HOMO   **LUMO**

Figure S1. The schematic diagram of frontier molecular orbitals for catalyst Au/C$_2$N. (The isovalue is setting as default 0.03 a.u.).
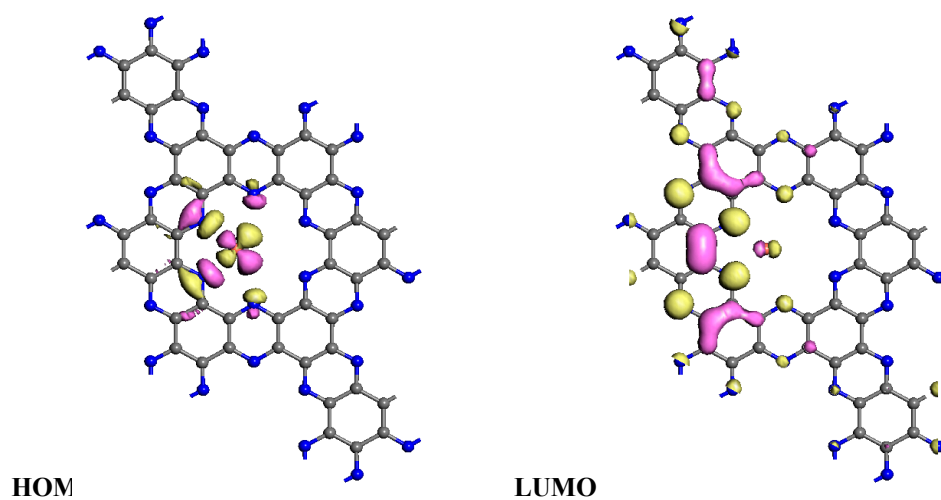

HOM   **LUMO**

Figure S2. The schematic diagram of frontier molecular orbitals for catalyst Cu/C$_2$N. (The isovalue is setting as default 0.03 a.u.).
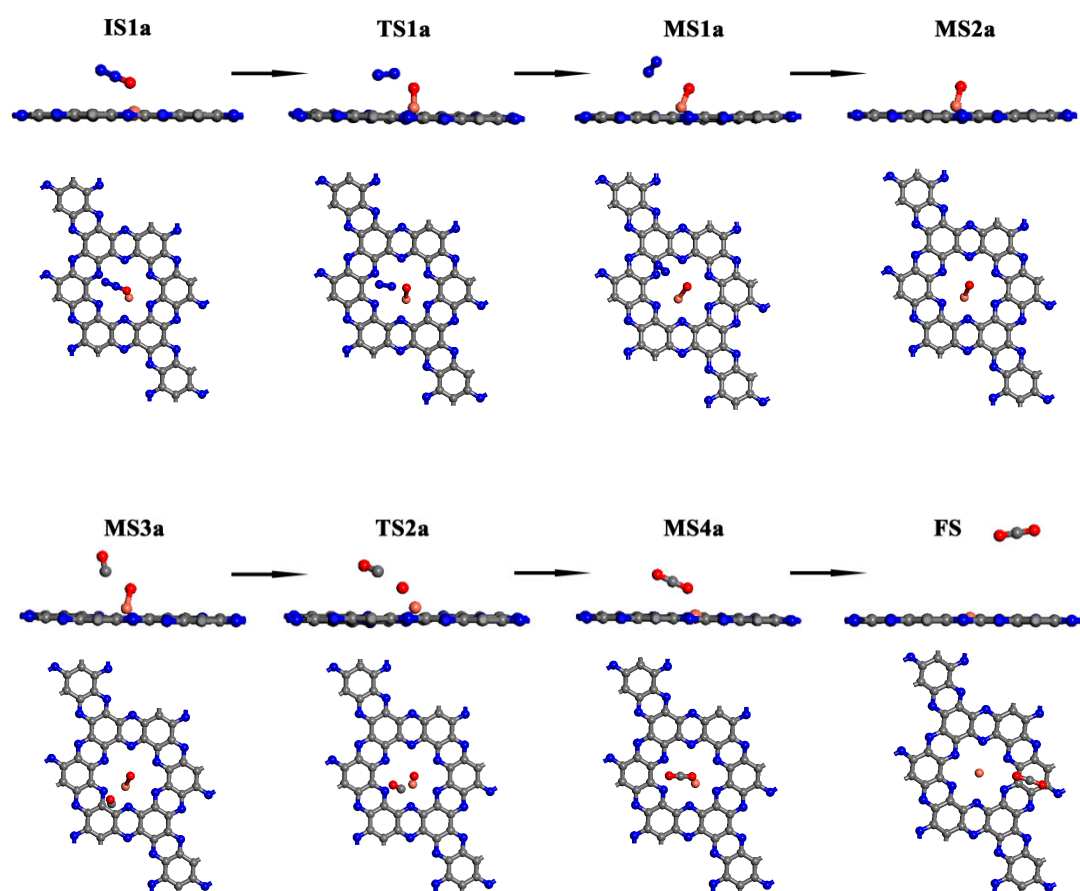
path I

Figure S3. The schematic diagram of all species with the MEP for the N₂O reduction on the Cu/C₂N monolayer via mechanism I. (Blue, grey, orange and red balls represent N, C, Cu and O atoms, respectively.).
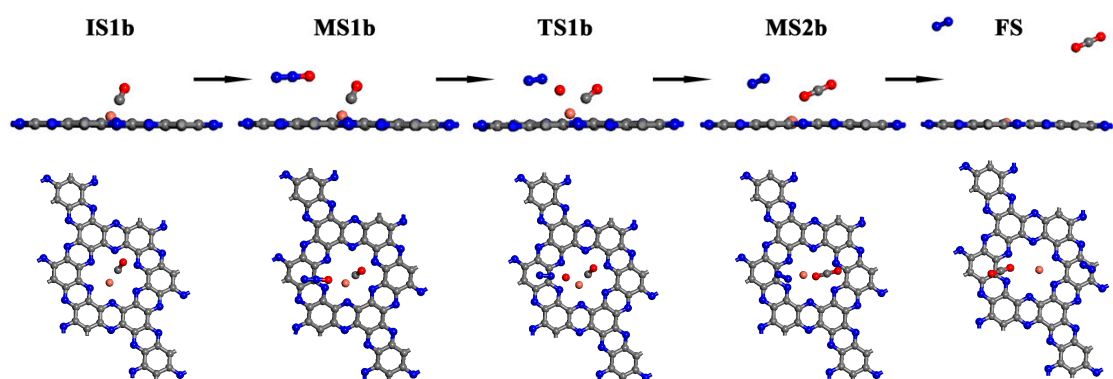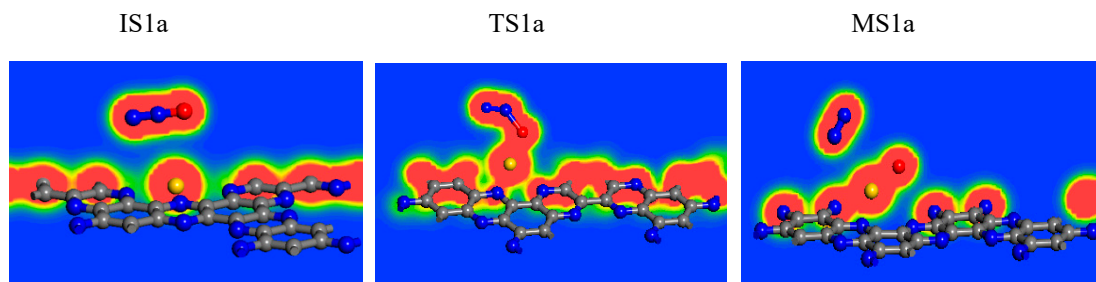
path II

Figure S4. The schematic diagram of all species and the MEP for the N₂O reduction on the Cu/C₂N monolayer via mechanism II. (Blue, grey, orange and red balls represent N, C, Cu and O atoms, respectively.).
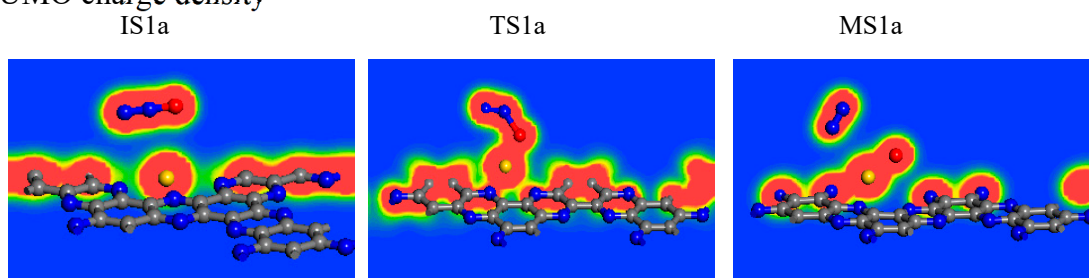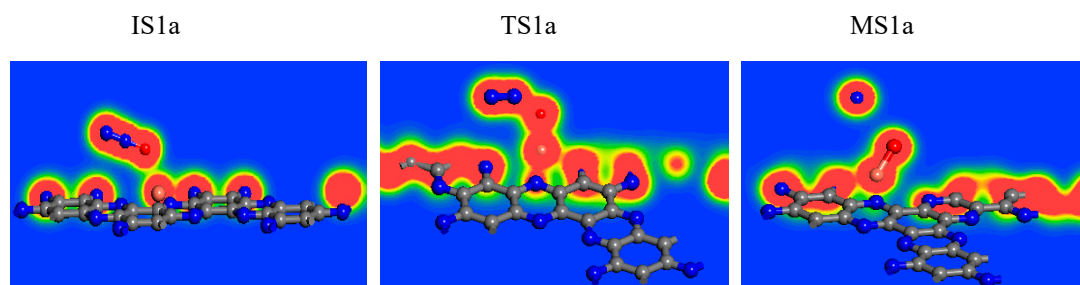
HOMO charge density

IS1a   TS1a   MS1a

LUMO charge density

IS1a   TS1a   MS1a

Figure S5. The HOMO and LUMO charge density plots for IS1a, TS1a and MS1a on **Au/C₂N.**

HOMO charge density

IS1a   TS1a   MS1a

LUMO charge density

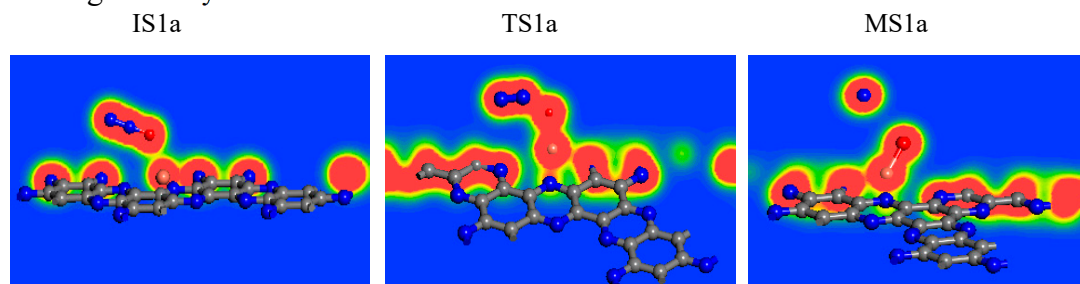IS1a   TS1a   MS1a

Figure S6. The HOMO and LUMO charge density plots for IS1a, TS1a and MS1a on **Cu/C₂N.**

Table S1. The Mulliken charge of species involved in N_2O reduction mechanism II.

Cat	Atom/ molecule	charges of the systems/e				
		Isolated systems	IS1b	MS1b	TS1b	MS2b
Au/C$_2$N	Au	0.548	0.532	0.528	0.545	0.565
	C	0.08	0.121	0.126	0.131	0.534
	O(CO)	−0.08	−0.075	−0.076	−0.081	−0.267
	O(N$_2$O)	−0.278		−0.284	−0.287	−0.263
	N(a)	0.420		0.426	0.333	0.007
	N(b)	−0.143		−0.138	−0.109	−0.006
Cu/C$_2$N	Cu	0.622	0.576	0.576	0.623	0.688
	C	0.08	0.154	0.154	0.156	0.532
	O(CO)	−0.08	−0.101	−0.100	−0.133	−0.237
	O(N$_2$O)	−0.278		−0.290	−0.271	−0.257
	N(a)	0.420		0.422	0.235	−0.001
	N(b)	−0.143		−0.131	−0.098	0.002