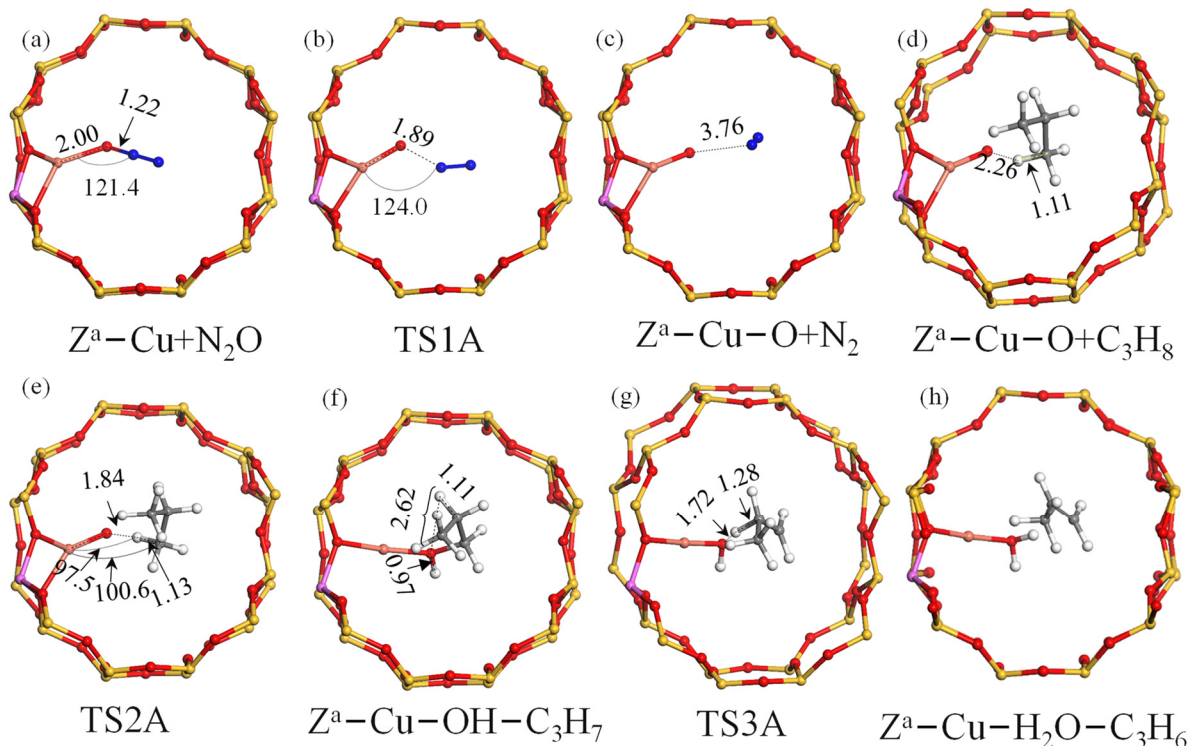


Figure 2. Optimized model of Cu-BEA with Z^a -Cu site for the N_2O -ODHP: (a) Z^a -Cu+N $_2$ O (adsorption for N_2O); (b) TS1A; (c) Z^a -Cu-O+N $_2$; (d) Z^a -Cu-O+C $_3$ H $_8$ (adsorption of C_3H_8); (e) TS2A; (f) Z^a -Cu-OH-C $_3$ H $_7$; (g) TS3A; (h) Z^a -Cu-H $_2$ O-C $_3$ H $_6$. Si (yellow), O (red), N (blue), Al (pink), Cu (orange).

2.1.2. N_2O -ODHP over Dimeric $[\text{Cu}-\text{Cu}]^{2+}$ Site of Route B

(a) Dissociation of N_2O to form αO (Reaction Step B1). In this part, the N_2O -ODHP was simulated over the dimeric $[\text{Cu}-\text{Cu}]^{2+}$ site (noted as Z^b -Cu). As shown in Figure 3a, the N_2O could be absorbed over Z^b -Cu through both its O and N end, with a Cu-ON $_2$ bond of 1.95 Å, a Cu-N $_2$ O bond of 1.80 Å, and an N-N-O bond angle of 175.0°. Much stronger structural distortion can be observed for the adsorbed N_2O relative to that of the N_2O being adsorbed over the monomeric $[\text{Cu}]^+$ site, and this is closely related to the strong synergistic effect of the dimeric $[\text{Cu}-\text{Cu}]^{2+}$. Moreover, due to such a synergistic effect, the N_2O can be readily ($\Delta E = 0.95$ eV, Figure 1b) dissociated to generate the αO ($[\text{Cu}-\text{O}-\text{Cu}]^{2+}$, Figure 3c) and the N_2 through the TS1B. Further comparing the structures of the adsorption state (Figure 3a) and the TS1B (Figure 3b), the bond length of Cu-ON $_2$ shrunk from 1.95 to 1.75 Å, while the N $_2$ -O bond enlarged from 1.79 to 1.80 Å, and the bond angle of N-N-O decreased from 112.9 to 118.9°.

(b) Propane dehydrogenation of αH (Reaction step B2). The C_3H_8 can be initially adsorbed over Z^b -Cu-O-Cu (Figure 3d). Subsequently, the αH would migrate from C_3H_8 to the αO through the TS2B (Figure 3e), which is characterized by the Cu $_a$ -O bond of 1.80 Å, the Cu $_b$ -O bond of 1.79 Å, and the Cu-O-Cu bond angle of 143.2°. This crosses a low energy barrier of 0.30 eV (Figure 1b). After that, an intermediate structure of Z^b -Cu $_2$ -C $_3$ H $_7$ -OH (Figure 3f) with a Cu $_a$ -OH bond of 1.92 Å, a Cu $_b$ -C bond of 2.11 Å, and a C-C-C bond angle of 115.9° can be formed, wherein the radical of the C_3H_7 - can be inserted into the Z^b -Cu-O-Cu site.

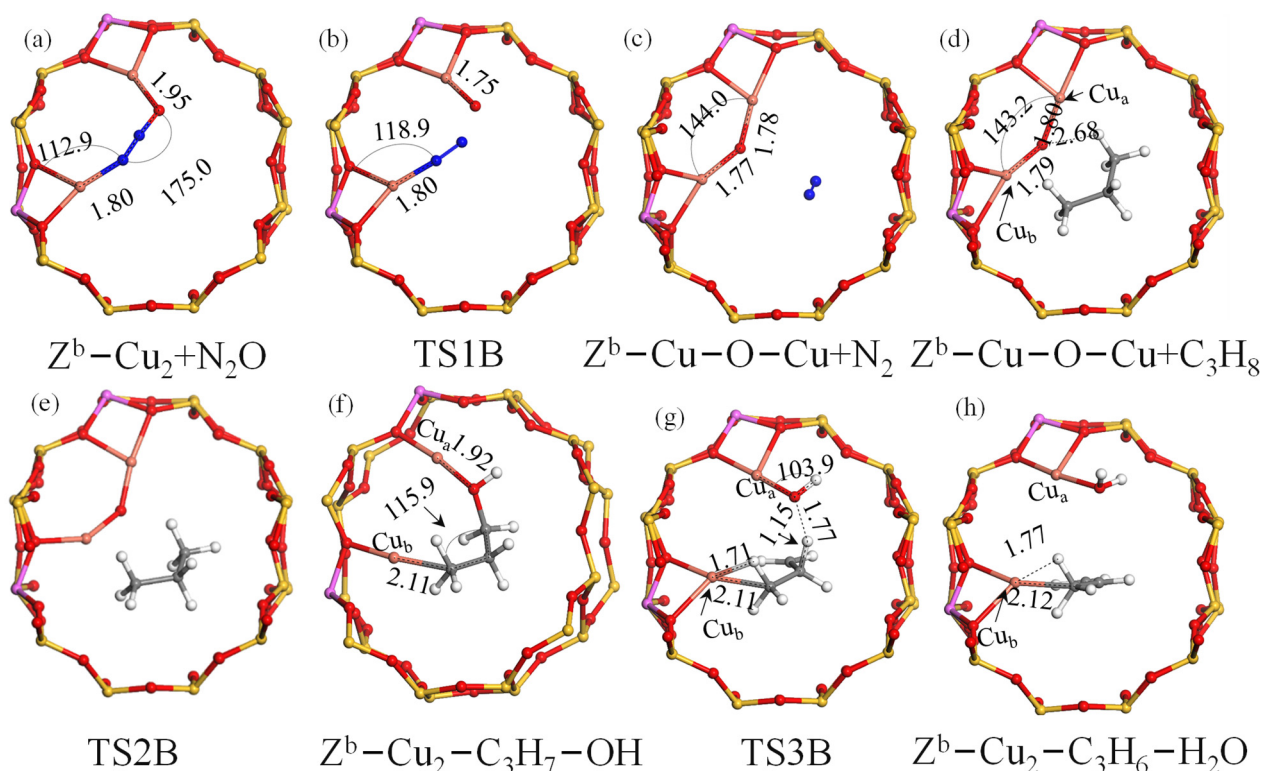


Figure 3. Optimized model of Cu-BEA with Z^b-Cu site for the N_2O -ODHP: (a) $Z^b-Cu_2+N_2O$ (adsorption for N_2O); (b) TS1B; (c) $Z^b-Cu-O-Cu+N_2$; (d) $Z^b-Cu-O-Cu+C_3H_8$ (adsorption of C_3H_8); (e) TS2B; (f) $Z^b-Cu_2-OH-C_3H_7$; (g) TS3B; (h) $Z^b-Cu_2-C_3H_6-H_2O$. Si (yellow), O (red), N (blue), Al (pink), Cu (orange).

(c) Propane dehydrogenation of βH to form propylene (Reaction Step B3). After Reaction Step B2, the βH further migrates to the αO of the $Z^b-Cu_2-C_3H_7-OH$ site, producing C_3H_6 and H_2O (Figure 3h), which, however, needs to overcome a significantly high barrier of 2.15 eV (Figure 1b) that is comparable to the value of 1.94 eV (Figure 1b) for the scenario of the monomeric $[Cu]^+$ site. The TS3B (Figure 3g) can be characterized by a Cu_a-O bond of 1.82 Å, an $O-\beta H$ bond of 1.77 Å, a $C-\beta H$ of 1.15 Å, and a $Cu-O-\alpha H$ bond angle of 103.9°. As noted, the Cu_b site forms a bridge with H and C in TS3B (Cu_b-H of 1.71 Å and Cu_b-C of 2.11 Å). Subsequently, the $C-H$ bond would expand from 1.71 to 1.77 Å, eventually leading to the $C-H$ bond being inviable in Figure 3h. Eventually, the C_3H_6 can be produced after the $C-\beta H$ bond breaking and the Cu_b-C bond formation that is associated with the formation of H_2O . As noted, such a high barrier of 2.15 eV also indicates that the dimeric Cu site of Z^b-Cu is not suitable for the N_2O -ODHP.

2.1.3. N_2O -ODHP over Distant $[Cu]^+-[Cu]^+$ Site of Route C

(a) Dissociation of N_2O to form αO (Reaction step C1). The N_2O -ODHP was further simulated over the distant $[Cu]^+-[Cu]^+$ site noted as Z^c-Cu and with the $Cu-Cu$ distance of 5.82 Å.

As shown in Figure 4a, given that it is similar to that of the dimeric $[Cu-Cu]^{2+}$ site, the N_2O molecule can also be adsorbed over Z^c-Cu through both its O and N end, with a bond length of 1.94 and 1.81 Å and a $N-N-O$ bond angle of 173.8°. Relatively stronger structural distortion can be observed for the adsorbed N_2O over the Z^c-Cu site in comparison to that of the Z^b-Cu site, which indicates a stronger synergistic effect of the Z^c-Cu site compared to the Z^b-Cu for N_2O preactivation. A similar finding can also be observed for the N_2O dissociation step to generate αO , wherein the Z^c-Cu exhibits a relatively lower N_2O -dissociation energy barrier (0.89 eV, Figure 1c) than that of the $[Cu-Cu]^{2+}$ dimeric site (Z^b-Cu of 0.95 eV, Figure 1b), which is due to this type of synergistic effect. The TSC1

(Figure 4b) can be characterized by a $\text{Cu}_a\text{—O}$ bond of the 1.81 Å, an N—N—O bond angle of 127.6° , and a $\text{Z}^c\text{—Cu—O}$ bond angle of 147.9° . Most importantly, the $\text{Z}^c\text{—Cu}$ site evolved into the motif structure of $[\text{Cu—O}]^+\text{—}[\text{Cu}]^+$ (Figure 4c, Cu—O bond of 1.71 Å), which contains two distant monomeric Cu sites that are greatly favorable to the further dehydrogenation of both the αH and the βH of the C_3H_8 molecule, as will be detailed below.

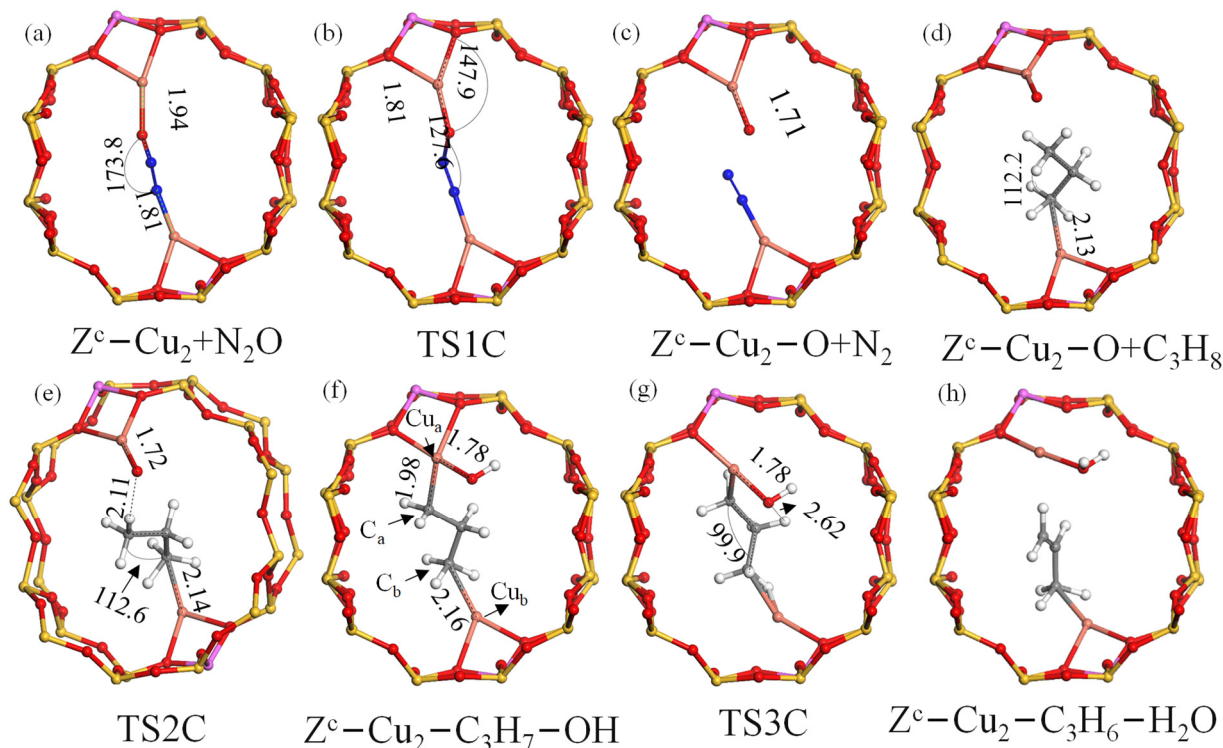


Figure 4. Optimized model of Cu-BEA with $\text{Z}^c\text{—Cu}$ site for the N_2O -ODHP: (a) $\text{Z}^c\text{—Cu}_2+\text{N}_2\text{O}$ (adsorption for N_2O); (b) TS1C; (c) $\text{Z}^c\text{—Cu—O—Cu}+\text{N}_2$; (d) $\text{Z}^c\text{—Cu}_2\text{—O}+\text{C}_3\text{H}_8$ (adsorption of C_3H_8); (e) TS2C; (f) $\text{Z}^c\text{—Cu}_2\text{—C}_3\text{H}_7\text{—OH}$; (g) TS3C; (h) $\text{Z}^c\text{—Cu}_2\text{—C}_3\text{H}_6\text{—H}_2\text{O}$. Si (yellow), O (red), N (blue), Al (pink), Cu (orange).

(b) Propane dehydrogenation of αH (Reaction step C2). The C_3H_8 can be adsorbed over the $[\text{Cu}]^+$ site of $[\text{Cu—O}]^+\text{—}[\text{Cu}]^+$ through the C end, forming a C—Cu bond of 2.13 Å and a C_3H_8 (C—C—C) bond angle of 112.2° . As noted, much stronger structural distortion of C_3H_8 can also be observed over the $\text{Z}^c\text{—Cu}$ site than that of the $\text{Z}^b\text{—Cu}$ site, which eventually leads to an extremely low barrier of 0.01 eV (Figure 1c) during the αH dehydrogenation through a transition state of TS2C (Figure 4e), and this is characterized by a Cu—C bond of 2.14 Å, a Cu—O bond of 1.72 Å, a $[\text{Cu—O}]\text{—}\alpha\text{H}$ bond of 2.11 Å, and a C—C—C bond angle of 112.6° . Finally, an intermediate structure of $\text{Z}^c\text{—Cu}_2\text{—C}_3\text{H}_7\text{—OH}$ (Figure 4f) can be formed with the $\text{Cu}_a\text{—OH}$ bond of 1.78 Å. As noted, it is interesting to see that the generated $\text{C}_3\text{H}_7\text{—}$ radical was well inserted between the distant $[\text{Cu—OH}]^+[\text{Cu}]^+$ site, forming, respectively, a $\text{Cu}_a\text{—C}$ bond of 1.98 Å and a $\text{Cu}_b\text{—C}$ bond of 2.16 Å. This would be greatly favorable for βH dehydrogenation by taking advantage of the synergistic effect of the distant $[\text{Cu—OH}]^+[\text{Cu}]^+$ site, as stated below in Reaction Step C3.

(c) Propane dehydrogenation of βH to form propylene (Reaction step C3). In this step, the βH would migrate from the $\text{C}_3\text{H}_7\text{—}$ to the $[\text{Cu}_a\text{—OH}]^+$ site, generating the adsorbed H_2O and C_3H_6 . Being totally different from the scenarios of both the monomeric and the dimeric Cu active sites ($\Delta E = 1.94$ and 2.15 eV, respectively; Figure 1a,b), the βH can be readily dehydrogenated from $\text{C}_3\text{H}_7\text{—}$ by crossing a significantly lower energy barrier of 0.33 eV (Figure 1c) over the $\text{Z}^c\text{—Cu}$ site due to its strong synergistic effect. The TS3C can be characterized by a Cu—OH bond of 1.78 Å, a $\beta\text{H—O}$ bond of 2.62 Å, and a C—C—C bond angle of 99.9° (Figure 4g). Carefully analyzing the motif structure of $\text{Z}^b\text{—Cu}_2\text{—C}_3\text{H}_7\text{—OH}$

(Figure 3f) and $Z^c\text{-Cu}_2\text{-C}_3\text{H}_7\text{-OH}$ (Figure 4f), one can find that although the radical of $\text{C}_3\text{H}_7\cdot$ can be inserted between both the $Z^b\text{-Cu}$ and the $Z^c\text{-Cu}$ site, the specific adsorption mode was different for the two. The $\text{C}_3\text{H}_7\cdot$ was adsorbed over the $Z^b\text{-Cu}$ site through the O-C_a and the $\text{Cu}_b\text{-C}_c$ bond, and was adsorbed through the $\text{Cu}_a\text{-C}_a$ and the $\text{Cu}_b\text{-C}_b$ bond over the $Z^c\text{-Cu}$ site. In this regard, the $\text{C}_3\text{H}_7\cdot$ has to break up the two bonds of O-C_a and $\beta\text{H-C}_b$ in order to generate the C_3H_6 and H_2O during the transition state of the TS3B (as seen in Figure 3g), whereas, on the contrary, the $\text{C}_3\text{H}_7\cdot$ only needs to break up one $\beta\text{H-C}_b$ bond during the transition state of the TS3C (seen in Figure 4g).

In the light of the above statements, we can therefore note that the $Z^c\text{-Cu}$ site possessing the lowest energy barrier for N_2O dissociation (0.89 eV) as well as αH (0.01 eV) and βH (0.33 eV) dehydrogenation (Figure 1c,d), relative to those of the $Z^b\text{-Cu}$ and the $Z^a\text{-Cu}$ sites (especially for the βH dehydrogenation step), is the most active site for $\text{N}_2\text{O-ODHP}$. Moreover, this finding also shows that modulating the Cu-Cu distance may constitute a promising strategy for highly-efficient zeolite-based $\text{N}_2\text{O-ODHP}$ catalyst design.

2.2. Microkinetic Modeling

Based on the above DFT simulations and transition state theory, microkinetic modeling was further conducted to explore the reaction dynamics (through the intermediate surface coverage variations) and to determine and compare the reaction rate of the rate of the determining step (RDS) over the three different Cu active sites. The $\text{N}_2\text{O-ODHP}$ reaction can be described by five elementary steps, given that it is associated with the kinetic equations listed in Table 1. The calculated kinetic parameters, including reaction rate constant, pre-exponential factor, and specific forward and reverse reaction rate, were listed in Table S1.

Table 1. Elementary steps of micro-dynamics and the equations of reaction rate for the $\text{N}_2\text{O-ODHP}$ over Cu-BEA.

Step	Elementary Steps	Reaction Rate Equations
R1	$Z\text{-Cu-N}_2\text{O}_{(g)} \leftrightarrow Z\text{-Cu-N}_2\text{O}$	$r_1 = k_1 P_{\text{N}_2\text{O}} \theta_v - k_{-1} \theta_{\text{N}_2\text{O}}$
R2	$Z\text{-Cu-N}_2\text{O} \rightarrow Z\text{-Cu-O+N}_{2(g)}$	$r_2 = k_2 \theta_{\text{N}_2\text{O}}$
R3	$Z\text{-Cu-O+C}_3\text{H}_{8(g)} \leftrightarrow Z\text{-Cu-O-C}_3\text{H}_8$	$r_3 = k_3 P_{\text{C}_3\text{H}_8} \theta_{\text{O}} - k_{-3} \theta_{\text{O-C}_3\text{H}_8}$
R4	$Z\text{-Cu-O-C}_3\text{H}_8 \leftrightarrow Z\text{-Cu-OH-C}_3\text{H}_7$	$r_4 = k_4 \theta_{\text{O-C}_3\text{H}_8} - k_{-4} \theta_{\text{C}_3\text{H}_7\text{-OH}}$
R5	$Z\text{-Cu-OH-C}_3\text{H}_7 \leftrightarrow Z\text{-Cu-H}_2\text{O-C}_3\text{H}_6$	$r_5 = k_5 \theta_{\text{C}_3\text{H}_7\text{-OH}} - k_{-5} \theta_{\text{C}_3\text{H}_6\text{-H}_2\text{O}}$

(a) Microkinetic modeling over $Z^a\text{-Cu}$. Figure 5a displays the intermediate coverage variations along with reaction time (t) over the $Z^a\text{-Cu}$ ($T = 823\text{ K}$). Initially, the unoccupied active site coverage (θ_v) would decrease from 1 to 0.8 ML as it is associated with the increase of adsorbed N_2O ($\theta_{\text{N}_2\text{O}}$) from 0 to 0.2 ML. This process corresponds with the N_2O dissociation step that generates αO , wherein the adsorbed N_2O ($\theta_{\text{N}_2\text{O}}$) constitutes the major active-site covered species over the $Z^a\text{-Cu}$ due to the relatively high energy barrier of R2 (1.40 eV, Figure 1a, N_2O dissociation to generate αO). Along with the reaction, both θ_v and $\theta_{\text{N}_2\text{O}}$ would quickly decrease to 0 ML as they are both accompanied with the rapid growth of the coverage of the intermediate of propanol ($\theta_{\text{C}_3\text{H}_7\text{-OH}}$), which finally reaches the equilibrium. This finding indicates that after the formation of αO , it would quickly participate in the ODHP reaction in order to generate the intermediate of propanol, and the intermediate of propanol ($\theta_{\text{C}_3\text{H}_7\text{-OH}}$) constitutes the major active-site covered species, which indicates that the R5 ($\Delta E = 1.94\text{ eV}$, Figure 1a) constitutes the RDS during $\text{N}_2\text{O-ODHP}$ over the $Z^a\text{-Cu}$ site, leading to the accumulation of $\text{C}_3\text{H}_7\text{-OH}$ over the active site.

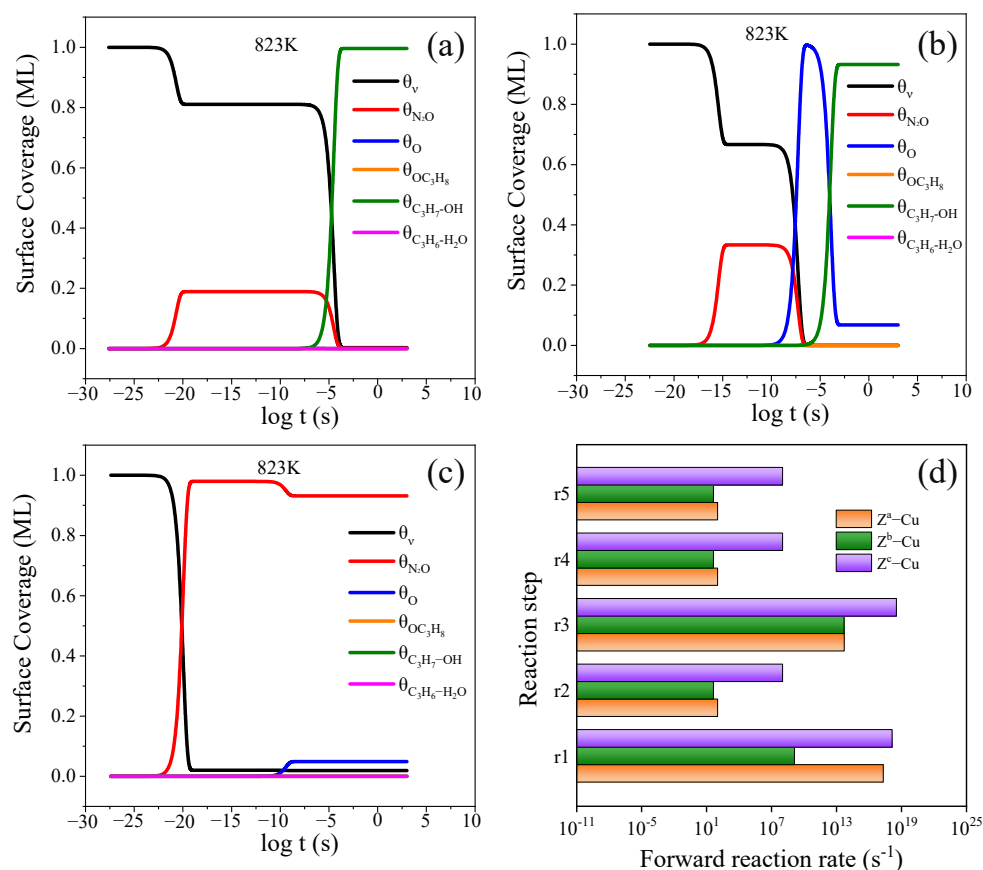


Figure 5. Microkinetic modeling results: the surface coverage variations along with reaction time (t) over the (a) Z^a -Cu, (b) Z^b -Cu, and (c) Z^c -Cu sites of Cu-BEA at 823 K, and (d) the forward reaction rate comparisons.

(b) Microkinetic modeling over Z^b -Cu. Figure 5b displays the variations of the intermediate coverages during the N_2O -ODHP over the Z^b -Cu site. Being similar to that of Z^a -Cu site, the adsorbed N_2O would initially cover the active site by displaying the θ_{N_2O} of 0.3 ML. However, the αO , given that it is in the form of $[Cu-O-Cu]^{2+}$, would shortly occupy the active site due to the relatively lower N_2O dissociation barrier (0.95 versus 1.40 eV of R2) and higher αH dehydrogenation barrier (0.3 versus 0.05 eV of R4) than that of Z^a -Cu site, which leads to the short accumulation of the αO over the active site. Along with the further reaction (reaching equilibrium), the active site would be eventually covered by the propanol ($\theta_{C_3H_7-OH}$), which is similar to the scenario of the Z^a -Cu site due to the extremely high barrier of R5 (2.15 eV). Thus, similar to that of Z^a -Cu, the R5 would constitute the RDS during the N_2O -ODHP over the Z^b -Cu site.

(c) Microkinetic modeling over Z^c -Cu. The surface coverage of the reactant as well as the generated intermediates during N_2O -ODHP over the Z^c -Cu site were both depicted in Figure 5c. Being totally different from the scenarios of the Z^a -Cu and the Z^b -Cu sites, the N_2O constitutes the major active-site covered species over the Z^c -Cu site at $T = 823$ K, wherein the θ_{N_2O} initially increases up to 1 ML and then decreases to a stable value of above 0.9 ML due to another intermediate αO ($\theta_o = 0.1$ ML) after the reaction, which reaches the equilibrium. This finding indicates that the N_2O dissociation step (R2) would constitute the RDS during the N_2O -ODHP over the Z^c -Cu site. This finding correlates well with the highest energy barrier of 0.89 eV of R2 during N_2O -ODHP (see Figure 1c).

(d) Reaction rate comparisons. Figure 5d displays the forward reaction rate comparisons of each elementary step during N_2O -ODHP over the different active sites of Z^a -Cu, Z^b -Cu, and Z^c -Cu. Obviously, the Z^c -Cu site displays much higher reaction rates than those of the Z^a -Cu and the Z^b -Cu. Moreover, in the net reaction rate (NRR) compar-

isons, which were further depicted in Figure S1, the Z^c -Cu displays an NRR of $1.25 \times 10^8 \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$, and it is five and six orders of magnitude higher, respectively, than those of the Z^a -Cu ($120.57 \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$) and the Z^b -Cu ($49.21 \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$) sites. These findings quantitatively verify the superior activity of the Z^c -Cu site relative to those of the Z^a -Cu and the Z^b -Cu sites.

2.3. Static Charge Difference PDOS and Analyses

To further illustrate the superior activity of the Z^c -Cu, the static charge difference and the partial density of state (PDOS) analyses were further conducted based on TS3 (corresponding to the β H dehydrogenation step). As shown in Figure 6a–d, large amounts of charge transfers occurred during the β H dehydrogenation, and the Cu of Z^c -Cu provided more charges relative to those of the Z^a -Cu and the Z^b -Cu (Figure 6d), which can be closely related to the smallest band gap between the Cu and C of C_3H_7 -, as shown by the PDOS analyses of Figure 6e–g (4.97 versus 5.82 and 5.29 eV). This finding indicates that the Z^c -Cu would exhibit a stronger electric field effect on C_3H_7 -, and that it is thereby greatly favorable for β H dehydrogenation.

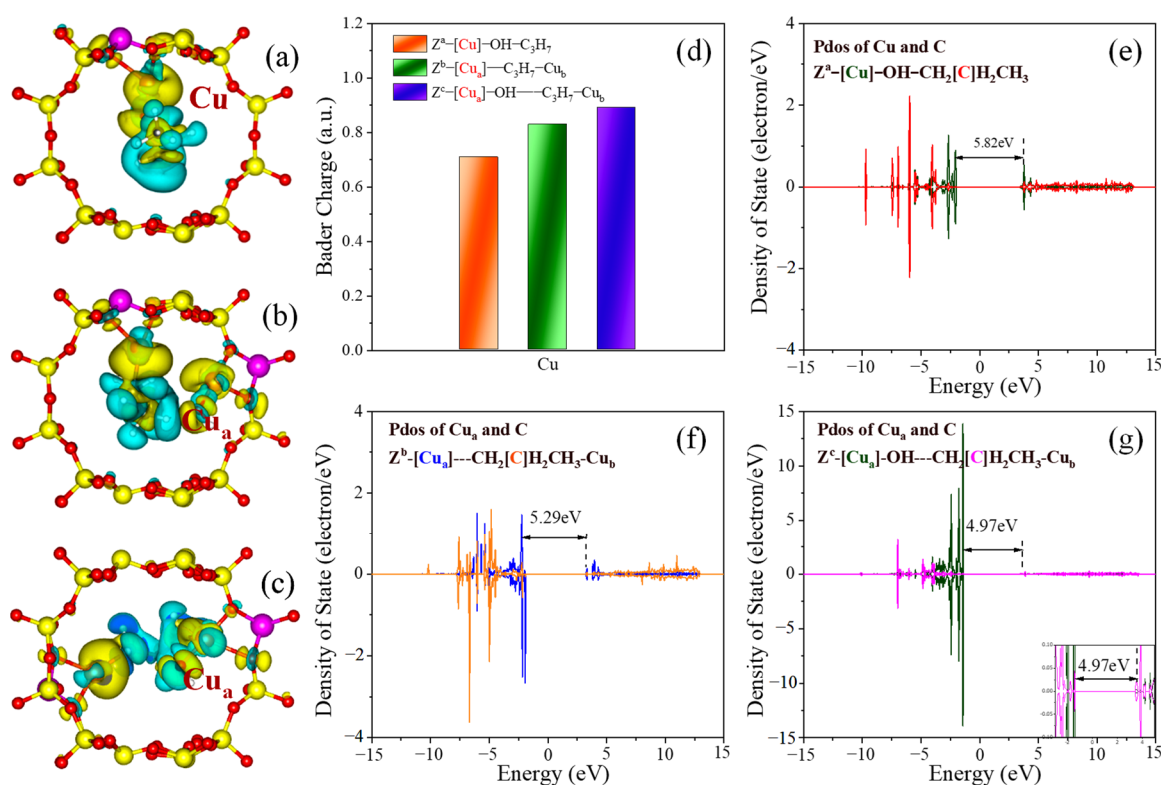


Figure 6. The static charge difference (a–c) and partial density of state (PDOS) analyses (e–g) of TS3 models for Z^a -, Z^b -, and Z^c -Cu-BEA; (d) bader charges analysis results; (e) partial density of state (PDOS) of atomic Cu and C over (e) Z^a -Cu; (f) Z^b -Cu; and (g) Z^c -Cu site. Yellow and blue colors represent the increase and decrease in electron density, respectively. Si (yellow), O (red), N (blue), Al (pink), Cu (orange).

3. N_2O -ODHP Activity Measurement

As is well known, in addition to the $[\text{Cu}]^+$ cations, the CuO_x species can also exist over Cu-modified zeolite catalyst (Cu-Zeolite) and shed more light on the activity behaviors of these different Cu species. The 1%Cu-BEA and 1%CuO-SiO₂ were prepared by the impregnation method (the metal loading of 1wt.%), and they were further evaluated for the N_2O -ODHP. In addition, the Fe-modified zeolites (Fe-Zeolite) have also been reported to possess excellent N_2O dissociation activity in order to produce αO [17], and to make a comparison with the Cu modified zeolite, the 1%Fe-BEA, and 1%Fe-ZSM-5 were also

prepared by the impregnation method (metal loading of 1 wt.%) and evaluated by N_2O -ODHP. The specific preparation method is stated in detail in the Supporting Information section of this paper. The activity measurement results, including the C_3H_8 and N_2O conversions as well as the product selectivity, were profiled in Figure 7a–c. As can be seen there, the 1%Cu-BEA displays a higher C_3H_8 conversion (31.5%) and a higher C_3H_6 selectivity (74.5%) than the other catalyst samples, especially in comparison with that of 1%CuO-SiO₂, displaying a C_3H_8 conversion of 3.5% and a C_3H_6 selectivity of 43.5%. This finding indicates that the CuO species would not constitute the major active species for the N_2O -ODHP.

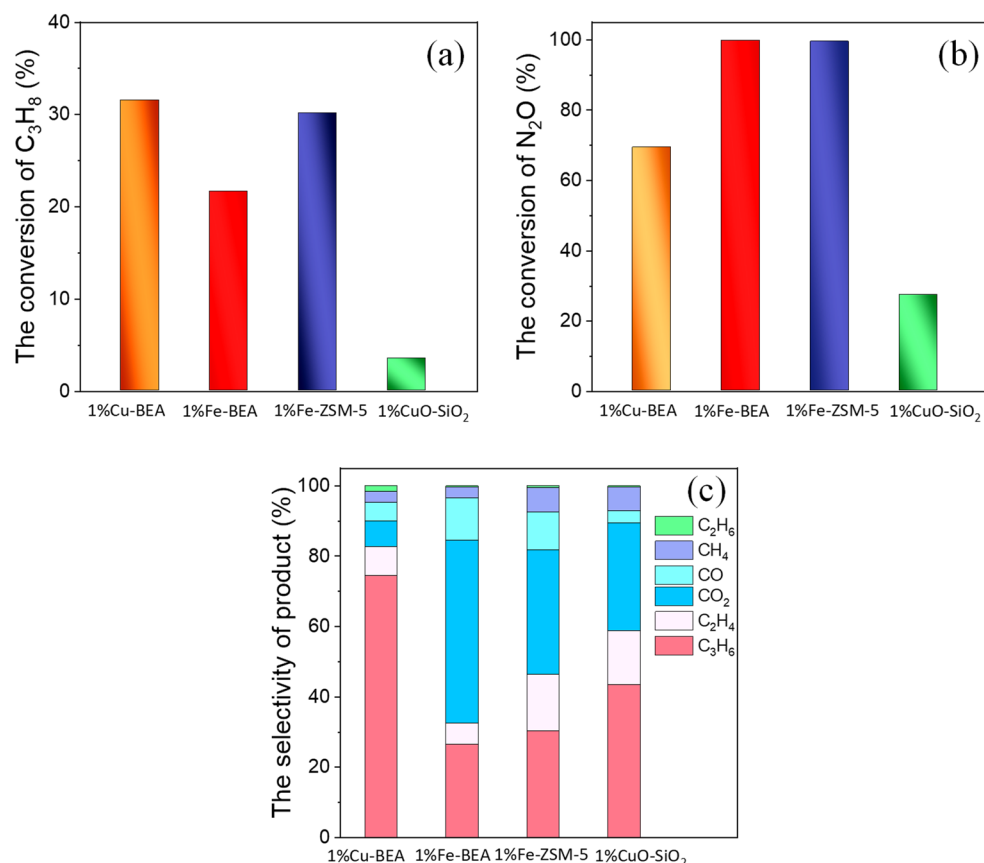


Figure 7. Activity measurement of N_2O -ODHP over 1%Cu-BEA (orange), 1%Fe-BEA (red), 1%Fe-ZSM-5 (dark blue), and 1%CuO-SiO₂ (green): (a) C_3H_8 conversion; (b) N_2O conversion; (c) product selectivity of C_2H_6 (light green), CH_4 (light purple), CO (light blue), CO_2 (blue), C_2H_4 (light pink), and C_3H_6 (light red). GHSV = 12,000 h^{−1}, C_3H_8 : N_2O :He = 10:10:80, T = 550 °C.

As further shown by the N_2O conversion of Figure 7b, the 1%CuO-SiO₂ displays a much lower N_2O conversion (27.2%) than the 1%Cu-BEA (69.4%). This finding shows that the lower N_2O dissociation activity of CuO species probably constitutes one of the major reactions that leads to the extremely low N_2O -ODHP activity of the 1%CuO-SiO₂. Conversely, the 1%Cu-BEA possessing active Cu cations for N_2O dissociation that generate αO exhibits a much higher level of N_2O -ODHP activity relative to the 1%CuO-SiO₂. As has also been reported on a theoretical level [22], the CuO exhibits a much high energy barrier (2.71 eV) for N_2O dissociation, which indicates that it is very difficult to decompose N_2O and produce αO over CuO.

As for the samples of 1%Fe-BEA and 1%Fe-ZSM-5, the nearly complete N_2O conversion (~100%) can be achieved due to the superior N_2O dissociation activity of Fe cations than those of the Cu cations [23], although this does lead to the ready overoxidation of C_3H_8 into CO_x (CO and CO_2 of 64.1 and 46.0%, respectively; see Figure 7c). This finding shows that the Fe cations are active for N_2O dissociation, although they suffer from the

overoxidation of C_3H_8 . The Cu-based zeolites would therefore probably be much more suitable for the N_2O -ODHP relative to that of the Fe-based zeolite catalyst. However, we would also like to emphasize that such works still need further investigation. We would also like to note that the TPR and UV-vis correlate with the active-site-structure in the theoretical calculation. This will be further studied in our research in the future, which will focus on the influence of a diversely structured topologized zeolite (MFI, FER, MOR, and BEA) on a specific structure, as well as on the location of $[Cu]^+$ cations and how they are related to N_2O -ODHP catalytic behaviors, both experimentally and theoretically.

4. Computational Modeling and Methodology

Density functional theory (DFT) adopts the Vienna ab-initio simulation package (VASP). The Projection Enhanced Wave (PAW) method utilizes the interaction between electrons and the core, and it uses Generalized Gradient Approximation (GGA) and Perdew Burke Ernzerhof (PBE) functions to achieve electron exchange correlation [24]. In the process of geometric optimization, the convergence achieved at the energy difference is 10^{-5} eV, with an ion relaxation convergence standard of $0.05 \text{ eV}/\text{\AA}$. The energy cutoff of the set plane wave is 400 eV. The K point of the Brillouin region is set to $2 \times 2 \times 1$ in the calculation of the structure, and it is set to $4 \times 4 \times 2$ in the partial wave density of states. In the International Zeolite Association (IZA) database, the cellular model data for BEA is $A = 12$, $B = 12.632$, and $C = 9.421 \text{ \AA}$ [25]. The calculation of the transition state (TS) uses the climbing image light pushing elastic bond (CI-NEB) and the dimer method. Four points are inserted between the initial state and the final state, and the saddle points corresponding to the transition state are located in order to find the lowest energy path. The TS state is only identified on one imaginary frequency [25–29]. The method of micro-dynamic modeling is included in the Supporting Information section of this paper.

5. Conclusions

The present work theoretically investigates N_2O -ODHP over Cu-BEA with three types of Cu sites—monomeric $[Cu]^+$ (Z^a -Cu), dimeric $[Cu-Cu]^{2+}$ (Z^b -Cu), and distant $[Cu]^+-[Cu]^+$ (Z^c -Cu). The Z^a -Cu is beneficial for αH dehydrogenation (0.05 eV), but it requires a high energy barrier in N_2O dissociation and βH dehydrogenation (1.40 and 1.94 eV) to be overcome. The Z^b -Cu, with a Cu—Cu distance of $4.91 \text{ \AA}$, is suitable for the N_2O dissociation step (0.95 eV), but it is highly resistant to the βH hydrogenation step because it displays an extremely high barrier of 2.15 eV. Being contrary to the scenarios of the Z^a -Cu and the Z^b -Cu, the Z^c -Cu site with the Cu—Cu distance of $5.82 \text{ \AA}$ is not only favorable for N_2O dissociation (0.89 eV) but also greatly active for the ODHP steps of αH (0.01 eV) and βH (0.33 eV) dehydrogenation. The microkinetic modeling further showed that the Z^c -Cu exhibits a five to six orders of magnitude higher net reaction rate than those of the Z^a -Cu and the Z^b -Cu sites. This is closely correlated with the specific structure of the Z^c -Cu, which possesses a much stronger electric field effect on the C_3H_8 molecule due to the synergic effect of Cu, as this possesses the smallest band gaps and they are favorable to the charge transfers between the Cu active site and the C_3H_8 molecule. Generally, we ultimately propose that modulating the Cu active site distance (Cu—Cu) probably constitutes a promising strategy for highly-efficient Cu-zeolite design for the N_2O -ODHP. Additionally, we would like to mention that it is not possible for there to be only one type of Z—Cu site (Cu cation site) experimentally, and other types of Cu site (such as $[Cu_3O_3]^{2+}$, which is proposed by Lercher et al. [30] for methane direct oxidation to methanol) may also be active for the N_2O -ODHP, which would be a good direction for further study of this subject.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13081212/s1>, Figure S1. Optimized Cu-BEA models with diverse Cu active site motifs (a) Z^a -Cu; (b) Z^b -Cu; (c) Z^c -Cu site; Si (yellow), O (red), N (blue), Al (pink), Cu (orange); Scheme S1. Schematic reaction for N_2O -ODHP over Z^a -Cu (reaction Route A), Z^b -Cu (reaction Route B) and Z^c -Cu (reaction Route C), respectively; Table S1. Micro-dynamics parameters of the reaction steps over Z^a -Cu, Z^b -Cu and Z^c -Cu site; Figure S2. The comparison of net reaction rate over Schematic reaction for N_2O -ODHP over Z^a -Cu, Z^b -Cu and Z^c -Cu site at 823 K [17,18,25,31–36].

Author Contributions: Methodology, N.W.; validation, C.D.; investigation, R.W.; resources, B.C.; data curation, R.X.; writing—original draft preparation, R.W.; writing—review and editing, N.L.; visualization, G.Y.; supervision, B.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China (No. 22178011 and 22176006).

Data Availability Statement: Data is available upon request to the corresponding authors.

Acknowledgments: We acknowledge the final support from National Natural Science Foundation of China (No. 22178011 and 22176006).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Pérez-Ramírez, J.; Gallardo-Llamas, A. Framework composition effects on the performance of steam-activated FeMFI zeolites in the N_2O -mediated propane oxidative dehydrogenation to propylene. *J. Phys. Chem. B* **2005**, *109*, 20529–20538. [\[CrossRef\]](#) [\[PubMed\]](#)
- Kondratenko, E.; Cherian, M.; Baerns, M.; Su, D.; Schlogl, R.; Wang, X.; Wachs, I. Oxidative dehydrogenation of propane over V/MCM-41 catalysts: Comparison of O_2 and N_2O as oxidants. *J. Catal.* **2005**, *234*, 131–142. [\[CrossRef\]](#)
- Sanchezgalofre, O.; Segura, Y.; Perezramirez, J. Deactivation and regeneration of iron-containing MFI zeolites in propane oxidative dehydrogenation by N_2O . *J. Catal.* **2007**, *249*, 123–133. [\[CrossRef\]](#)
- Wei, W.; Moulijn, J.A.; Mul, G. FAPO and Fe-TUD-1: Promising catalysts for N_2O mediated selective oxidation of propane. *J. Catal.* **2009**, *262*, 1–8. [\[CrossRef\]](#)
- Kondratenko, E.V.; Brückner, A. On the nature and reactivity of active oxygen species formed from O_2 and N_2O on VO_x /MCM-41 used for oxidative dehydrogenation of propane. *J. Catal.* **2010**, *274*, 111–116. [\[CrossRef\]](#)
- Orlyk, S.; Kyriienko, P.; Kapran, A.; Chedryk, V.; Balakin, D.; Gurgul, J.; Zimowska, M.; Millot, Y.; Dzwigaj, S. CO_2 -assisted dehydrogenation of propane to propene over Zn-BEA zeolites: Impact of acid–base characteristics on catalytic performance. *Catalysts* **2023**, *13*, 681. [\[CrossRef\]](#)
- Vogt, E.T.; Weckhuysen, B.M. Fluid catalytic cracking: Recent developments on the grand old lady of zeolite catalysis. *Chem. Soc. Rev.* **2015**, *44*, 7342–7370. [\[CrossRef\]](#) [\[PubMed\]](#)
- Chen, J.Q.; Bozzano, A.; Glover, B.; Fuglerud, T.; Kvisle, S. Recent advancements in ethylene and propylene production using the UOP/Hydro MTO process. *Catal. Today* **2005**, *106*, 103–107. [\[CrossRef\]](#)
- Bulánek, R.; Wichterlová, B.; Novoveská, K.; Kreibich, V. Oxidation of propane with oxygen and/or nitrous oxide over Fe-ZSM-5 with low iron concentrations. *Appl. Catal. A* **2004**, *264*, 13–22. [\[CrossRef\]](#)
- Novoveská, K.; Bulánek, R.; Wichterlová, B. Oxidation of propane with oxygen, nitrous oxide and oxygen/nitrous oxide mixture over Co- and Fe-zeolites. *Catal. Today* **2005**, *100*, 315–319. [\[CrossRef\]](#)
- Wu, G.; Hao, Y.; Zhang, N.; Guan, N.; Li, L.; Grünert, W. Oxidative dehydrogenation of propane with nitrous oxide over Fe–O–Al species occluded in ZSM-5: Reaction and deactivation mechanisms. *Microporous Mesoporous Mater.* **2014**, *198*, 82–91. [\[CrossRef\]](#)
- Jiang, X.; Sharma, L.; Fung, V.; Park, S.J.; Jones, C.W.; Sumpter, B.G.; Baltusaitis, J.; Wu, Z. Oxidative dehydrogenation of propane to propylene with soft oxidants via heterogeneous catalysis. *ACS Catal.* **2021**, *11*, 2182–2234. [\[CrossRef\]](#)
- Patet, R.E.; Koehle, M.; Lobo, R.F.; Caratzoulas, S.; Vlachos, D.G. General acid-type catalysis in the dehydrative aromatization of furans to aromatics in H-[Al]-BEA, H-[Fe]-BEA, H-[Ga]-BEA, and H-[B]-BEA zeolites. *J. Phys. Chem. C* **2017**, *121*, 13666–13679. [\[CrossRef\]](#)
- Chalupka, K.; Thomas, C.; Millot, Y.; Averseng, F.; Dzwigaj, S. Mononuclear pseudo-tetrahedral V species of VSiBEA zeolite as the active sites of the selective oxidative dehydrogenation of propane. *J. Catal.* **2013**, *305*, 46–55. [\[CrossRef\]](#)
- Mauvezin, M.; Delahay, G.; Kißlich, F.; Coq, B.; Kieger, S. Catalytic reduction of N_2O by NH_3 in presence of oxygen using Fe-exchanged zeolites. *Catal. Lett.* **1999**, *62*, 41–44. [\[CrossRef\]](#)
- Sobalik, Z.; Sazama, P.; Dedecek, J.; Wichterlová, B. Critical evaluation of the role of the distribution of Al atoms in the framework for the activity of metallo-zeolites in redox N_2O/NO_x reactions. *Appl. Catal. A* **2014**, *474*, 178–185. [\[CrossRef\]](#)

17. Liu, N.; Zhang, R.; Chen, B.; Li, Y.; Li, Y. Comparative study on the direct decomposition of nitrous oxide over M (Fe, Co, Cu)–BEA zeolites. *J. Catal.* **2012**, *294*, 99–112. [\[CrossRef\]](#)
18. Xu, R.; Liu, N.; Dai, C.; Li, Y.; Zhang, J.; Wu, B.; Yu, G.; Chen, B. H₂O-built proton transfer bridge enhances continuous methane oxidation to methanol over Cu-BEA zeolite. *Angew. Chem.* **2021**, *60*, 16634–16640. [\[CrossRef\]](#)
19. Widmann, D.; Behm, R.J. Dynamic surface composition in a Mars-van Krevelen type reaction: CO oxidation on Au/TiO₂. *J. Catal.* **2018**, *357*, 263–273. [\[CrossRef\]](#)
20. Wang, C.; Gu, X.-K.; Yan, H.; Lin, Y.; Li, J.; Liu, D.; Li, W.-X.; Lu, J. Water-mediated Mars–Van Krevelen mechanism for CO oxidation on ceria-supported single-atom Pt₁ catalyst. *ACS Catal.* **2016**, *7*, 887–891. [\[CrossRef\]](#)
21. Jan, F.; Lian, Z.; Zhi, S.; Yang, M.; Si, C.; Li, B. Revealing the role of HBr in propane dehydrogenation on CeO₂(111) via DFT-based microkinetic simulation. *Phys. Chem. Chem. Phys.* **2022**, *24*, 9718–9726. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Suo, W.; Sun, S.; Liu, N.; Li, X.; Wang, Y. The adsorption and dissociation of N₂O on CuO(111) surface: The effect of surface structures. *Surf. Sci.* **2020**, *696*, 121596. [\[CrossRef\]](#)
23. Li, Y.; Liu, N.; Dai, C.; Xu, R.; Yu, G.; Wang, N.; Zhang, J.; Chen, B. Synergistic Effect of neighboring Fe and Cu cation sites boosts FeCu-BEA activity for the continuous direct oxidation of Methane to Methanol. *Catalysts* **2021**, *11*, 1444. [\[CrossRef\]](#)
24. Jianwen, Z.; Zhifeng, H.; Ziqian, Y.; Meijuan, L.; Fei, C.; Qiang, S. The influence of alkaline earth elements on electronic properties of α -Si₃N₄ via DFT calculation. *J. Wuhan Univ. Technol. Mater. Sci. Ed.* **2020**, *35*, 863–871.
25. Zhou, Z.; Qin, B.; Li, S.; Sun, Y. A DFT-based microkinetic study on methanol synthesis from CO₂ hydrogenation over the In₂O₃ catalyst. *Phys. Chem. Chem. Phys.* **2021**, *23*, 1888–1895. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Montejo-Valencia, B.D.; Curet-Arana, M.C. Periodic DFT study of the opening of fructose and glucose rings and the further conversion of fructose to trioses catalyzed by M-BEA (M = Sn, Ti, Zr, or Hf). *J. Phys. Chem. C* **2019**, *123*, 3532–3540. [\[CrossRef\]](#)
27. Mahyuddin, M.H.; Staykov, A.; Shiota, Y.; Yoshizawa, K. Direct conversion of methane to methanol by metal-exchanged ZSM5 zeolite (Metal = Fe, Co, Ni, Cu). *ACS Catal.* **2016**, *6*, 8321–8331. [\[CrossRef\]](#)
28. Liu, N.; Zhang, R.; Li, Y.; Chen, B. Local electric field effect of TMI (Fe, Co, Cu)-BEA on N₂O direct dissociation. *J. Phys. Chem. C* **2014**, *118*, 10944–10956. [\[CrossRef\]](#)
29. Konsolakis, M. Recent advances on nitrous oxide (N₂O) decomposition over non-noble-metal oxide catalysts: Catalytic performance, mechanistic considerations, and surface chemistry aspects. *ACS Catal.* **2015**, *5*, 6397–6421. [\[CrossRef\]](#)
30. Ikuno, T.; Grundner, S.; Jentys, A.; Li, G.; Pidko, E.A.; Fulton, J.L.; Sanchez-Sanchez, M.; Lercher, J.A. Formation of Active Cu-oxo Clusters for Methane Oxidation in Cu-Exchanged Mordenite. *J. Phys. Chem. C* **2019**, *123*, 8759–8769. [\[CrossRef\]](#)
31. Liu, N.; Yuan, X.; Zhang, R.; Xu, R.; Li, Y. Mechanistic insight into selective catalytic combustion of acrylonitrile (C₂H₃CN): NCO formation and its further transformation towards N₂. *Phys. Chem. Chem. Phys.* **2017**, *19*, 7971–7979. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Liu, N.; Yuan, X.; Zhang, R.; Li, Y.; Chen, B. Mechanistic insight into selective catalytic combustion of HCN over Cu-BEA: Influence of different active center structures. *Phys. Chem. Chem. Phys.* **2017**, *19*, 23960–23970. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Dixit, M.; Baruah, R.; Parikh, D.; Sharma, S.; Bhargav, A. Autothermal reforming of methane on rhodium catalysts: Microkinetic analysis for model reduction. *Comput. Chem. Eng.* **2016**, *89*, 149–157. [\[CrossRef\]](#)
34. Ke, C.; Lin, Z. Density Functional Theory Based Micro- and Macro-Kinetic Studies of Ni-Catalyzed Methanol Steam Reforming. *Catalysts* **2020**, *10*, 349. [\[CrossRef\]](#)
35. Gokhale, A.A.; Kandoi, S.; Greeley, J.P.; Mavrikakis, M.; Dumesic, J.A. Molecular-level descriptions of surface chemistry in kinetic models using density functional theory. *Chem. Eng. Sci.* **2004**, *59*, 4679–4691. [\[CrossRef\]](#)
36. Cai, Q.-X.; Wang, J.-G.; Wang, Y.-G.; Mei, D. Mechanistic insights into the structure-dependent selectivity of catalytic furfural conversion on platinum catalysts. *AIChE J.* **2015**, *61*, 3812–3824. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.