Supplementary information

Experimental and Theoretical Insight into the Support-Dependent N_2 Selectivity of CuO-based NH_3-SCO Catalysts

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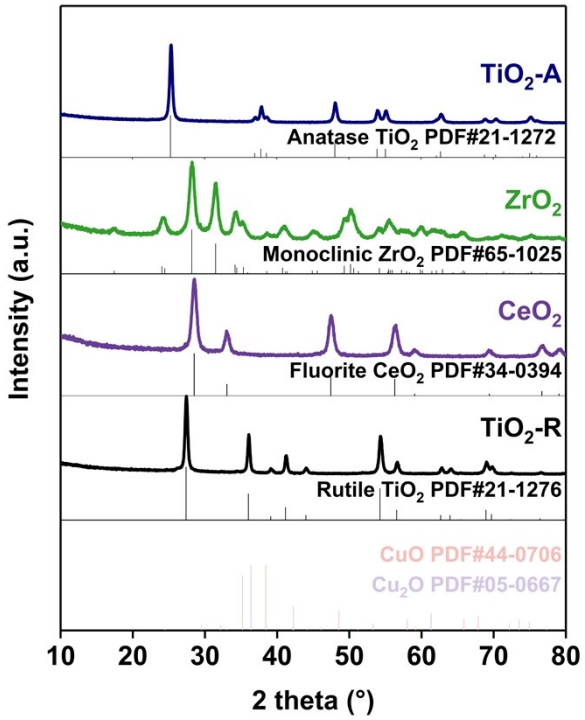


Figure S1. XRD patterns of the supports.

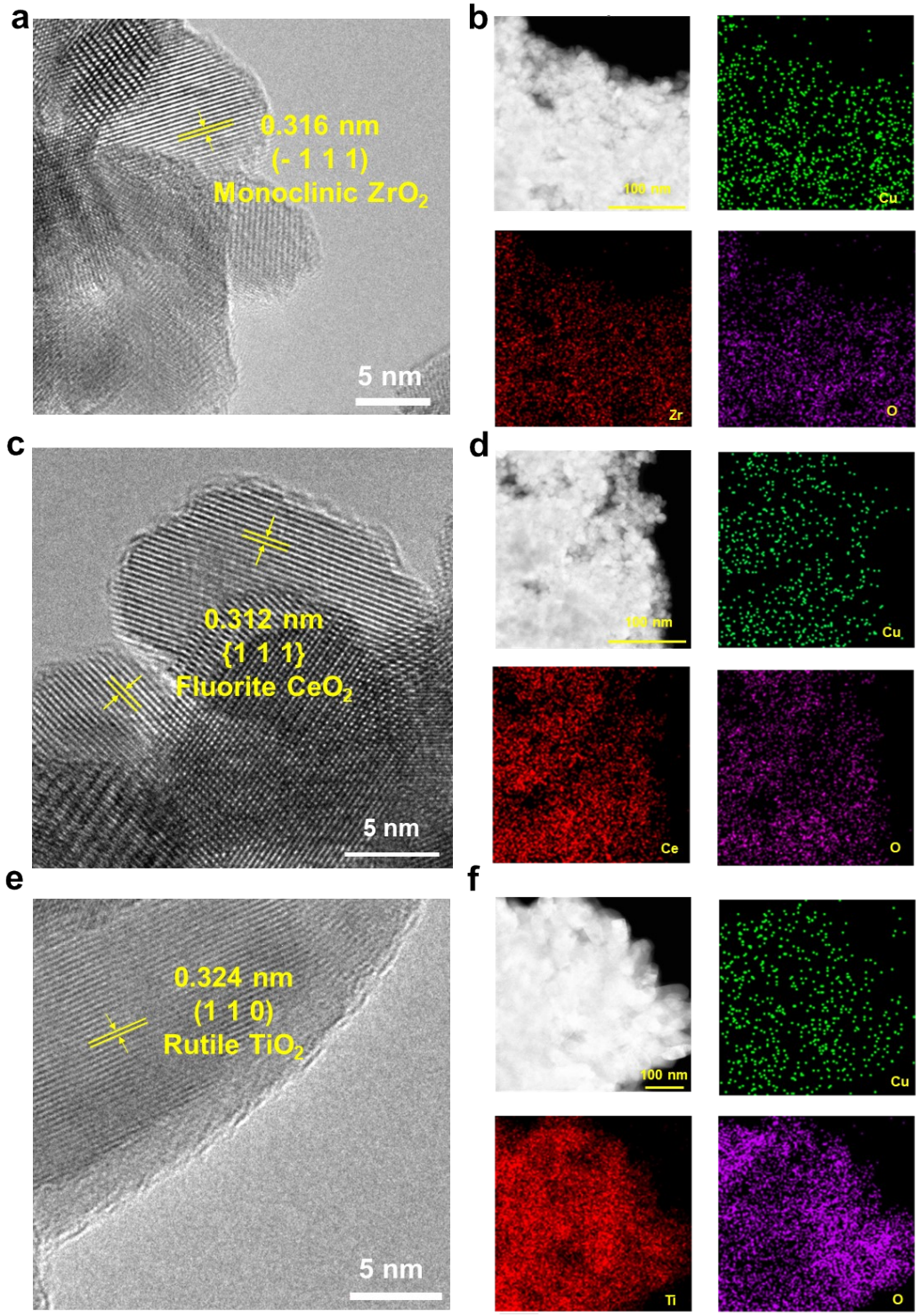


Figure S2. (a, c, e) HRTEM image of CuO/ZrO_2, CuO/CeO_2 and CuO/TiO_2-R. (b, d, f) EDS mapping of CuO/ZrO_2, CuO/CeO_2 and CuO/TiO_2-R.

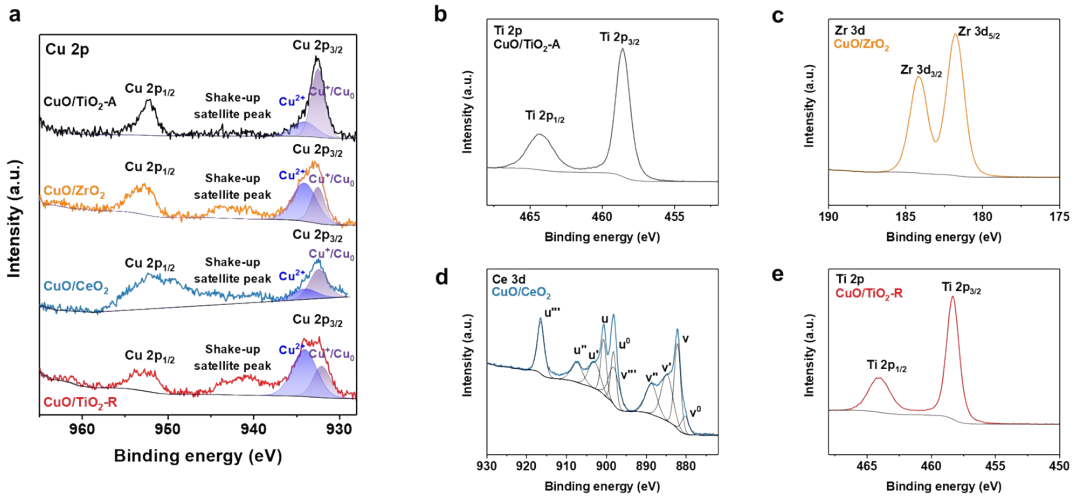


Figure S3. XPS results. (a) Cu 2p spectrum. (b) Ti 2p spectrum of CuO/TiO_2-A. (c) Zr 3d spectrum of CuO/ZrO_2. (d) Ce 3d spectrum of CuO/CeO_2. (e) Ti 2p spectrum of CuO/TiO_2-R.

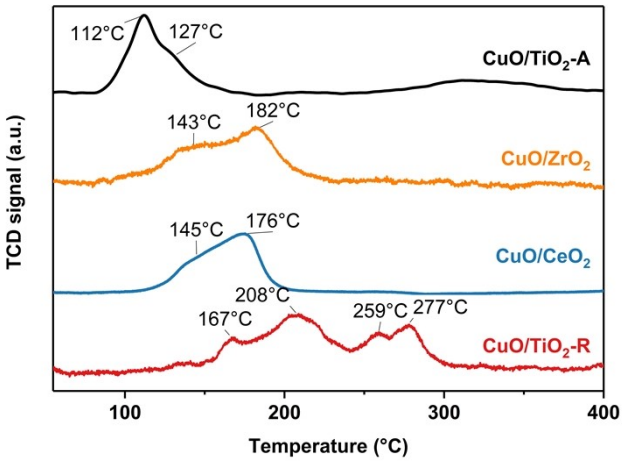


Figure S4. H_2-TPR results of the catalysts.

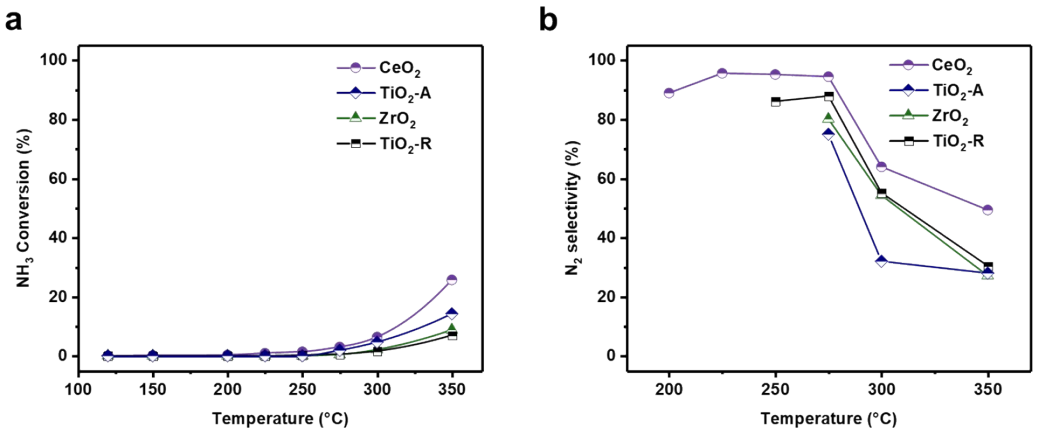


Figure S5. Catalytic performance evaluation of the metal oxide supports. (a) NH_3 conversion. (b) N_2 selectivity. Reaction conditions: 500 ppm NH_3, 5 vol% O_2, Ar as balance gas, total flow rate = 200 sccm, GHSV = 60000 $cm^3\ g_{cat}^{-1}\ h^{-1}$.

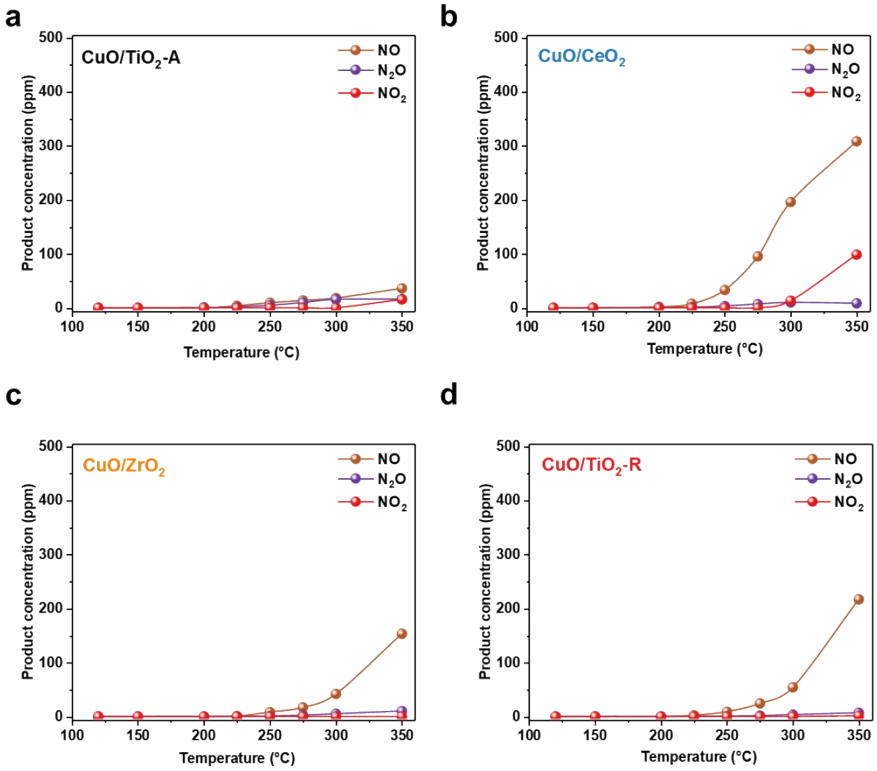


Figure S6. Byproduct analysis of different catalysts.

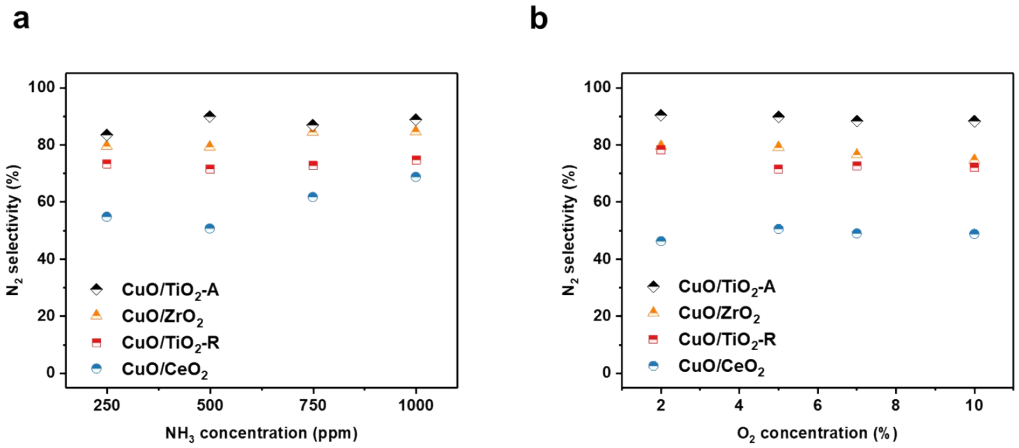


Figure S7 Influence of reactant concentration on the N_2 selectivity at 250°C.

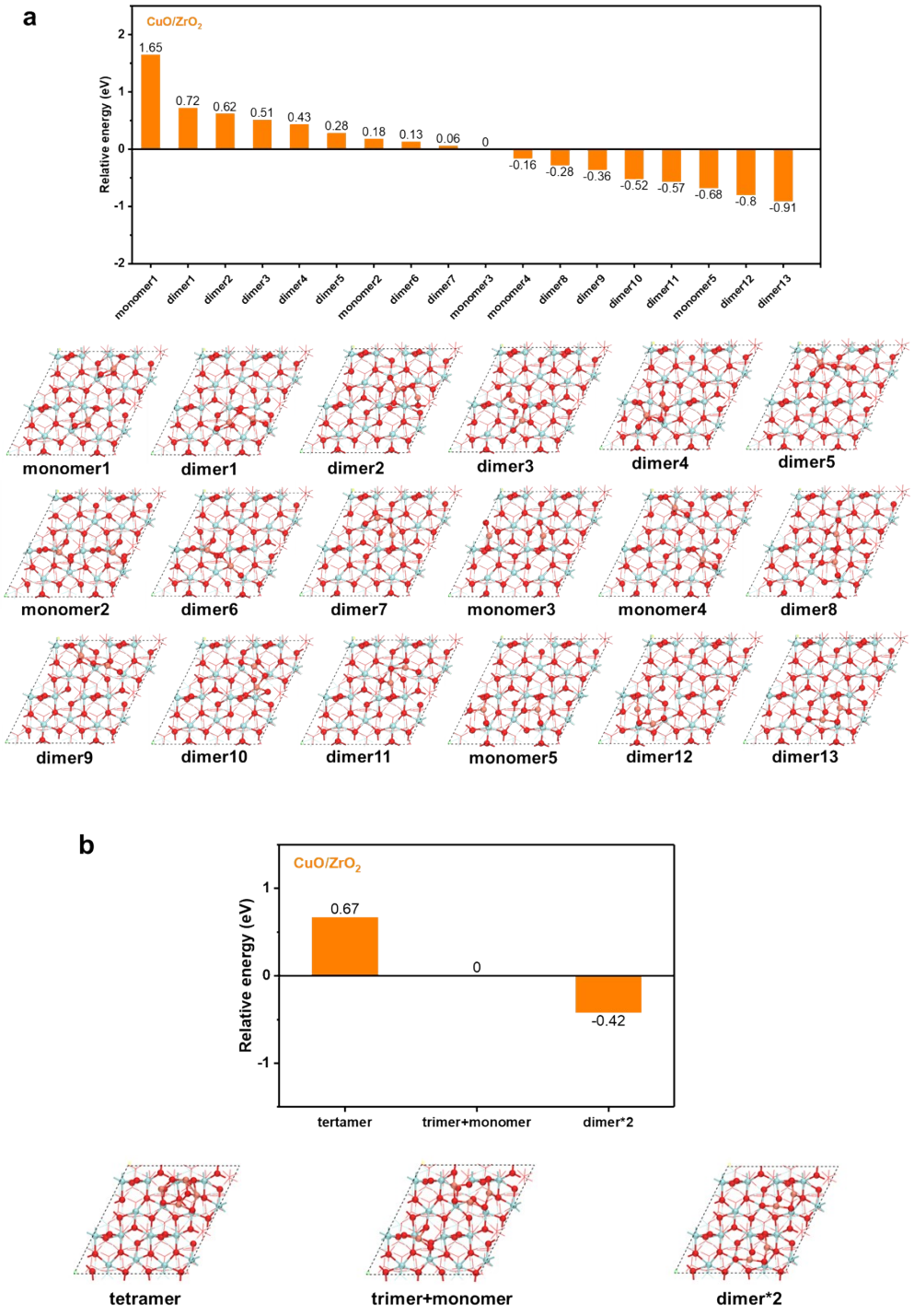


Figure S8. Energy comparison of different configurations of CuO/ZrO_2 at different surface Cu density. (a) 2 CuO in each periodic cell. (b) 4 CuO in each periodic cell. Red, orange and green balls represent O, Cu, and Zr respectively.

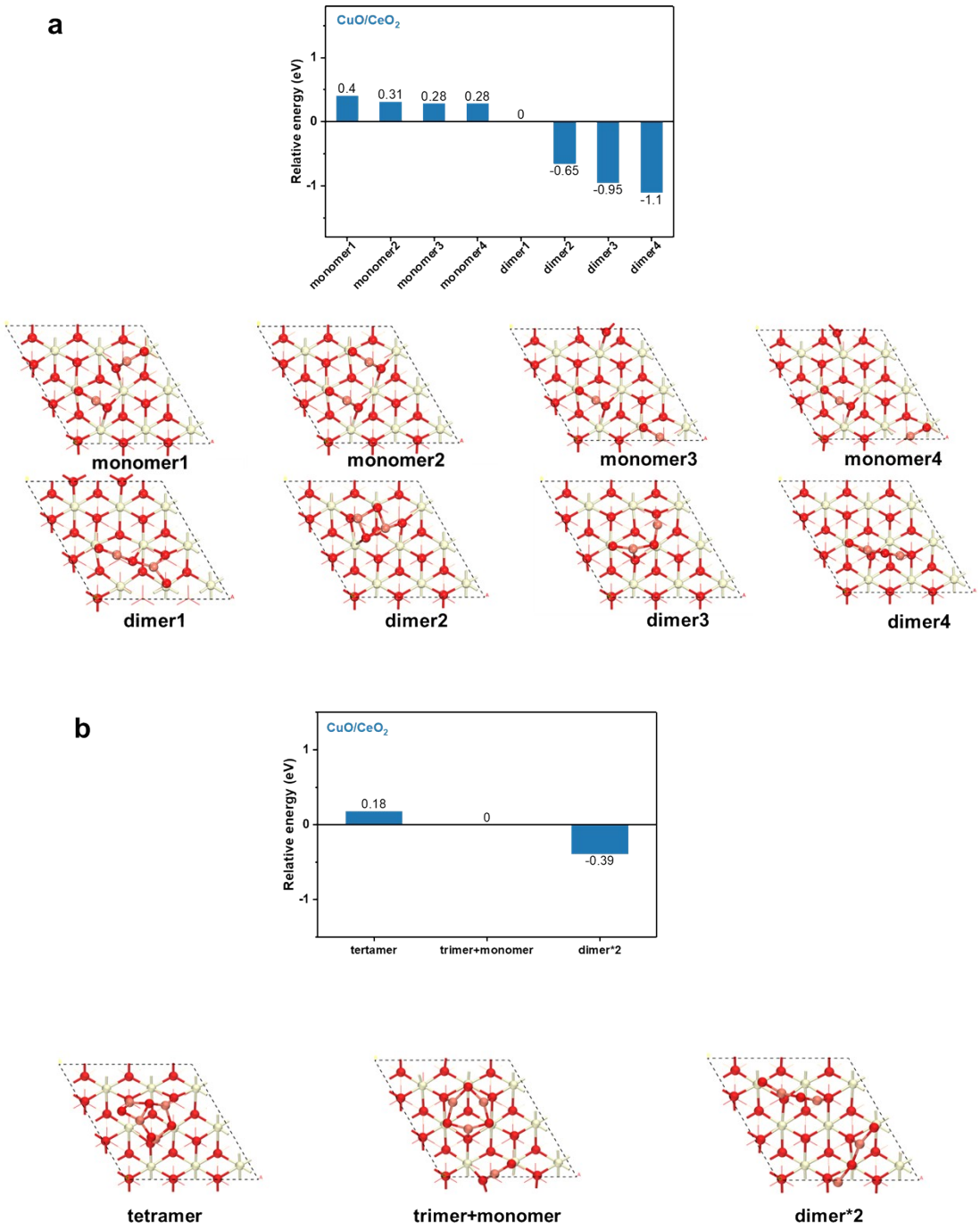


Figure S9. Energy comparison of different configurations of CuO/CeO_2 at different surface Cu density. (a) 2 CuO in each periodic cell. (b) 4 CuO in each periodic cell. Red, orange and yellow balls represent O, Cu and Ce respectively.

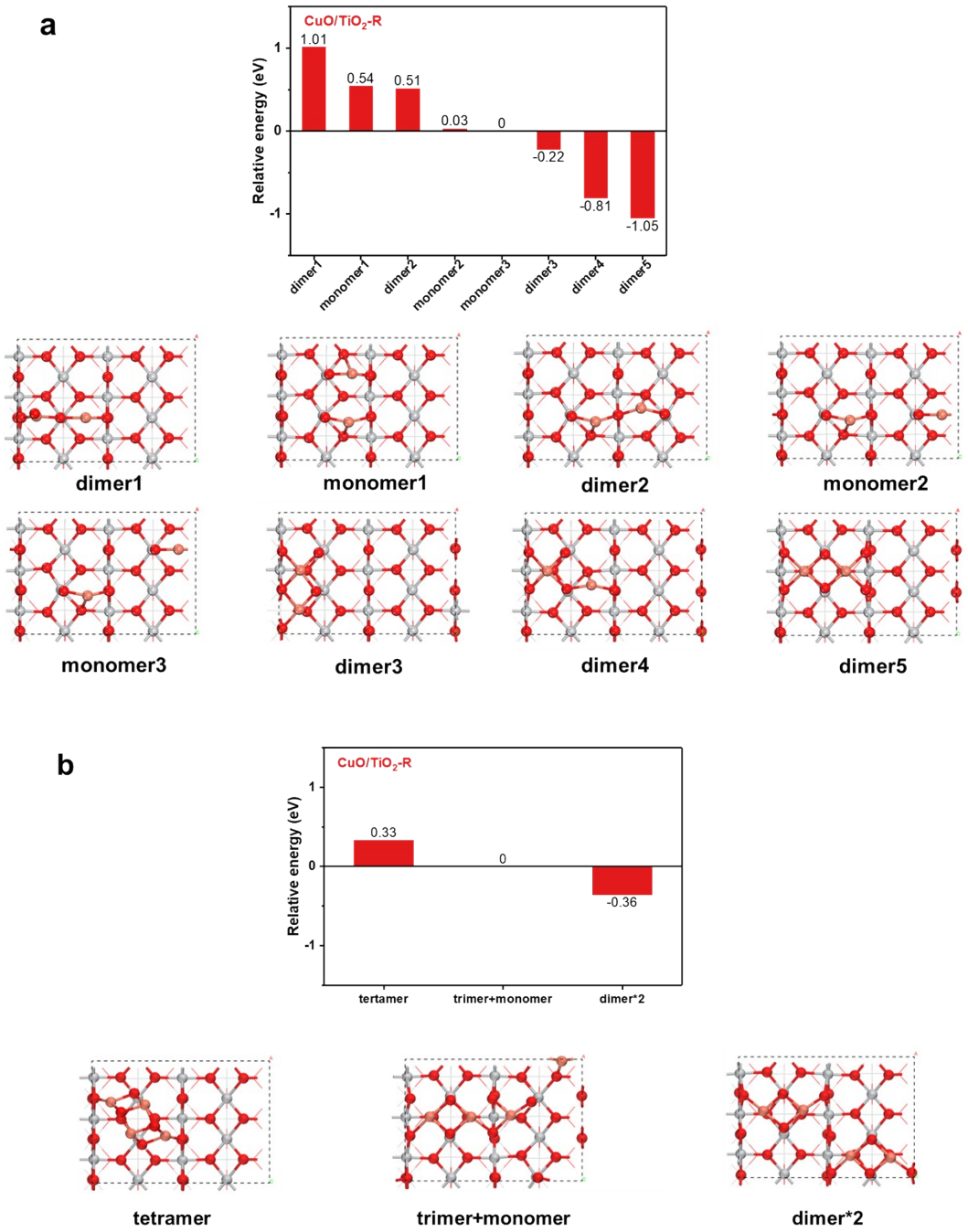


Figure S10. Energy comparison of different configurations of CuO/TiO_2-R at different surface Cu density. (a) 2 CuO in each periodic cell. (b) 4 CuO in each periodic cell. Red, orange and gray balls represent O, Cu and Ti respectively.

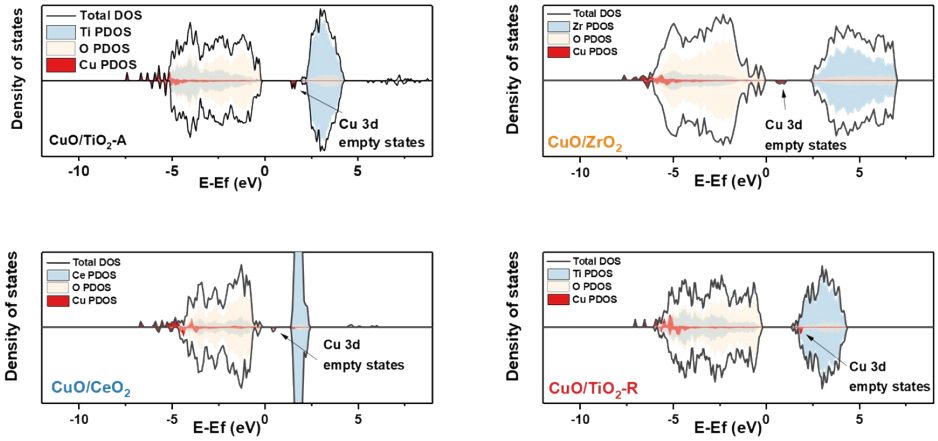


Figure S11. Projected density of states results of CuO/TiO_2-A, CuO/ZrO_2, CuO/CeO_2 and CuO/TiO_2-R theoretical models.

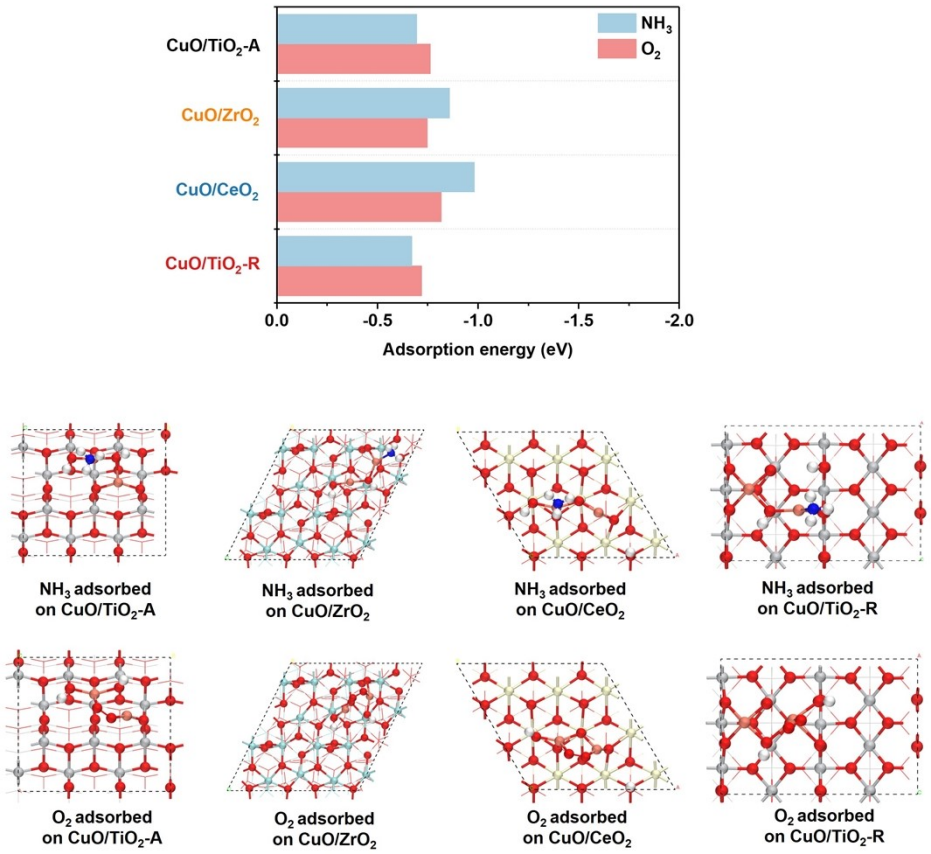


Figure S12. Energy of NH_3 and O_2 adsorption on catalysts during NH_3-SCO. Red, orange, blue, white, gray, green and yellow balls represent O, Cu, N, H, Ti, Zr and Ce respectively.

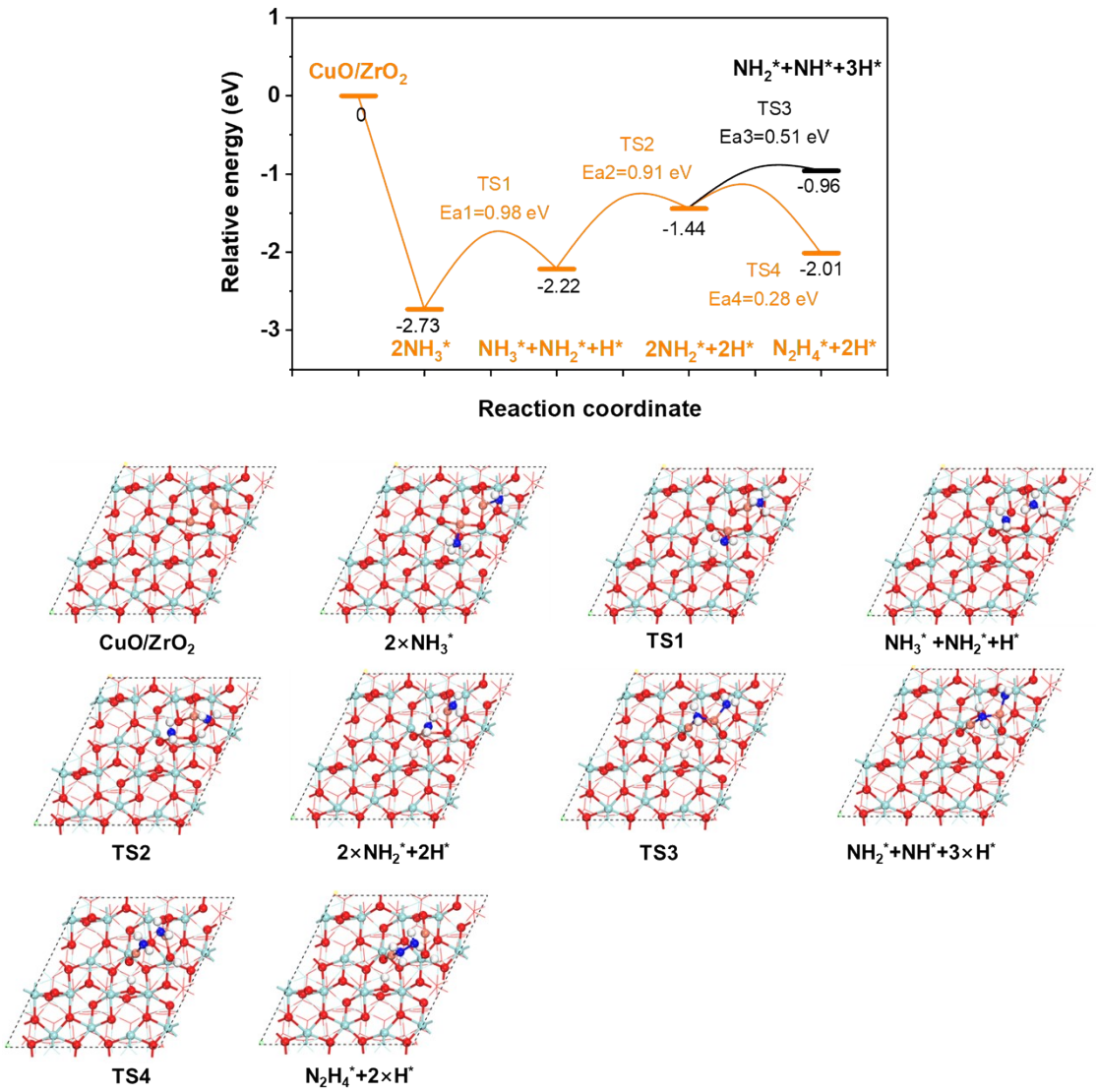
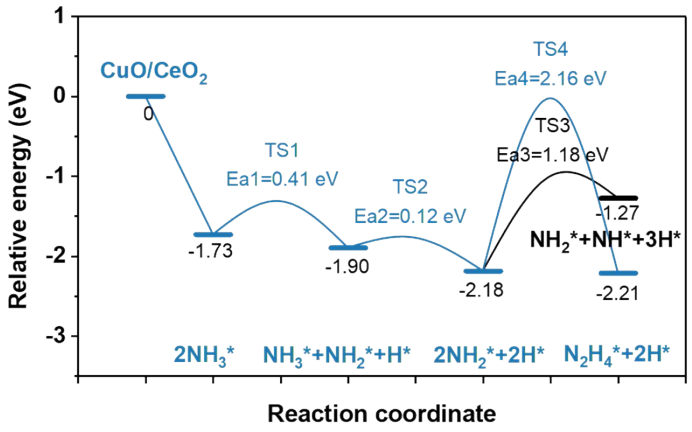


Figure S13. Energy diagram and optimized structures of all the intermediates and transition states for NH_3 transformation to N_2H_4* or NH* over CuO/ZrO_2 in this manuscript. Red, orange, blue, white and green balls represent O, Cu, N, H, and Zr respectively.



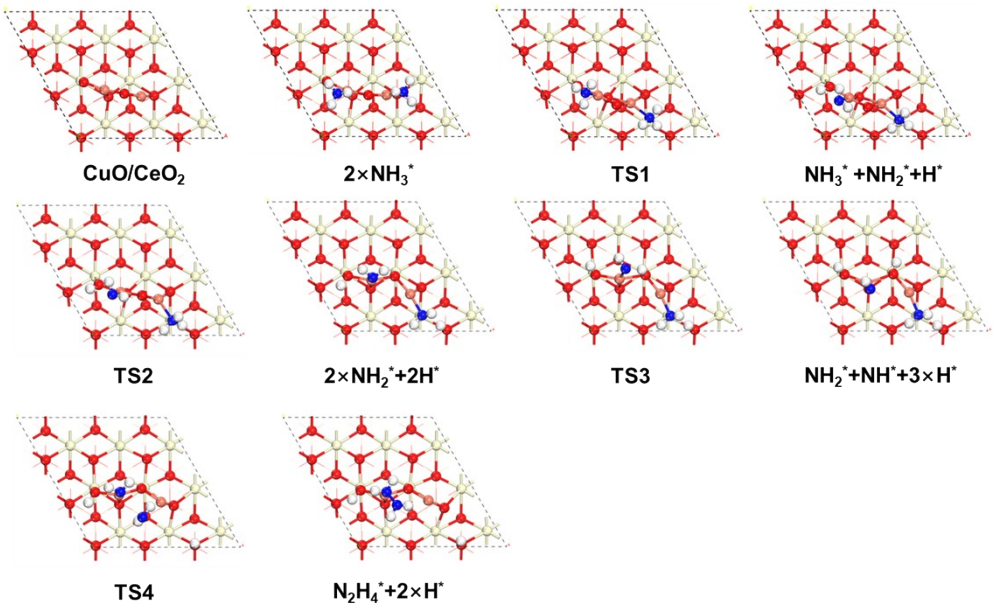


Figure S14. Energy diagram and optimized structures of all the intermediates and transition states for NH_3 transformation to N_2H_4* or NH* over CuO/CeO_2 in this manuscript. Red, orange, blue, white and yellow balls represent O, Cu, N, H, and Ce respectively.

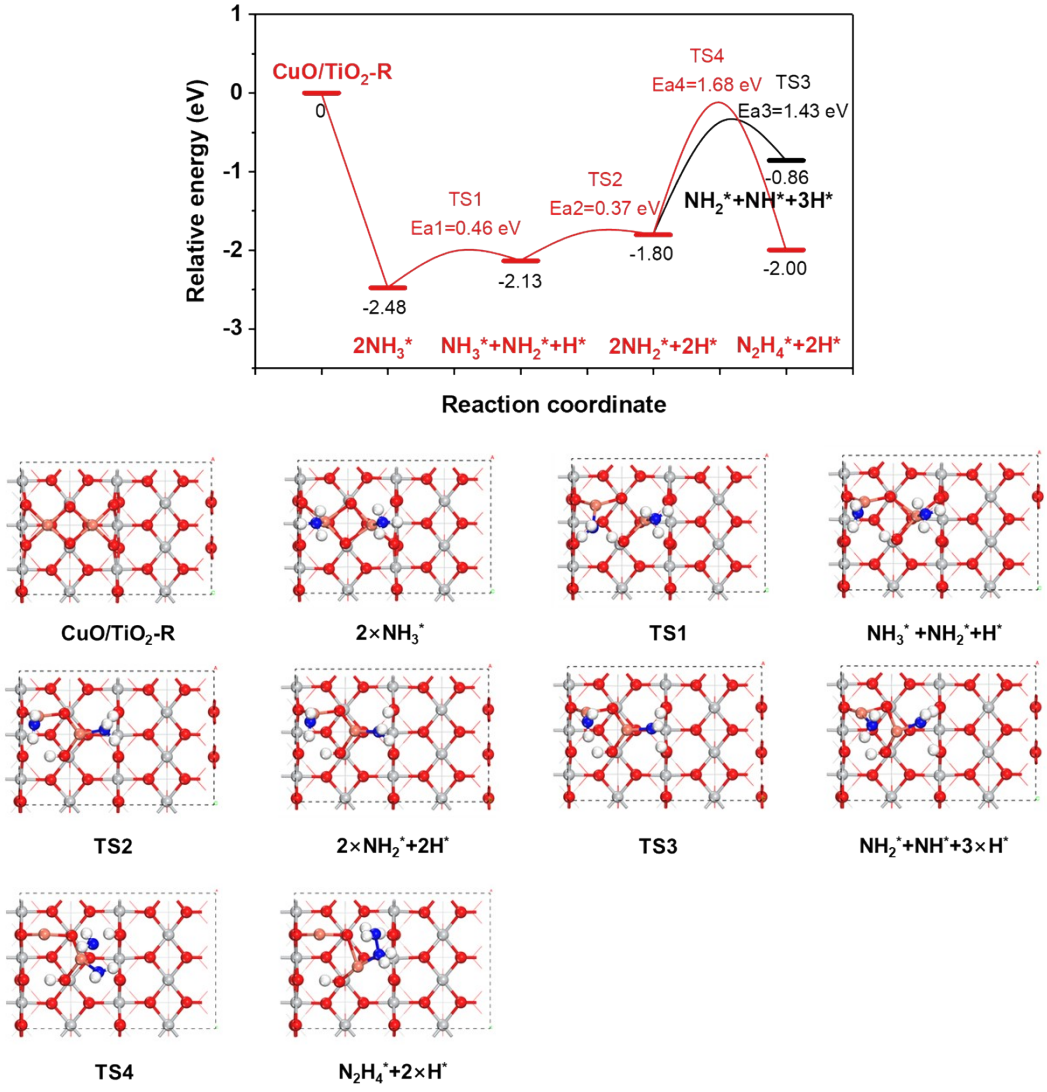


Figure S15. Energy diagram and optimized structures of all the intermediates and transition states for NH_3 transformation to N_2H_4* or NH* over CuO/TiO_2-R in this manuscript. Red, orange, blue, white and gray balls represent O, Cu, N, H, and Ti respectively.

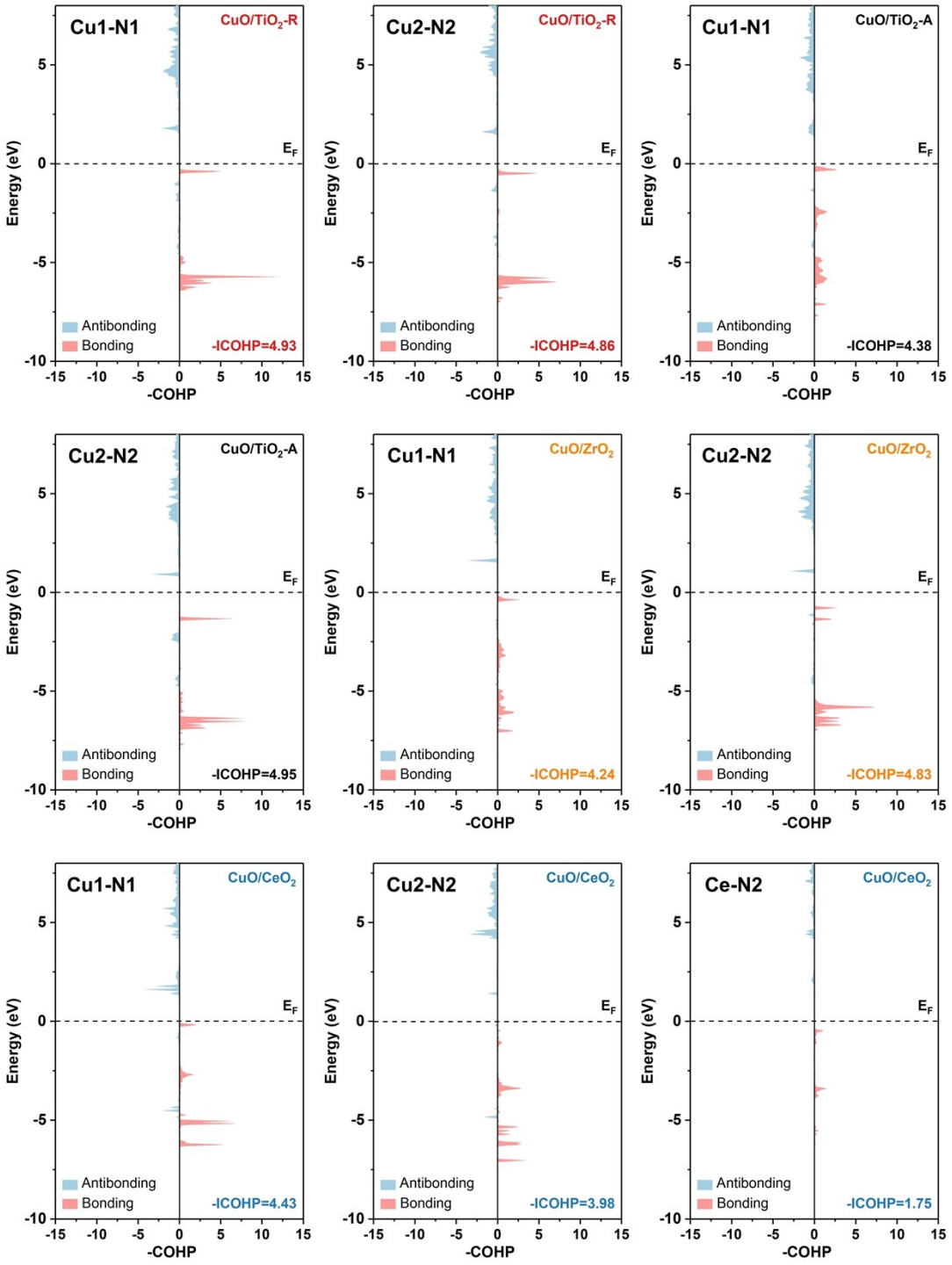


Figure S16. Crystal orbital Hamilton population analysis of N-Cu and N-Ce bonds in $2NH_2$*+2H* intermediate states of different catalysts.

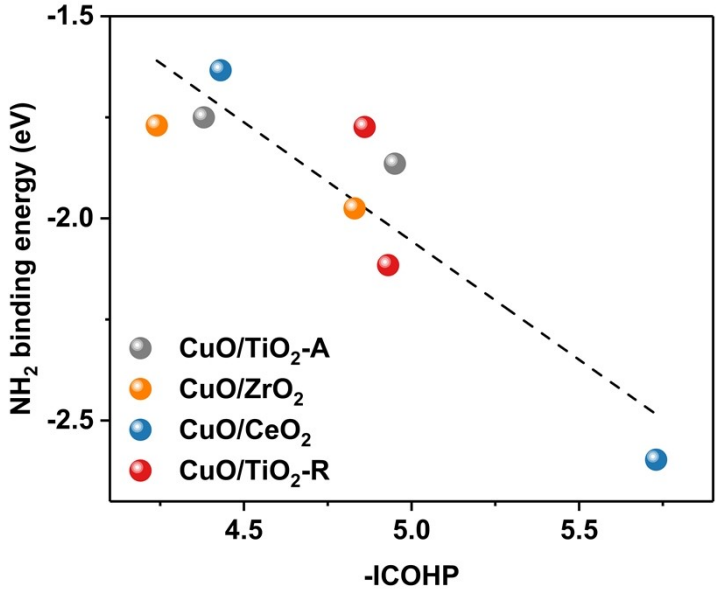


Figure S17. Relations between -ICOHP of catalyst-N and NH_2 binding energy.

Table S1 Cu mass ratio obtained by ICP-OES.

Sample	Cu(wt%)
CuO/TiO_2-A	0.91
CuO/ZrO_2	0.85
CuO/CeO_2	0.89
CuO/TiO_2-R	0.83

Table S2 BET surface area, pore diameter and pore value of the catalysts and supports evaluated by N_2 adsorption.

Sample	BET specific surface area ($m^2\ g^{-1}$)	Pore diameter (nm)	Pore volume ($cm^3\ g^{-1}$)
CuO/TiO_2-A	60	12.22	0.19
CuO/ZrO_2	65	13.96	0.22
CuO/CeO_2	70	5.76	0.10
CuO/TiO_2-R	26	23.18	0.14
TiO_2-A	87	9.72	0.23
ZrO_2	78	12.44	0.23
CeO_2	70	5.72	0.10
TiO_2-R	27	25.63	0.13

Table S3 Surface Cu density of the catalysts

Sample	Surface Cu density in experiment [a] (Cu nm^2)	Surface Cu density in computation [b] (Cu nm^2)
CuO/TiO_2-A	1.44	1.67
CuO/ZrO_2	1.24	1.22
CuO/CeO_2	1.12	1.75
CuO/TiO_2-R	3.02	1.67

[a] Obtained combining ICP-OES result and BET surface area.

[b] Obtained by calculating the Cu density in each periodic cell of theoretical model.

Table S4. Reaction energy (eV) and energy barriers (eV).

	CuO/TiO_2-A[a]		**CuO/ZrO_2**		**CuO/CeO_2**		**CuO/TiO_2-R**	
Reaction step	E	Ea	E	Ea	E	Ea	E	Ea
R1: $2NH_3$ (g)→$2NH_3$*	-2.40	\	-2.73	\	-1.73	\	-2.48	\
R2: $2NH_3$*→NH_3*+NH_2*+H*	-0.02	0.65	0.51	0.98	-0.17	0.41	0.35	0.46
R2': NH_3*+NH_2*+H*→$2NH_2$*+2H*	1.05	1.07	0.78	0.91	-0.28	0.12	0.33	0.37
R3: $2NH_2$*+2H*→NH_2*+NH*+3H*	1.75	2.66	0.48	0.51	0.91	1.18	0.94	1.43
R4: $2NH_2$*+2H*→N_2H_4*+2H*	-0.61	0.88	-0.57	0.28	-0.03	2.16	-0.20	1.68

[a] Details of energy diagram and intermediate structure of CuO/TiO_2-A could be found in our previous research.[1]

REFERENCES

1. M. C. Ran, Y. Dong, X. Zhang, W. X. Li, Z. Wang, S. S. Lin, Y. Yang, H. Song, W. H. Wu, S. J. Liu, Y. H. Zhu, C. H. Zheng and X. Gao, *Environ. Sci. Technol.*, 2024, **58**, 12249–12259.