

Electronic Supplementary Information

Unveiling intrinsic active sites and pivotal intermediate species in N₂O decomposition over Co₃O₄-based catalysts

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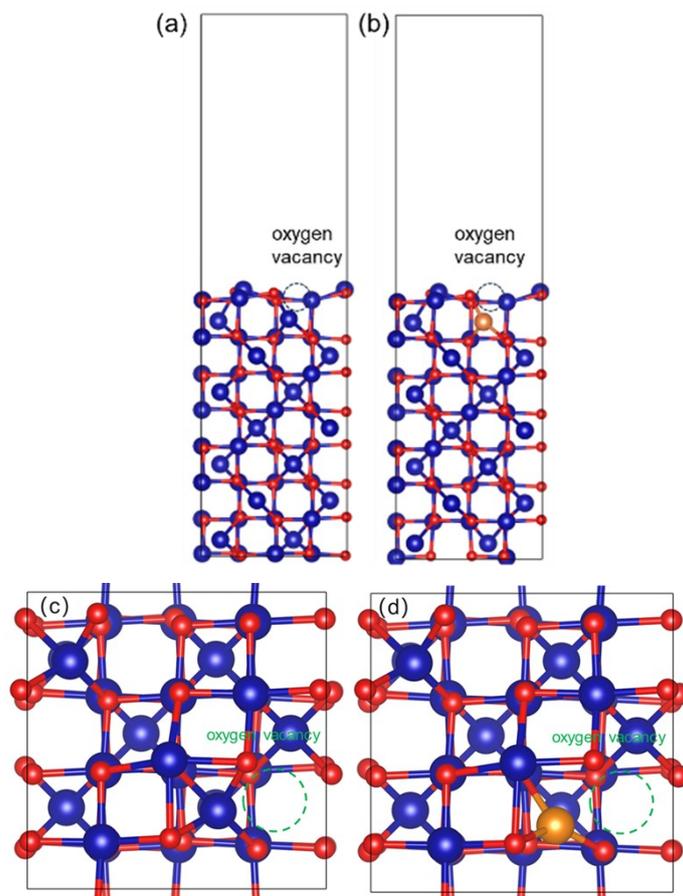


Fig. S1 Optimized slab models of (a) the Co₃O₄ (100) surface and (b) Cu²⁺ replaces Co²⁺ sites. Top views of (c) the Co₃O₄ (100) and (d) Cu doped Co₃O₄ (100). Red, blue, gray and orange balls represent O, Co, N and Cu atoms, respectively.

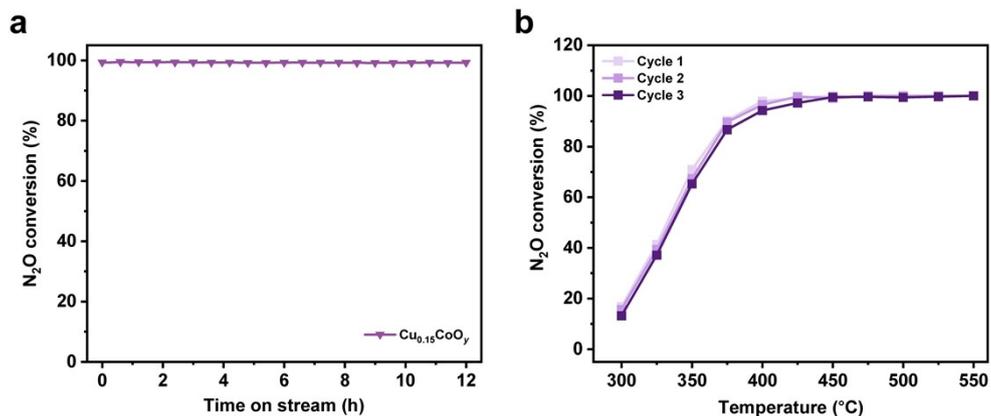


Fig. S2 (a) N_2O decomposition performance of the $\text{Cu}_{0.15}\text{CoO}_y$ at 400 °C for 12 h; (b) N_2O decomposition performance of the $\text{Cu}_{0.15}\text{CoO}_y$ after multiple cycles. Reaction conditions: $[\text{N}_2\text{O}] = 500$ ppm, Ar balance, flow rate = 200 mL min^{-1} , GHSV = 120,000 h^{-1} .

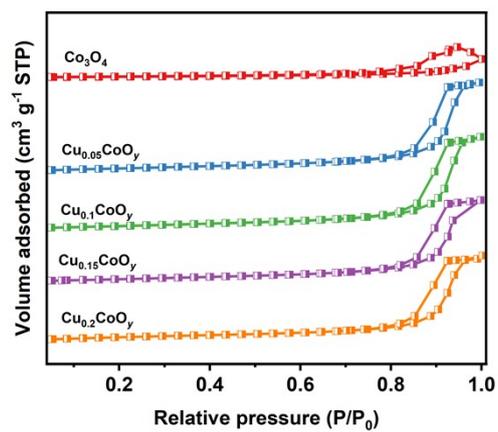


Fig. S3 N₂ adsorption-desorption isotherms of Co-based catalysts.

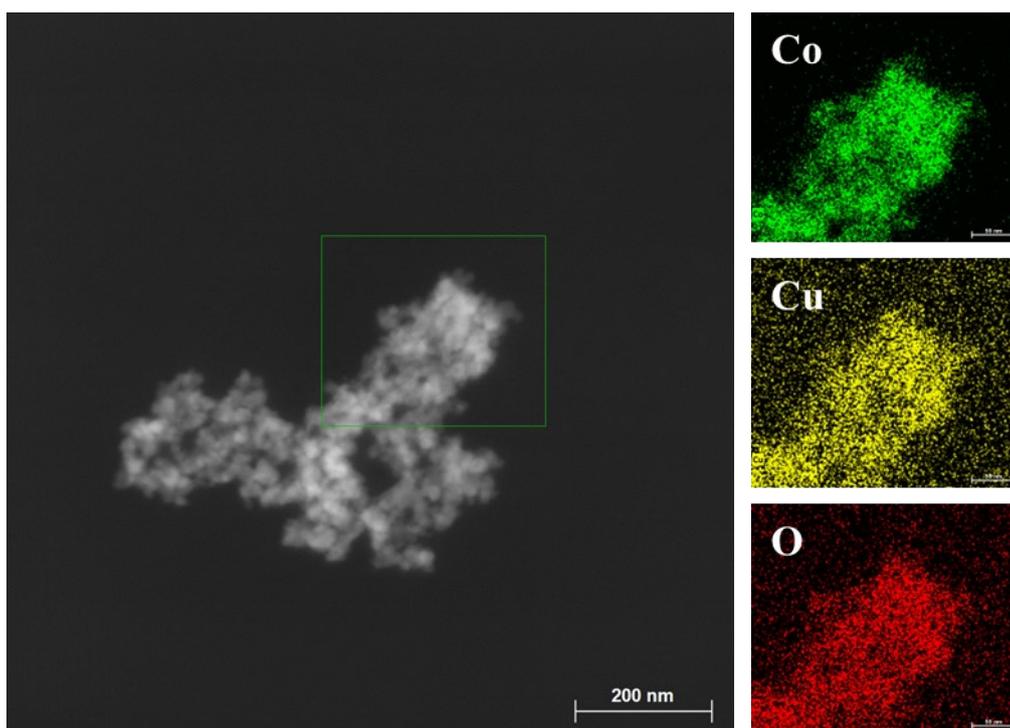


Fig. S4 HAADF-STEM image and EDS mappings of $\text{Cu}_{0.15}\text{CoO}_y$ catalyst.

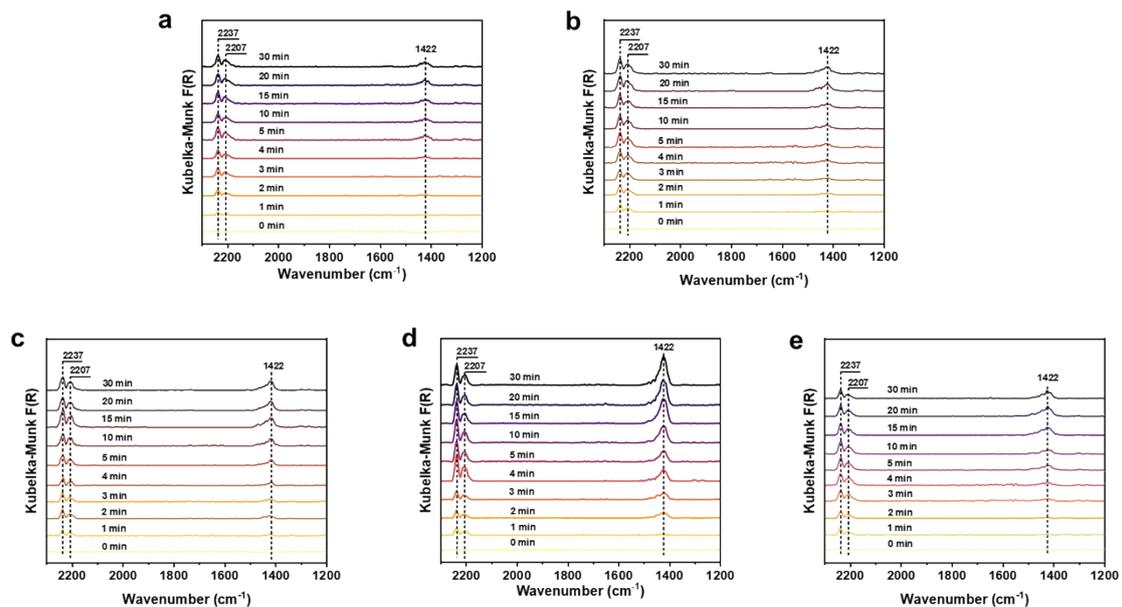


Fig. S5 *In situ* DRIFTS spectra of N_2O decomposition over (a) Co_3O_4 , (b) $\text{Cu}_{0.05}\text{CoO}_y$, (c) $\text{Cu}_{0.1}\text{CoO}_y$, (d) $\text{Cu}_{0.15}\text{CoO}_y$, and (e) $\text{Cu}_{0.2}\text{CoO}_y$ catalysts at $325\text{ }^\circ\text{C}$ for 30 min.

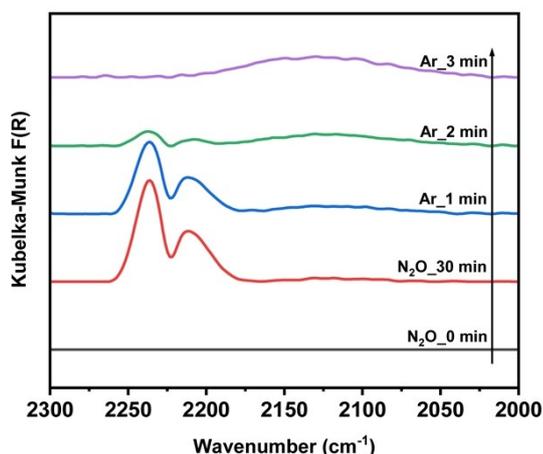


Fig. S6. *In situ* DRIFTS spectra spectral evolution of $\text{Cu}_{0.15}\text{CoO}_y$ catalyst under varied atmospheres at room temperature. N_2O atmosphere: 500 ppm N_2O , balanced with Ar, 50 mL min^{-1} . Ar atmosphere: pure Ar, 50 mL min^{-1} .

As shown in Fig. S6, after stopping the N_2O flow and purging the cell with pure Ar at 50 mL min^{-1} , the characteristic N_2O -related IR bands at 2237 and 2207 cm^{-1} gradually weakened and completely disappeared after approximately 3 min of Ar purging. Considering that the internal volume of the DRIFTS cell is very small ($\sim 3 \text{ mL}$) and the gas flow rate is relatively high (50 mL min^{-1}), gas-phase N_2O should have been flushed out almost immediately. Therefore, the fact that the characteristic bands persisted for some time before disappearing suggests that these bands are mainly associated with surface-adsorbed species rather than free gas-phase N_2O .

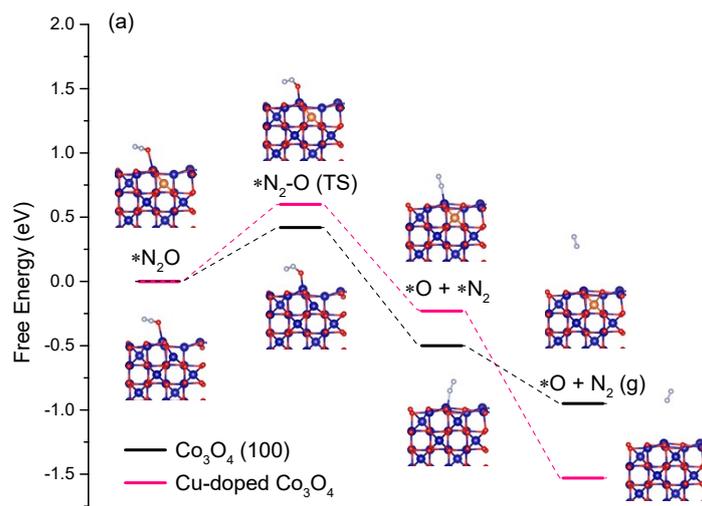


Fig. S7 Splitting of adsorbed N_2O on Co_3O_4 (100) and Cu-doped Co_3O_4 (100). Red, blue, gray and orange balls represent O, Co, N and Cu atoms, respectively. The pink dotted circle indicates an oxygen vacancy.

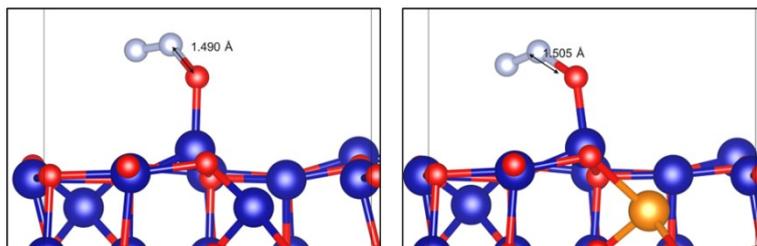


Fig. S8. Bond lengths in transition states.

Table S1. Frequency values of transition state (TS) over Co_3O_4

Mode	Type	Frequency (THz)	Angular frequency ($2\pi \cdot \text{THz}$)	Wavenumbe r (cm^{-1})	Energy (meV)
...
170	f	1.751693	11.006213	58.430195	7.244418
171	f	1.548416	9.728987	51.649613	6.403733
172	f	1.453885	9.135027	48.496373	6.012781
173	f	1.344003	8.444620	44.831113	5.558347
174	f/i	20.040608	125.918855	668.482732	82.881258

Table S2. Frequency values of transition state (TS) over Cu-doped Co₃O₄

Mode	Type	Frequency (THz)	Angular frequency ($2\pi \cdot$ THz)	Wavenumber (cm ⁻¹)	Energy (meV)
...
170	f	1.115155	7.006728	37.197582	4.611910
171	f	0.938572	5.897222	31.307391	3.881620
172	f	0.448436	4.186647	22.226230	2.755700
173	f/i	1.547817	9.725221	51.629619	6.401254
174	f/i	17.879424	112.339732	596.393378	73.943322