# Supporting Information

## Theoretical insights into the catalytic mechanism of propylene hydroformylation over Co-N-C materials

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**Section1.**

Formula for product selectivity

$$N_i = A_i - B_i \tag{S1}$$

$$S_{propane} = \frac{N_{propane}}{N_{isobutyraldehyde} + N_{n-butyraldehyde} + N_{propane}} \tag{S2}$$

$$S_{aldehyde} = \frac{N_{n-butyraldehyde} + N_{isobutyraldehyd}}{N_{n-butyraldehyde} + N_{isobutyraldehyd} + N_{propane}} \tag{S3}$$

$$S_{n\text{-}butyraldehyde} = \frac{N_{n-butyraldehyde}}{N_{n-butyraldehyde} + N_{isobutyraldehyd} + N_{propane}} \tag{S4}$$

$$S_{isobutyraldehyde} = \frac{N_{isobutyraldehyd}}{N_{n-butyraldehyde} + N_{isobutyraldehyd} + N_{propane}} \tag{S5}$$

where ***N*** represents the actual occurrence frequency of species generated per unit time, the ***i*** represents propane, n-butyraldehyde, and isobutyraldehyde, ***A*** represents the total occurrence frequency for all reactions that generate the species, and ***B*** represents the occurrence frequency for all reactions that consume the species.

**Section2.**

**Table S1** The activation energy of each elementary process of propylene hydroformylation.

| Serial Number | elementary process | Activation barrier /eV | | |
|---|---|---|---|---|
| | | I | II | III |
| 1 | $H_2 \nsim H^* + H^*$ | 0 | 0 | 0 |
| 2 | $H^* + * \nsim * + H^*$ | \ | 0.1 | 0.2 |

| | | | | |
|---|---|---|---|---|
| 3 | $CO \gtrless CO^*$ | 0 | 0 | 0 |
| 4 | $CH_3CH=CH_2 \gtrless CH_3CH=CH_2^*$ | 0 | 0 | 0 |
| 5 | $CH_3CH=CH_2^* + H^* \gtrless CH_3CH_2CH_2^*$ | 0.33 | 0.58 | 0.49 |
| 6 | $CH_3CH_2CH_2^* \gtrless CH_3CH=CH_2^* + H^*$ | 0.8 | 1.66 | 1.28 |
| 7 | $CH_3CH=CH_2^* + H^* \gtrless CH_3CHCH_3^*$ | 0.16 | 0.57 | 0.13 |
| 8 | $CH_3CHCH_3^* \gtrless CH_3CH=CH_2^*+H^*$ | 0.67 | 0.84 | 1.01 |
| 9 | $CH_3CH_2CH_2^* + H^* \gtrless CH_3CH_2CH_3^*$ | 0.77 | 0.83 | 0.88 |
| 10 | $CH_3CH_2CH_3^* \gtrless CH_3CH_2CH_2^* + H^*$ | 0.26 | 0.95 | 0.43 |
| 11 | $CH_3CHCH_3^* + H^* \gtrless CH_3CH_2CH_3^*$ | 0.66 | 0.86 | 0.72 |
| 12 | $CH_3CH_2CH_3^* \gtrless CH_3CHCH_3^* + H^*$ | 0.25 | 0.98 | 0.49 |
| 13 | $CH_3CH_2CH_2^* + CO^* \gtrless CH_3CH_2CH_2CO^*$ | 0.79 | 0.52 | 0.70 |
| 14 | $CH_3CH_2CH_2CO^* \gtrless CH_3CH_2CH_2^*+CO^*$ | 0.85 | 1.03 | 1.11 |
| 15 | $CH_3CHCH_3^* + CO^* \gtrless CH_3CHCH_3CO^*$ | 0.41 | 0.62 | 0.45 |
| 16 | $CH_3CHCH_3CO^* \gtrless CH_3CHCH_3^* + CO^*$ | 0.11 | 0.82 | 0.88 |
| 17 | $CH_3CH_2CH_2CO^* + H^* \gtrless CH_3CH_2CH_2CHO^*$ | 0.42 | 0.72 | 0.95 |
| 18 | $CH_3CH_2CH_2CHO^* \gtrless CH_3CH_2CH_2CO^* + H^*$ | 0.60 | 0.77 | 1.30 |
| 19 | $CH_3CHCH_3CO^* + H^* \gtrless CH_3CHCH_3CHO^*$ | 0.59 | 0.70 | 1.01 |
| 20 | $CH_3CHCH_3CHO^* \gtrless CH_3CHCH_3CO^*+H^*$ | 0.67 | 0.14 | 1.70 |
| 21 | $H^*+H^* \gtrless H_2$ | 0.75 | 0.95 | 0.55 |
| 22 | $CO^* \gtrless CO$ | 2.11 | 2.72 | 1.07 |
| 23 | $CH_3CH=CH_2^* \gtrless CH_3CH=CH_2$ | 1.54 | 1.83 | 0.32 |
| 24 | $CH_3CH_2CH_2^* \gtrless CH_3CH_2CH_2$ | 3.24 | 2.36 | 2.28 |
| 25 | $CH_3CHCH_3^* \gtrless CH_3CHCH_3$ | 3.04 | 2.16 | 2.10 |
| 26 | $CH_3CH_2CH_2CO^* \gtrless CH_3CH_2CH_2CO$ | 3.35 | 2.76 | 2.34 |
| 27 | $CH_3CHCH_3CO^* \gtrless CH_3CHCH_3CO$ | 3.07 | 3.89 | 2.09 |
| 28 | $CH_3CH_2CH_3^* \gtrless CH_3CH_2CH_3$ | 1.62 | 1.85 | 0.77 |
| 29 | $CH_3CH_2CH_2CHO^* \gtrless CH_3CH_2CH_2CHO$ | 1.86 | 1.16 | 0.93 |

| | | | | |
|---|---|---|---|---|
| 30 | $CH_3CHCH_3CHO^* \not\asymp CH_3CHCH_3CHO^*$ | 1.70 | 1.08 | 0.96 |

*I, II, and III in the table represent the three catalyst models of Co-N3-C, 0N-bridged and 2N-bridged, respectively.

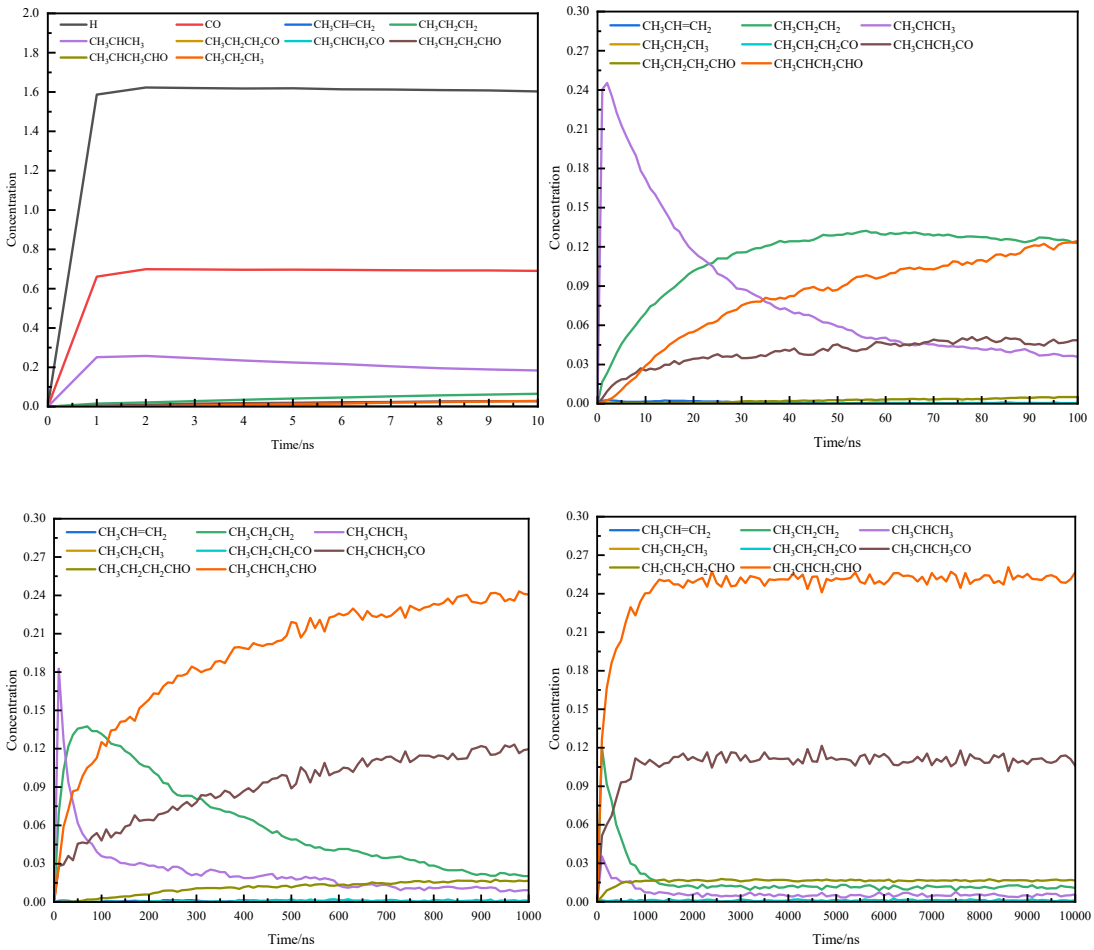


**Figure S1** The change of coverage over time within 10, 100, 1000 and 10000 ns on Co-$N_3$-C

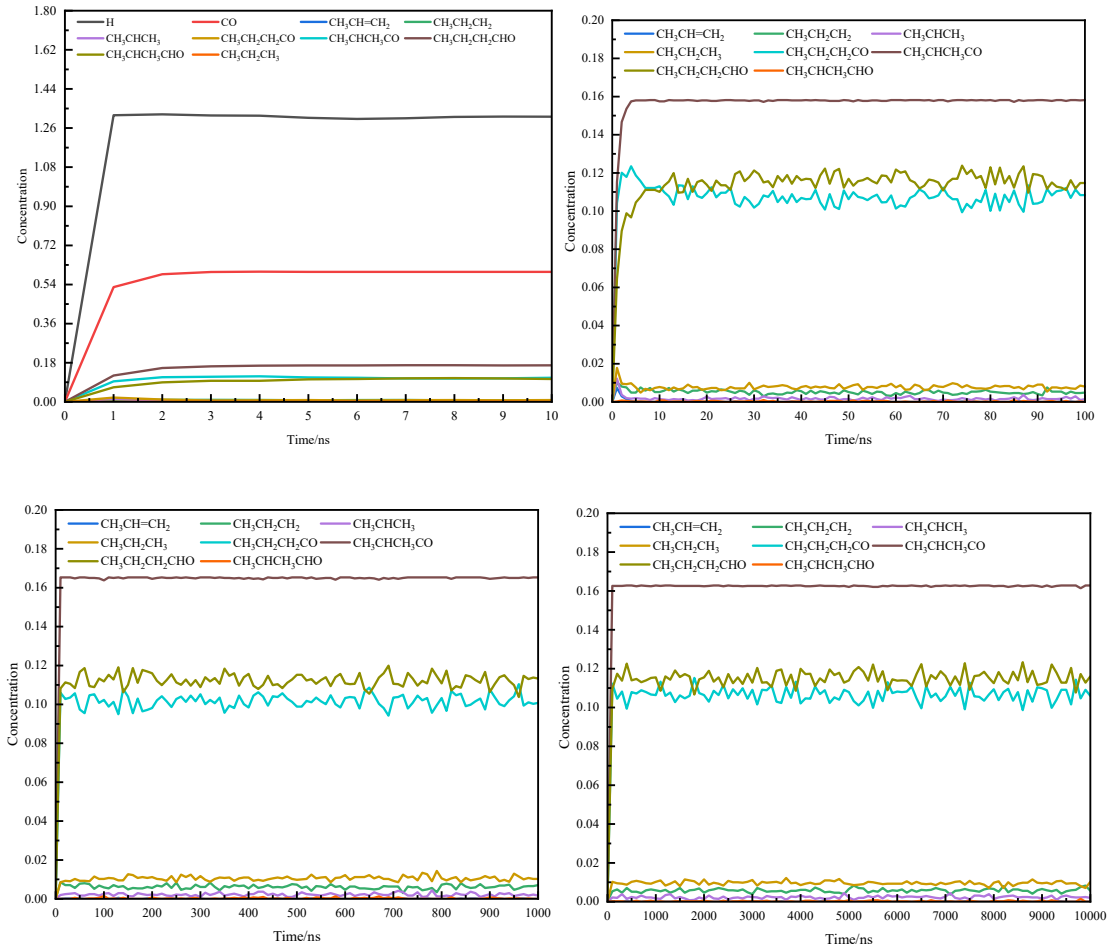


**Figure S2** The change of coverage over time within 10, 100, 1000 and 10000 ns on 0N-bridged

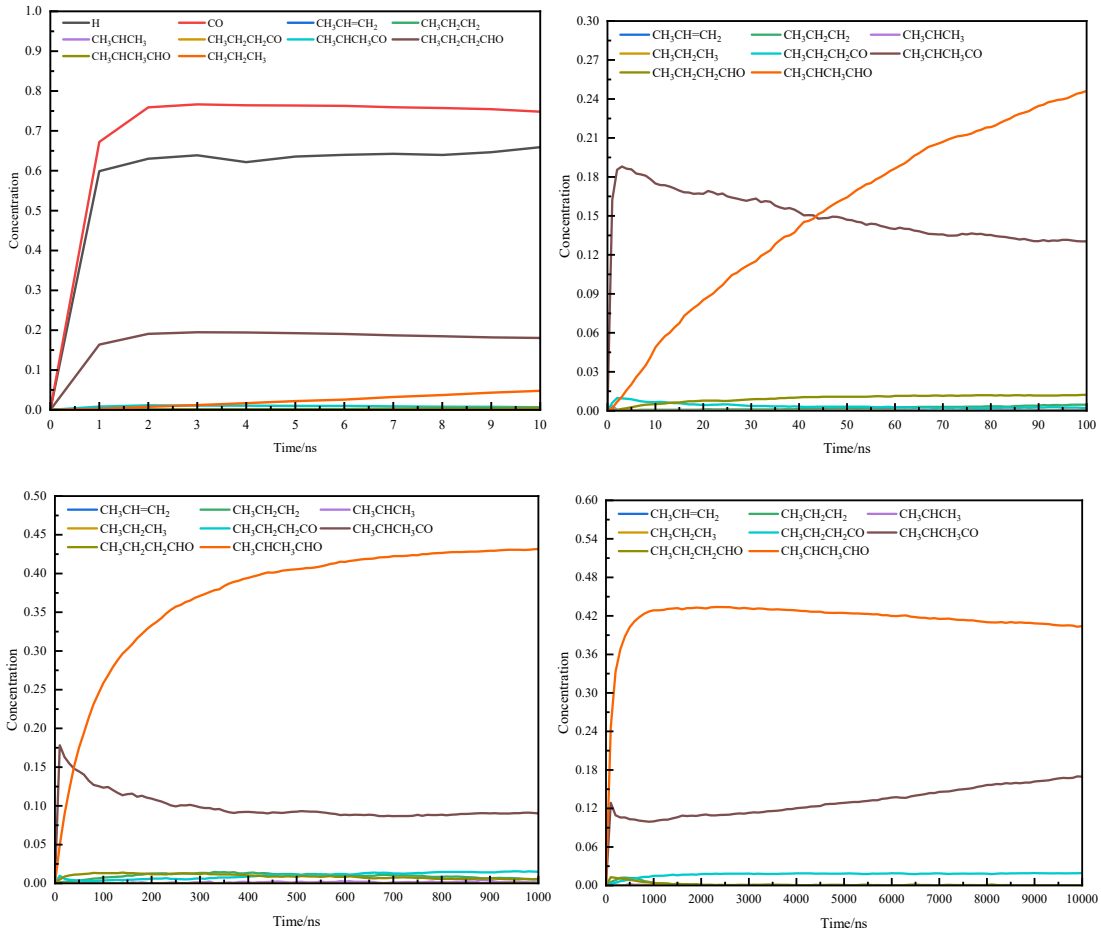


**Figure S3** The change of coverage over time within 10,100, 1000 and 10000 ns on 2N-bridged

**Table S2** The occurrence frequency of each elementary process in propylene hydroformylation on three models during 10000 ns simulation time.

| Serial Number | elementary process | Activation barrier /eV | | |
|---|---|---|---|---|
| | | I | II | III |
| 1 | $H_2$ ✂ $H^*$ + $H^*$ | 303289 | 1529254 | 3547111 |
| 2 | $H^*$ + * ✂ * + $H^*$ | \ | 325373 | 1079617 |
| 3 | CO ✂ $CO^*$ | 4028 | 4033 | 404489 |
| 4 | $CH_3CH=CH_2$ ✂ $CH_3CH=CH_2^*$ | 1626 | 1672 | 164709 |
| 5 | $CH_3CH=CH_2^*$ + $H^*$ ✂ $CH_3CH_2CH_2^*$ | 910 | 8071 | 50 |
| 6 | $CH_3CH_2CH_2^*$ ✂ $CH_3CH=CH_2^*$ + $H^*$ | 3433 | 9 | 235 |
| 7 | $CH_3CH=CH_2^*$ + $H^*$ ✂ $CH_3CHCH_3^*$ | 23517 | 8921 | 4209 |
| 8 | $CH_3CHCH_3^*$ ✂ $CH_3CH=CH_2^*$+$H^*$ | 19368 | 15311 | 1595 |
| 9 | $CH_3CH_2CH_2^*$ + $H^*$ ✂ $CH_3CH_2CH_3^*$ | 3696 | 29578 | 447 |
| 10 | $CH_3CH_2CH_3^*$ ✂ $CH_3CH_2CH_2^*$ + $H^*$ | 6336 | 22506 | 712 |
| 11 | $CH_3CHCH_3^*$ + $H^*$✂ $CH_3CH_2CH_3^*$ | 10269 | 9076 | 265 |
| 12 | $CH_3CH_2CH_3^*$ ✂ $CH_3CHCH_3^*$ + $H^*$ | 7629 | 16123 | 0 |
| 13 | $CH_3CH_2CH_2^*$ + $CO^*$ ✂ $CH_3CH_2CH_2CO^*$ | 73 | 1027 | 203 |
| 14 | $CH_3CH_2CH_2CO^*$ ✂ $CH_3CH_2CH_2^*$+$CO^*$ | 0 | 64 | 124 |
| 15 | $CH_3CHCH_3^*$ + $CO^*$ ✂ $CH_3CHCH_3CO^*$ | 623542 | 1356 | 22176 |
| 16 | $CH_3CHCH_3CO^*$ ✂ $CH_3CHCH_3^*$ + $CO^*$ | 622057 | 710 | 19827 |
| 17 | $CH_3CH_2CH_2CO^*$ + $H^*$ ✂ $CH_3CH_2CH_2CHO^*$ | 158389 | 2260731 | 270 |
| 18 | $CH_3CH_2CH_2CHO^*$ ✂ $CH_3CH_2CH_2CO^*$ + $H^*$ | 158321 | 2260214 | 270 |
| 19 | $CH_3CHCH_3CO^*$ + $H^*$ ✂ $CH_3CHCH_3CHO^*$ | 639722 | 385517 | 2211 |

| | | | | |
|---|---|---|---|---|
| 20 | $CH_3CHCH_3CHO^* \nsim CH_3CHCH_3CO^*+H^*$ | 638671 | 385516 | 556 |
| 21 | $H^*+H^* \nsim H_2$ | 299200 | 1525471 | 3543024 |
| 22 | $CO^* \nsim CO$ | 0 | 0 | 400417 |
| 23 | $CH3CH=CH2^* \nsim CH3CH=CH2$ | 0 | 0 | 162280 |
| 24 | $CH_3CH_2CH_2^* \nsim CH_3CH_2CH_2$ | 0 | 0 | 0 |
| 25 | $CH_3CHCH_3^* \nsim CH_3CHCH_3$ | 0 | 0 | 0 |
| 26 | $CH_3CH_2CH_2CO^* \nsim CH_3CH_2CH_2CO$ | 0 | 0 | 0 |
| 27 | $CH_3CHCH_3CO^* \nsim CH_3CHCH_3CO$ | 0 | 0 | 0 |
| 28 | $CH_3CH_2CH_3^* \nsim CH_3CH_2CH_3$ | 0 | 0 | 0 |
| 29 | $CH_3CH_2CH_2CHO^* \nsim CH_3CH_2CH_2CHO$ | 0 | 0 | 0 |
| 30 | $CH_3CHCH_3CHO^* \nsim CH_3CHCH_3CHO^*$ | 0 | 0 | 0 |

*I, II, and III in the table represent the three catalyst models of Co-$N_3$-C, 0N-bridged and 2N-bridged, respectively.

**Table S3** The product selectivity on three models

| | Co-$N_3$ | 0N-bridged | 2N-bridged |
|---|---|---|---|
| $S_{propane}$/% | 0 | 4.6 | 0 |
| $S_{aldehyde}$ /% | 100 | 95.4 | 100 |
| $S_{n\text{-}butyraldehyde}$ /% | 6.1 | 95.2 | 0 |
| $S_{isobutyraldehyde}$ /% | 93.9 | 0.2 | 100 |