Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary Information

## Mechanistic Insight into Selective Catalytic Combustion of HCN over Cu-BEA: Influence of Different Active Center Structures

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**Mulliken Charge Transfer Analysis**

In present work, the Mulliken charge transfer (CT) analysis was employed to quantitatively describe the electric effects of Cu-BEA with different active center structures of single $[Cu]^+$, double $[Cu]^+$, and $[Cu\text{-}O\text{-}Cu]^{2+}$ during HCN-SCC. The Route I (Route IA, IB, IC), including HCN adsorption and further oxidation into HNCO or NCO, was taken into account during the CT analysis. Firstly, based on the DFT calculation results of Mulliken atomic population analysis, the atomic charge of each component of the constructed 24T-Cu-BEA model was collected and listed in Table S2. As noted, herein the atomic Si, Al, O, and H of zeolite framework were considered as a whole part, with the related atomic Mulliken charges being added together and represented as Zeolite.

In order to clearly display the charge transfer (CT) routes of each reaction step, atomic charge transfer (ACT) and Mulliken charge ratio (MCR) are cited and formulated as follows:

$$Q(ACT)_M = Q(M)_P - Q(M)_R \qquad \text{Eq. (S1.1)}$$

$$MCR_A = \frac{Q(ACT)_A}{\sum Q(ACT)_A} \times 100\% \qquad \text{Eq. (S1.2)}$$

$$MCR_D = \frac{Q(ACT)_D}{\sum Q(ACT)_D} \times 100\% \qquad \text{Eq. (S1.3)}$$

In Eq.(S1.1) $Q(M)_P$ and $Q(M)_R$ respectively delegate the Mulliken atomic charges of the component M in a product state and reactant state; $Q(ACT)_M$ is the CT amount of the component M in each reaction step. The component M acting as a charge acceptor generally associates with a negative value of $Q(ACT)_A$, vice versa for $Q(ACT)_D$. As formulated by Eq.(S1.2) and Eq.(S1.3), which individually describe the MCR calculations for the charge acceptor ($MCR_A$) and charge donor ($MCR_D$). The $\Sigma Q(ACT)_A$ and $\Sigma Q(ACT)_D$ respectively represent the total CT of all the charge acceptors and donors. Obviously, $MCR_D$ is positive yielding a ΣMCRD of 100%,

whereas $MCR_A$ is negative resulting in a $\Sigma MCR_A$ of -100%. The sum of $MCR_A$ and $MCR_D$ is thus equal to zero. The calculated MCR values of each component involved in the constructed models of Route I were listed in Table S3. The CT profiles of Figures 4a-4i of the main text was derived from the MCR data listed in Table S3.

**Table S1a.** Optimized structural parameters of HCN-SCC mechanism over 24T-[Cu]-Z (energy in kcal·mol$^{-1}$， diameter in Å, angle in °)

| Reaction Routes | Energy Barrier (kcal mol$^{-1}$) | Structures | Gas Phase | AS[a] | TS[b] | Product |
|---|---|---|---|---|---|---|
| Route IA | 23.8 | Cu-N | - | 1.92 | - | - |
| | | Cu-O | - | 1.90 | 2.0 | - |
| | | C-N | 1.16 | 1.29 | 1.26 | 1.20 |
| | | C-O | - | 1.32 | 1.25 | 1.19 |
| | | C-H | 1.07 | 1.09 | 1.17 | - |
| | | N-H | - | - | - | 1.01 |
| | | ∠N-C-H | 180.0 | 128.0 | 93.0 | - |
| | | ∠H-N-C | - | - | - | 129.2 |
| | | ∠N-C-O | - | 109.6 | 142.5 | 171.4 |
| Route IIA | 7.1 | Cu-N | - | 1.91 | 1.80 | 1.77 |
| | | N-H | 1.01 | 1.04 | 1.03 | 1.03 |
| | | N-C | 1.22 | 1.42 | 2.0 | - |
| | | C-$O_1$ | 1.17 | 1.18 | 1.17 | 1.17 |
| | | C-$O_2$ | - | 1.31 | 1.20 | 1.17 |
| | | ∠$O_1$-C-$O_2$ | - | 143.2 | 162.1 | 178.5 |
| | | ∠H-N-C | 124.5 | 114.2 | - | - |
| | | ∠N-C-O | 172.2 | 143.9 | - | - |

| Route IIIA | 7.9<br>72.3 | Structures | Gas Phase | AS | TS1 | IM[c] | TS2 | Product |
|---|---|---|---|---|---|---|---|---|
| | | Cu-N | - | 1.92 | 1.88 | 1.98 | - | - |
| | | N-$H_1$ | - | 1.03 | 1.02 | 1.02 | 1.03 | 1.04 |
| | | N-O | - | 1.61 | 1.77 | 1.44 | 1.53 | 1.32 |
| | | N-$H_2$ | - | - | 1.31 | 1.02 | 1.02 | 1.04 |
| | | N-$H_3$ | - | - | - | - | 1.07 | 1.10 |
| | | O-$H_2$ | 0.97 | 0.98 | 1.11 | - | - | - |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | $O\text{-}H_3$ | 0.97 | 1.01 | 0.99 | 0.98 | 1.48 | 2.05 |
| | $\angle H_2\text{-}O\text{-}H_3$ | 103.7 | 106.1 | 109.3 | - | - | - |

[a] Adsorption state
[b] Transition state
[c] Intermediate

**Table S1b.** Optimized structural parameters of HCN-SCC mechanism over 24T-$[Cu]_2$-Z (energy in kcal $mol^{-1}$，diameter in Å, angle in °)

| Reaction routes | Energy Barrier (kcal $mol^{-1}$) | Structures | Gas phase | AS[a] | TS[b] | Product |
|---|---|---|---|---|---|---|
| Route IB | 1.6 | $Cu_1$-N | - | 1.80 | 1.82 | 1.92 |
| | | $Cu_2$-$O_2$ | - | - | 1.85 | 2.03 |
| | | C-N | 1.16 | 1.28 | 1.27 | 1.25 |
| | | C-$O_1$ | - | 1.26 | 1.18 | 1.16 |
| | | C-$O_2$ | - | 1.39 | 1.81 | 2.29 |
| | | $O_2$-H | - | 0.99 | 0.98 | 1.01 |
| | | ∠N-C-$O_1$ | - | 128.5 | 157.1 | 174.9 |
| | | C-H | 1.07 | - | - | - |
| | | ∠N-C-H | 180.0 | 95 | - | - |
| Route IIB | 6.0 | Cu-N | - | 1.97 | 1.95 | - |
| | | N-C | 1.23 | 1.29 | 1.56 | - |
| | | C-$O_1$ | 1.18 | 1.15 | 1.15 | 1.14 |
| | | N-$O_2$ | - | 1.31 | 1.21 | 1.15 |
| | | ∠N-C-$O_1$ | 180.0 | 171.3 | 135.8 | - |
| Route IIIB | 1.4 | Cu-$N_1$ | | 1.91 | 1.91 | 1.92 |
| | | $N_1$-C | 1.23 | 1.50 | 1.64 | - |
| | | C-$O_1$ | 1.18 | 1.17 | 1.17 | 1.17 |
| | | $N_1$-$N_2$ | - | 1.26 | 1.20 | 1.11 |
| | | C-$O_2$ | - | 1.39 | 1.31 | 1.16 |
| | | $N_2$-$O_2$ | 1.16 | 1.47 | 1.73 | - |
| | | ∠$N_1$-C-$O_1$ | 180.0 | 136.8 | 128.0 | - |
| | | ∠$O_1$-C-$O_2$ | - | 134.2 | 139.1 | 179.0 |

[a] Adsorption state
[b] Transition state

**Table S1c.** Optimized structural parameters of HCN-SCC mechanism over 24T-$[Cu]_2$-O-Z (energy in kcal $mol^{-1}$， diameter in Å, angle in °).

| Reaction Routes | Energy Barrier (kcal $mol^{-1}$) | Structures | Gas Phase | AS[a] | TS[b] | Product |
|---|---|---|---|---|---|---|
| Route IC | 21.5 | $Cu_1$-N | - | 1.93 | - | - |
| | | $Cu_1$-O | - | 1.98 | 1.99 | 2.12 |
| | | $Cu_2$-O | - | 1.95 | 1.98 | 2.10 |
| | | C-N | 1.16 | 1.27 | 1.24 | 1.17 |
| | | C-O | - | 1.35 | 1.33 | 1.22 |
| | | C-H | 1.07 | 1.09 | 1.12 | - |
| | | N-H | - | - | - | 1.03 |
| | | ∠N-C-H | 180.0 | 128.2 | 103.4 | - |
| | | ∠H-N-C | - | - | - | 156.6 |
| | | ∠N-C-O | - | 110.3 | 142.0 | 175.9 |
| Route IIC | 14.7 | $Cu_1$-N | - | 1.94 | 1.84 | 1.83 |
| | | $Cu_2$-N | - | 1.97 | 2.00 | 1.84 |
| | | N-H | 1.01 | 1.03 | 1.03 | 1.03 |
| | | N-C | 1.22 | 1.45 | - | - |
| | | C-$O_1$ | 1.17 | 1.20 | 1.17 | 1.17 |
| | | C-$O_2$ | - | 1.30 | 1.21 | 1.17 |
| | | ∠$O_1$-C-$O_2$ | - | 130.3 | 157.2 | 179.1 |
| | | ∠H-N-C | 124.5 | 109.0 | - | - |
| | | ∠N-C-O | 172.2 | 124.7 | - | - |

| Reaction Routes | Energy Barrier (kcal $mol^{-1}$) | Structures | Gas Phase | AS | TS1 | IM[c] | TS2 | Product |
|---|---|---|---|---|---|---|---|---|
| Route IIIC | 26.3<br>74.3 | $Cu_1$-N | - | 1.83 | 1.90 | 1.97 | - | - |
| | | $Cu_2$-N | - | 1.85 | 2.02 | - | - | - |

| | | | | | | |
|---|---|---|---|---|---|---|
| $N\text{-}H_1$ | - | 1.03 | 1.02 | 1.02 | 1.02 | 1.04 |
| N-O | - | 2.34 | 2.03 | 1.44 | 1.52 | 1.41 |
| $N\text{-}H_2$ | - | - | 1.08 | 1.02 | 1.02 | 1.03 |
| $N\text{-}H_3$ | - | - | - | - | 1.11 | 1.03 |
| $O\text{-}H_2$ | 0.97 | 0.97 | 1.47 | - | - | - |
| $O\text{-}H_3$ | 0.97 | 0.97 | 0.98 | 0.98 | 1.48 | - |
| $\angle H_2\text{-}O\text{-}H_3$ | 103.7 | 104.5 | - | - | - | - |

[a] Adsorption state
[b] Transition state
[c] Intermediate

**Table S2** Mulliken atomic charges of each component in the models involved in RouteI over 24T-Cu-BEA with different active centers.

| Mulliken atomic charge/a.u. | 24T-[Cu]-Z[a]+O +HCN | 24T-[Cu]-O-Z-HCN | TSA1 | 24T-[Cu]-Z-HNCO |
|---|---|---|---|---|
| Q(Zeolite) | -0.2046 | -0.3224 | -0.3281 | -0.4291 |
| Q(Cu) | 0.6175 | 0.5339 | 0.3291 | 0.2894 |
| Q(O) | -0.4129 | -0.4745 | -0.4536 | -0.3777 |
| Q(H) | 0.2496 | 0.19 | 0.2332 | 0.3977 |
| Q(C) | 0.1086 | 0.4359 | 0.342 | 0.657 |
| Q(N) | -0.3582 | -0.3629 | -0.1226 | -0.5373 |
| Mulliken atomic charge/a.u. | 24T-$[Cu]_2$-Z[b]+2O +HCN | 24T-$[Cu]_2$-2O-Z-HCN | TSB1 | 24T-$[Cu]_2$-NCO-OH |
| Q(Zeolite) | -0.4947 | -0.5451 | -0.524 | -0.6237 |
| Q(Cu1) | 0.5414 | 0.4585 | 0.4079 | 0.2477 |
| Q(O1) | -0.2916 | -0.4609 | -0.329 | -0.2278 |
| Q(Cu2) | 0.5432 | 0.2847 | 0.3921 | 0.2164 |
| Q(O2) | -0.2983 | -0.581 | -0.7398 | -0.5644 |
| Q(H) | 0.2496 | 0.4984 | 0.5078 | 0.5343 |
| Q(C) | 0.1086 | 0.7824 | 0.7247 | 0.6764 |
| Q(N1) | -0.3582 | -0.437 | -0.4397 | -0.2589 |
| Mulliken atomic charge/a.u. | 24T-$[Cu]_2$-O-Z[c] +HCN | 24T-$[Cu]_2$-O-Z-HCN | TSC1 | 24T-$[Cu]_2$-HNCO |
| Q(Zeolite) | -0.3336 | -0.5061 | -0.4628 | -0.5126 |
| Q(Cu1) | 0.4283 | 0.4579 | 0.2455 | 0.1374 |
| Q(Cu2) | 0.5071 | 0.3268 | 0.3359 | 0.2045 |
| Q(O) | -0.6018 | -0.5708 | -0.5773 | -0.4667 |
| Q(H) | 0.2496 | 0.2104 | 0.2749 | 0.4389 |
| Q(C) | 0.1086 | 0.4203 | 0.2903 | 0.6478 |
| Q(N) | -0.3582 | -0.3385 | -0.1065 | -0.4493 |

[a]24T-[Cu]-Z represents Cu-BEA with single $[Cu]^+$ active center

[b]24T-$[Cu]_2$-Z represents Cu-BEA with double $[Cu]^+$ active center

[c]24T-$[Cu]_2$-O-Z represents Cu-BEA with double $[Cu\text{-}O\text{-}Cu]^{2+}$ active center

**Table S3** Mulliken charge ratio (MCR) of each component in the models involved in Route I over 24T-Cu-BEA with different active centers.

| Model | MCR/% | Reaction Step A1 | Reaction Step A2 | Reaction Step A3 |
|---|---|---|---|---|
| 24T-[Cu]-Z[a] | Zeolite | -35.99 | -1.87 | -18.19 |
| | Cu | -25.54 | -67.28 | -7.15 |
| | O | -18.82 | 6.87 | 13.67 |
| | H | -18.21 | 14.19 | 29.62 |
| | C | 100 | -30.85 | 56.72 |
| | N | -1.44 | 78.94 | -74.67 |
| Model | MCR/% | Reaction Step B1 | Reaction Step B2 | Reaction Step B3 |
| 24T-$[Cu]_2$-Z[b] | Zeolite | -5.46 | 7.82 | -20.6 |
| | Cu1 | -8.99 | -18.75 | -33.11 |
| | O1 | -18.35 | 48.89 | 20.91 |
| | Cu2 | -28.02 | 39.81 | -36.31 |
| | O2 | -30.64 | -58.86 | 36.25 |
| | H | 26.97 | 3.48 | 5.48 |
| | C | 73.03 | -21.39 | -9.98 |
| | N1 | -8.54 | -1 | 37.36 |
| Model | MCR/% | Reaction Step C1 | Reaction Step C2 | Reaction Step C3 |
| 24T-$[Cu]_2$-O-Z[c] | Zeolite | -44.01 | 12.41 | -7.88 |
| | Cu1 | 7.55 | -60.88 | -17.1 |
| | Cu2 | -45.99 | 2.61 | -20.79 |
| | O | 7.91 | -1.86 | 17.5 |
| | H | -10 | 18.49 | 25.94 |
| | C | 79.51 | -37.26 | 56.56 |
| | N | 5.03 | 66.49 | -54.23 |

[a]24T-[Cu]-Z represents Cu-BEA with single $[Cu]^+$ active center

[b]24T-$[Cu]_2$-Z represents Cu-BEA with double $[Cu]^+$ active center

[c]24T-$[Cu]_2$-O-Z represents Cu-BEA with double $[Cu\text{-}O\text{-}Cu]^{2+}$ active center

**Table S4a** DFT energy calculation of each reaction step during HCN-SCCover 24T-[Cu]-Z.

| | Reaction steps | Energy/ kcal·mol$^{-1}$ |
|---|---|---|
| Route IA | Step A1 | -55.8 |
| | Step A2 | 23.8 |
| | Step A3 | -86 |
| Route IIA | Step A4 | -95.6 |
| | Step A5 | 7.1 |
| | Step A6 | -4.6 |
| Route IIIA | Step A7 | -8.3 |
| | Step A8 | 7.9 |
| | Step A9 | -50.5 |
| | Step A10 | 72.3 |
| | Step A11 | -20.9 |

**Table S4b** DFT energy calculation of each reaction step during HCN-SCC over24T-$[Cu]_2$-Z.

| | Reaction steps | Energy/ kcal·mol$^{-1}$ |
|---|---|---|
| Route IB | Step B1 | -97.7 |
| | Step B2 | 1.6 |
| | Step B3 | -11 |
| Route IIB | Step B4 | -94.5 |
| | Step B5 | 6 |
| | Step B6 | -38.2 |
| Route IIIB | Step B7 | 11.7 |
| | Step B8 | 1.4 |
| | Step B9 | -114.5 |

**Table S4c** DFT energy calculation of each reaction step during HCN-SCC over 24T-$[Cu]_2$-O-Z.

| | Reaction steps | Energy/ kcal·mol$^{-1}$ |
|---|---|---|
| Route IC | Step C1 | -18.8 |
| | Step C2 | 21.5 |
| | Step C3 | -78.2 |
| Route IIC | Step C4 | -134 |
| | Step C5 | 14.7 |
| | Step C6 | -16.1 |
| Route IIIC | Step C7 | -2.1 |
| | Step C8 | 26.3 |
| | Step C9 | -35.4 |
| | Step C10 | 74.3 |
| | Step C11 | -87 |