

Supporting Information

Phosphate Modification Promotes Low-Temperature NH₃-SCO over Cu/CeO₂ through Coupled Regulation of Surface Acidity and Oxygen Species

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1. Characterization of catalysts

X-ray diffraction (XRD): The phase composition and crystal structure of the catalysts were characterized using an Empyrean X-ray diffractometer (Malvern Panalytical, Netherlands) with Cu K α radiation ($\lambda = 0.15406$ nm). The tube voltage and current were 40 kV and 15 mA, respectively. The diffraction patterns were collected over the 2θ range of 20–80° at a scanning rate of 10 °/min.

X-ray photoelectron spectroscopy (XPS): The surface elemental composition and chemical states of Cu/CeO₂ and Acid-Cu/CeO₂ were analyzed by X-ray photoelectron spectroscopy using a Nexsa spectrometer (Thermo Scientific, USA) equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV). The spot size was 400 μ m. The valence states and surface coordination environment of the catalysts were evaluated based on peak fitting analysis. All binding energies were calibrated using the adventitious carbon C 1s peak at 284.9 eV as the internal reference.

Oxygen temperature-programmed desorption (O₂-TPD): O₂-TPD measurements were performed on an in situ reaction system coupled with a TPD/TDS ultra-high-vacuum thermal desorption mass spectrometer (Hiden, UK). Typically, 0.1 g of catalyst was pretreated in high-purity He at 200 °C for 1 h with a flow rate of 30 mL/min to remove surface impurities. After cooling to room temperature, the sample was saturated with O₂, followed by He purging to remove physically adsorbed oxygen. Once a stable baseline was obtained, the sample was heated to 900 °C at a ramping rate of 10 °C/min, and the oxygen desorption signal was continuously recorded.

Pyridine adsorption infrared spectroscopy (Py-IR): Pyridine adsorption infrared spectra were collected using a Nicolet iS50 FTIR spectrometer (Thermo Scientific, USA) equipped with an in situ transmission cell to identify and quantify Brønsted and Lewis acid sites. Prior to pyridine adsorption, the catalyst wafer was activated in vacuum at 400 °C for 2 h, then cooled to the desired adsorption temperature (50, 100, or 150 °C). Background spectra were recorded at each target temperature after stabilization for 30 min. Pyridine vapor was then introduced and allowed to adsorb for 30 min, followed by evacuation for 30 min to remove physically adsorbed pyridine, and

spectra were collected at the same temperature. The concentration of acid sites was calculated from the integrated areas of the characteristic bands after subtracting the background spectrum recorded at the corresponding temperature. Spectra were recorded in the range of 1400-1700 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans.

The Py-IR spectra were reprocessed using the same baseline-correction procedure for all samples. The Lewis and Brønsted acid-site concentrations were calculated from the baseline-corrected integrated peak areas of the characteristic pyridine adsorption bands. The same catalyst wafer mass and wafer diameter were used for CeO_2 , Cu/CeO_2 , and Acid-Cu/CeO_2 . Specifically, the catalyst wafer mass was 23 mg and the wafer radius was 0.65 cm for all samples. Therefore, the mass-area normalization factor (R^2/W) was identical among the three samples, allowing direct comparison of the calculated acid-site concentration after baseline correction.

The acid-site concentrations were calculated according to the following equations:

$$C_{\text{LAS}} = 1.42 \times A_{\text{LAS}} \times R^2/W$$

$$C_{\text{BAS}} = 1.88 \times A_{\text{BAS}} \times R^2/W$$

where C_{LAS} and C_{BAS} represent the concentrations of Lewis and Brønsted acid sites, respectively, in $\mu\text{mol g}^{-1}$; A_{LAS} and A_{BAS} are the integrated areas of the characteristic Lewis and Brønsted pyridine adsorption bands after baseline correction; R is the wafer radius in cm; and W is the catalyst wafer mass in mg.

Operando DRIFTS: Operando DRIFTS measurements were carried out on a VERTEX 70 FTIR spectrometer (Bruker, Germany) in diffuse reflectance mode to investigate the surface reaction process and intermediate evolution during $\text{NH}_3\text{-SCO}$. The spectra were recorded over the range of 800-4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. The CeO_2 , Cu/CeO_2 , and Acid-Cu/CeO_2 samples were placed in an in situ reaction chamber and pretreated in He ($\geq 99.999\%$) at 300 $^\circ\text{C}$ for 30 min to remove surface impurities. After cooling to the target temperature, the background spectrum was collected under He flow. Subsequently, the reaction gas containing 500 ppm NH_3 and 2 vol% O_2 balanced with He was introduced into the reaction chamber. The total gas flow rate was maintained at 50 mL min^{-1} , and the operando DRIFTS measurements were performed at atmospheric pressure. The spectra were collected at different

reaction temperatures to monitor the real-time adsorption, activation, and transformation of NH_3 -derived surface species under $\text{NH}_3 + \text{O}_2$ reaction conditions.

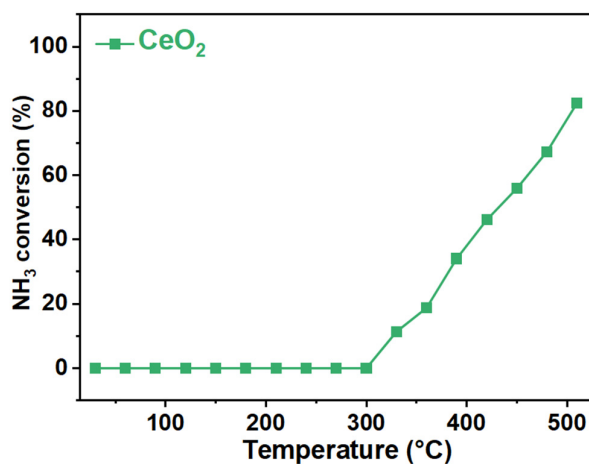


Figure S1. NH_3 conversion over CeO_2 catalyst as a function of temperature

Table S1. ICP-OES elemental analysis results of Cu/CeO_2 and Acid-Cu/CeO_2 catalysts.

Sample	Element	Replicate 1 (mg kg^{-1})	Replicate 2 (mg kg^{-1})	Average (mg kg^{-1})	Average content (wt%)
Cu/CeO_2	Cu	13227	14075	13651	1.37
Cu/CeO_2	Ce	745454	755946	750700	75.07
Acid- Cu/CeO_2	Cu	10095	12080	11088	1.11
Acid- Cu/CeO_2	Ce	771428	739095	755262	75.53

Table S2. Relative Ce^{3+} and Ce^{4+} contents calculated from the Ce 3d XPS spectra of Cu/CeO_2 and Acid-Cu/CeO_2 catalysts.

Samples	Ce^{3+}	Ce^{4+}	$\text{Ce}^{3+}/\text{Ce}^{4+}$
Cu/CeO_2	20.52 %	79.48 %	0.258
Acid- Cu/CeO_2	18.44 %	81.56 %	0.226

Table S3 Relative Cu¹⁺ and Cu²⁺ contents calculated from the Cu 2p XPS spectra of Cu/CeO₂ and Acid-Cu/CeO₂ catalysts.

Samples	Cu ⁺	Cu ²⁺
Cu/CeO ₂	33.73%	66.27 %
Acid-Cu/CeO ₂	49.82 %	50.18 %

Table S4. Relative contents of O_α, O_β, O_γ and O_{rela} obtained from the O 1s XPS fitting results of Cu/CeO₂ and Acid-Cu/CeO₂ catalysts.

Samples	O _α	O _β	O _γ	O _{rela}
Cu/CeO ₂	33.89%	55.56%	10.55%	66.11%
Acid-Cu/CeO ₂	55.25%	24.86%	19.89%	44.75%

Table S5. Surface elemental composition of Acid-Cu/CeO₂ estimated from XPS survey spectra.

Sample	C 1s (at.%)	Ce 3d (at.%)	Cu 2p (at.%)	O 1s (at.%)	P 2p (at.%)	Surface P:Cu atomic ratio
Acid-Cu/CeO ₂	18.9	13.63	4.91	58.81	3.75	0.76

Note: The XPS-derived values represent surface semi-quantitative elemental compositions. The C 1s signal is mainly attributed to adventitious carbon.

Table S6. Comparison of Ammonia Selective Catalytic Oxidation Performance of Different Catalysts

Catalyst	T ₉₀ or activity temperature	N ₂ selectivity	Reaction conditions	Ref.
Acid-Cu/CeO ₂	T ₉₀ =260 °C	>75%	500 ppm NH ₃ , 2 vol% O ₂ , WHSV = 30,000 mL gcat ⁻¹ h ⁻¹	This work
CuO/TiO ₂	T ₉₀ =270 °C	>80%	500 ppm NH ₃ , 5 vol% O ₂ , N ₂ balance, GHSV = 50,000 h ⁻¹ for activity;	[3]
CuO/CeO ₂ -NR	T ₉₀ =250 °C	90%	1000 ppm NH ₃ , 10 vol% O ₂ , GHSV = 40,000 h ⁻¹	[16]
Cu-Mg-Fe-O-(Ce)	>300 °C	/	NH ₃ -SCO over Cu-Mg-Fe-O-(Ce) mixed oxides	[26]
Cu/CeO ₂ -ZrO ₂ (IW)	T ₉₀ =260 °C	100%	1000 ppm NH ₃ , 10 vol% O ₂ , GHSV = 40,000 h ⁻¹	[38]
Cu-ATP	T ₉₀ =300 °C	100%	500 ppm NH ₃ , 5 vol% O ₂ , N ₂ balance, GHSV = 50,000-80,000 h ⁻¹	[42]
Cu/HAPOPS	T ₉₀ ≈350 °C	84%	NH ₃ /O ₂ = 0.03, N ₂ balance, GHSV = 120,000 h ⁻¹	[43]

Table S7. Quantitative acid site results of CeO₂, Cu/CeO₂ and Acid-Cu/CeO₂ catalysts measured by Py-IR at different desorption temperatures

Catalyst	Temperature (°C)	W (mg)	BAS area	LAS area	BAS concentration (μmol/g)	LAS concentration (μmol/g)	Total acid concentration (μmol/g)
CeO ₂	50	23	0.013	0.028	0.45	7.30	7.75
	100		0.006	0.13	0.21	3.39	3.60
	150		0.002	0.05	0.09	1.30	1.39
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Cu/CeO ₂	50	23	0.057	1.12	1.97	29.22	31.19
	100		0.034	0.64	1.17	16.70	17.87
	150		0.013	0.17	0.45	4.43	4.88
Acid-Cu/CeO ₂	50	23	0.086	1.34	2.97	34.95	37.92
	100		0.054	0.81	1.87	21.13	23.00
	150		0.029	0.33	1.00	8.61	9.61