

Supplementary Materials

Table S1. Structural parameters of optimized models in the N₂O decomposition process (diameter in Å, angle in °) (The first N₂O molecule is noted as O1–N1–N2. The second N₂O molecule is labelled as O2–N3–N4).

Model	Spin	Cu1-Cu2	Cu1-O1	Cu2-O1	O1-N1
Z-CuCu	1	2.46	-	-	-
Z-Cu-ONN-Cu	1	2.65	2.11	2.24	1.22
Z-Cu-ONN-Cu-TS	1	2.85	1.90	1.94	1.52
Z-Cu-O-N ₂ -Cu	3	2.62	1.83	1.83	-
Z-CuOCu	3	2.69	1.84	1.82	-
Model	N1-N2	∠O1-N1-N2	∠Cu1-O1-Cu2		
Z-CuCu	-	-	-		
Z-Cu-ONN-Cu	1.12	178.03	-		
Z-Cu-ONN-Cu-TS	1.12	142.98	95.67		
Z-Cu-O-N ₂ -Cu	1.10	-	115.05		
Z-CuOCu	-	-	113.83		
Model	Spin	Cu1-Cu2	Cu1-O1	Cu2-O1	Cu1-O2
Z-Cu-O-ONN-Cu	3	2.7	1.84	1.81	-
Z-Cu-O-ONN-Cu-TS	3	2.8	1.84	1.82	-
Z-Cu-OO-N ₂ -Cu	3	2.86	-	1.9	1.93
Z-Cu-OO-Cu	3	2.86	-	1.9	1.93
Model	O2-N3	N3-N4	O1-O2	∠O2-N3-N4	
Z-Cu-O-ONN-Cu	1.21	1.13	3.26	178.56	
Z-Cu-O-ONN-Cu-TS	1.64	1.11	1.83	153.52	
Z-Cu-OO-N ₂ -Cu	-	1.1	1.4	-	
Z-Cu-OO-Cu	-	1.1	1.4	-	

Table S2. Structural parameters of optimized models in the NO-NH₃-SCR process (diameter in Å, angle in °) (The O atom of the Z-2Cu-O is noted as O. The NO is labelled as N2-O2. The NH₃ is shorted as N1-H1-H2-H3).

Model	Spin	Cu1-Cu2	Cu1-O	Cu2-O	N1-Cu2	N2-Cu1
Z-CuOCu-NH ₃	3	2.81	1.81	1.83	2.08	-
Z-Cu-OH-NH ₂ -Cu-TS	4	2.78	1.86	1.93	2	-
Z-Cu-OH-NH ₂ -Cu	4	2.92	1.92	1.93	2.08	-
Z-Cu-OH-NH ₂ -NO-Cu	4	3	1.9	1.93	2.09	2.64
Z-Cu-OH-NH ₂ -NO-Cu-TS	4	2.9	1.89	2	2.94	2.01
Z-Cu-OH-NH-NOH-Cu	4	2.92	1.9	1.95	2.81	1.97
Z-Cu-OH-NH-NOH-Cu-TS	4	3.34	1.9	1.91	-	2.3
Z-Cu-OH-N ₂ -H ₂ O-Cu	4	3.15	1.88	1.91	-	4.41
Z-CuOHCu	2	2.81	1.9	1.92	-	-
Model	H1-O	H1-N1	N1-N2	O2-H1	∠Cu1-O-Cu2	
Z-CuOCu-NH ₃	-	-	-	-	100.98	
Z-Cu-OH-NH ₂ -Cu-TS	1.23	1.29	-	-	94.47	
Z-Cu-OH-NH ₂ -Cu	0.97	-	-	-	98.69	
Z-Cu-OH-NH ₂ -NO-Cu	0.97	-	-	-	100.19	
Z-Cu-OH-NH ₂ -NO-Cu-TS	0.97	-	1.43	1.26	96.16	
Z-Cu-OH-NH-NOH-Cu	0.97	-	1.33	0.98	99.09	
Z-Cu-OH-NH-NOH-Cu-TS	0.97	-	1.18	0.97	122.56	
Z-Cu-OH-N ₂ -H ₂ O-Cu	0.97	-	1.1	0.97	112.46	

Table S3. Structural parameters of optimized models in the NO₂-NH₃-SCR process (diameter in Å, angle in °) (The O atom of the Z-2Cu-OH is noted as O. The NO₂ is labelled as O1-N1-O2. The NH₃ is shorted as N2-H1-H2-H3).

Model	Spin	Cu1-Cu2	Cu2-O	Cu1-O	O-H	∠Cu1-O-Cu2	N2-Cu2
Z-Cu-OH-NO ₂ -Cu	3	2.88	1.94	1.90	-	97.14	-
Z-Cu-OH-NO ₂ -NH ₃ -Cu	3	3.12	1.96	1.89	0.97	108.21	2.15
Z-Cu-OH-NO ₂ -NH ₃ -Cu-TS	3	2.63	2.00	2.00	0.98	82.07	-
Z-Cu-NH ₄ NO ₂ -Cu	3	3.31	-	1.95	0.97	-	-
Z-Cu-NH ₂ NO-Cu	3	2.75	1.98	1.95	-	88.94	-
Model	O1-Cu2	N2-Cu1	H1-O	N2-H1	N-N	O-N	N-O
Z-Cu-OH-NO ₂ -Cu	2.09	-	-	-	-	-	-
Z-Cu-OH-NO ₂ -NH ₃ -Cu	2.18	-	-	-	-	-	-
Z-Cu-OH-NO ₂ -NH ₃ -Cu-TS	2.93	-	1.18	1.34	-	-	-
Z-Cu-NH ₄ NO ₂ -Cu	1.94	-	1.00	-	1.43	-	-
Z-Cu-NH ₂ NO-Cu	-	-	-	-	1.51	1.37	1.15

Table S4. Structural parameters of optimized models of NO_x-assisted reduction of active center (diameter in Å, angle in °) (The NO is labelled as N1-O1. The NO₂ is noted as O2-N2-O3.).

Model	Spin	Cu1-Cu2	Cu1-O	Cu2-O	∠Cu1-O-Cu2	N1-O	N1-O1
Z-Cu-O-NO-Cu-TS	2	2.66	1.92	1.89	88.34	1.58	1.20
Z-Cu-ONO-Cu	2	2.64	1.92	-	-	1.43	1.23
Model	Spin	Cu1-Cu2	Cu1-O	Cu2-O	O2-Cu2	O-O2	N2-O2
Z-Cu-O-NO ₂ -Cu-TS	4	2.78	1.87	1.94	-	1.70	1.85
Z-Cu-OO-NO-Cu	4	2.86	1.90	-	1.93	1.40	-
Model	∠Cu1-O-Cu2		∠O2-N2-O3		N2-O3		
Z-Cu-O-NO ₂ -Cu-TS	93.72		111.69		1.16		
Z-Cu-OO-NO-Cu	-		-		1.16		