

Appendix A. Supplementary data

Tuning degradation activity and pathways of chlorinated organic pollutants over CeO₂ catalyst with acid sites: Synergistic effect of Lewis and Brønsted acid sites

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1. Procedures of Characterization

1.1 NH₃ temperature programmed desorption (NH₃-TPD)

The strength and number of surface acid sites of samples were measured by using temperature programmed desorption of ammonia (NH₃-TPD). Prior to the NH₃-TPD analysis, about 100 mg amount of sample was first pre-treated at 550 °C for 1 h under 5 vol.% O₂/He flow (30 mL/min), cooled to 50 °C, and swept by He for another 2 h. And subsequently, the sample was treated by the 5 vol.% NH₃/He (30 mL/min) for 30 min. After sweeping with He flow (30 mL/min), the sample was heated from 50 to 600 °C with a heating rate of 10 °C/min under He flow (30 mL/min), and the TCD signal was simultaneously recorded.

1.2 O₂ temperature programmed desorption (O₂-TPD)

Before testing, about 50 mg sample were pretreated at 550 °C for 1 h with 30 mL/min 5 vol.% O₂/He, followed by cooling to 50 °C. The O₂-TPD profile was obtained during the temperature increase from 50 to 800 °C with a rate of 10 °C/min under He atmosphere (30 mL/min).

1.3 H₂ temperature programmed reduction (H₂-TPR)

The pretreatment of 50 mg sample was carried out by using 5 vol.% O₂/He gas flow of 30 mL/min at 550 °C for 1 h. After cooling down to 50 °C, the H₂-TPR profile was obtained under 5 vol.% H₂/Ar flow (30 mL/min) during the temperature rise from 50 to 800 °C with a rate of 10 °C/min. H₂ consumption was estimated according to the calibration of reduction peak area against a work curve obtained from the standard CuO sample.

1.4 In situ DRIFTS of pyridine adsorption (pyridine-DRIFTS)

Prior to the pyridine-DRIFTS test, sample was pre-treated at 300 °C with He (30 mL/min) for 1 h, and then cooled to 120 °C to record the backgrounds. The pyridine vapor (30 mL/min) was then introduced to the IR cell for 10 min at 120 °C, after being purged for 30 min with He flow (30 mL/min), the spectra of adsorbed pyridine were collected.

1.5 In situ DRIFTS of NH₃ adsorption (NH₃-DRIFTS)

For the NH₃-DRIFTS test, the operation was taken similar with pyridine-DRIFTS. The pyridine vapor was substituted with the 5 vol.% NH₃/He (30 mL/min), and the spectral collection temperature was change to 100 °C.

1.6 In situ DRIFTS of chlorobenzene oxidation

The oxidation intermediates of chlorobenzene (CB) on the catalyst surface were detected by the *in situ* DRIFTS analysis. Firstly, the sample was purged at 300 °C for 1h with 20 vol.% O₂/He flow (30 mL/min) and then cooled to 50 °C. Subsequently, the sample was exposed to 1000 ppm CB/He feed to saturation. After sweeping for 30 min with He flow (30 mL/min), the backgrounds were record. And then the temperature was raised step by step to each predetermined value (200, 250, 300, 350, 400, and 420 °C) and maintained for 10 min to ensure the spectra did not change. Finally, the stable CB oxidation spectra at each temperature were obtained.

1.7 The characterization of used samples

All temperature-programmed desorption and reaction measurements and NH₃-DRIFTS tests of used samples are similar to the fresh samples. To ensure the obtained

data can accurately reflect the influence of reaction conditions, all used samples were not pretreated prior to testing.

2. Figures and Tables

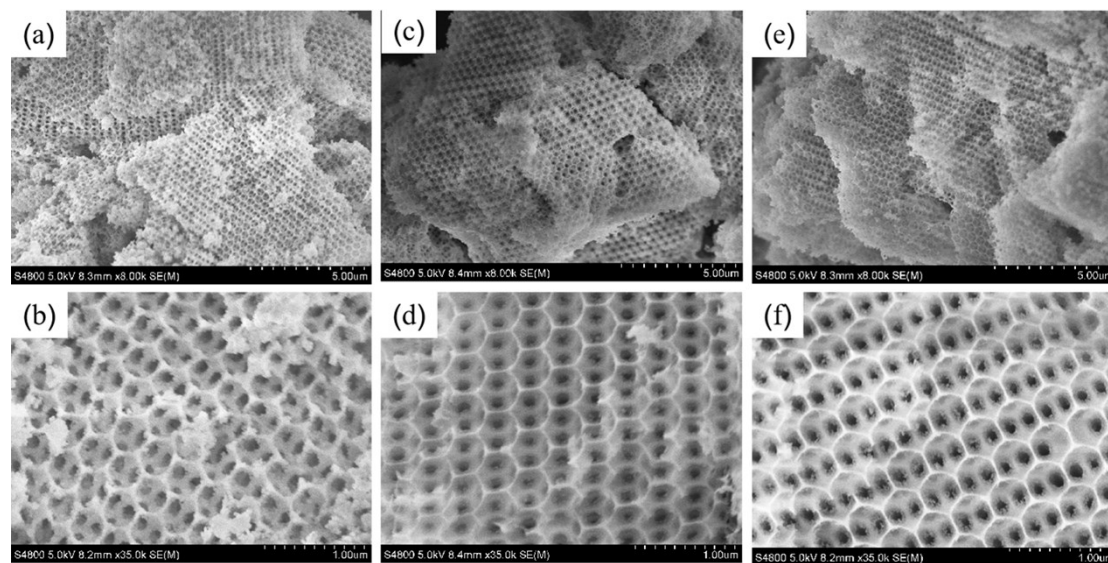


Fig. S1 SEM images of used (a, b) CeO₂, (c, d) Ce_{0.7}Zr_{0.3}O₂, and (e, f) S-Ce_{0.7}Zr_{0.3}O₂ samples.

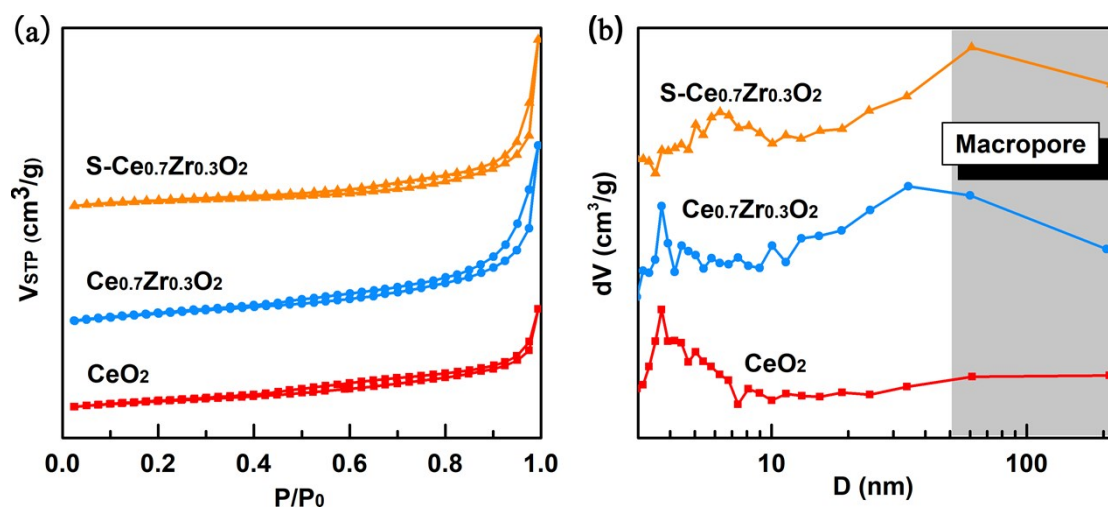


Fig. S2 N₂ static physisorption of three samples (a) isotherm curves, (b) pore size distribution.

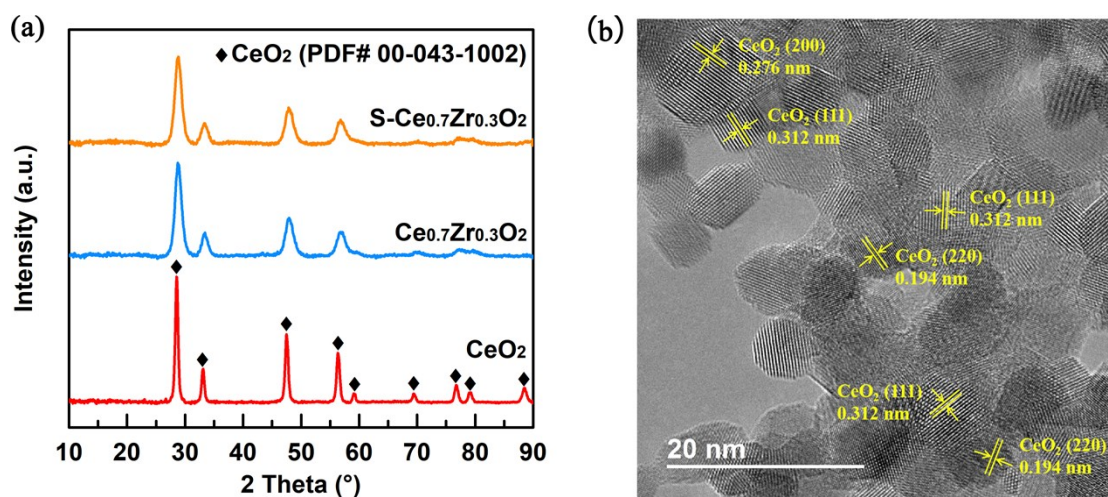


Fig. S3 (a) XRD patterns of used samples and HRTEM image of used S-Ce_{0.7}Zr_{0.3}O₂ sample.

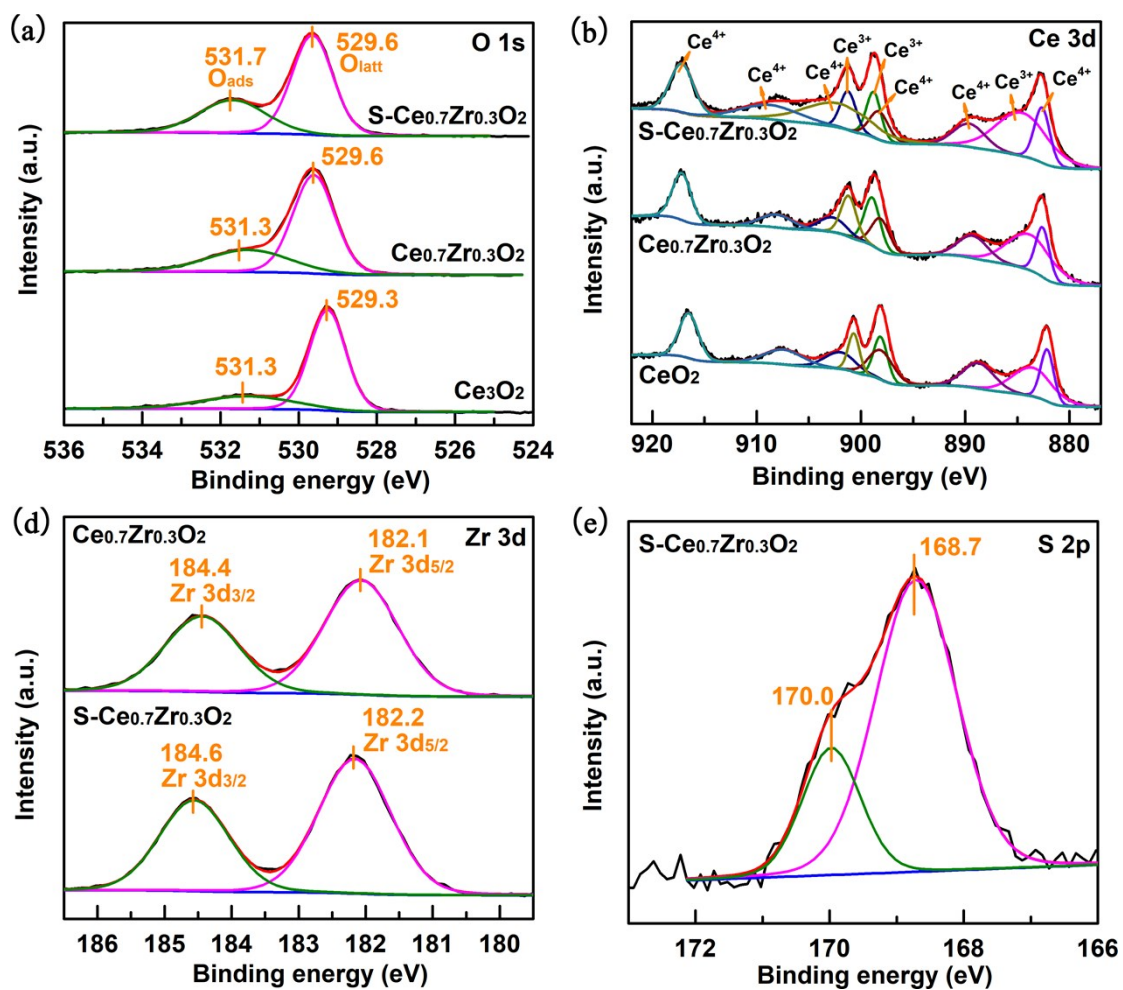


Fig. S4 (a) O 1s XPS spectra and (b) Ce 3d XPS spectra of used CeO₂, Ce_{0.7}Zr_{0.3}O₂, and S-Ce_{0.7}Zr_{0.3}O₂; (c) Zr 3d XPS spectra of used Ce_{0.7}Zr_{0.3}O₂, and S-Ce_{0.7}Zr_{0.3}O₂; and (d) S 2p XPS spectra of used S-Ce_{0.7}Zr_{0.3}O₂.

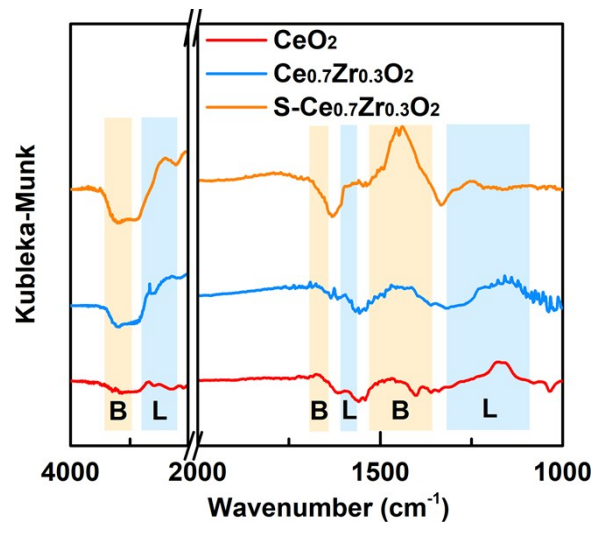


Fig. S5 NH₃-DRIFTS spectra of used samples.

Table S1 Acid elements (S, P, W, or Mo) content of M-Ce_{0.7}Zr_{0.3}O₂ samples

Sample	S-Ce _{0.7} Zr _{0.3} O ₂	P-Ce _{0.7} Zr _{0.3} O ₂	W-Ce _{0.7} Zr _{0.3} O ₂	Mo-Ce _{0.7} Zr _{0.3} O ₂
Acid element content (wt.%)	1.00	0.97	1.16	1.13

These values were determined by XRF.

Table S2 Summary of physicochemical characteristics of used samples

Catalysis	XPS		A_B^a/A_L^b
	$O_{\text{latt}}/O_{\text{ads}}$	Ce^{4+}/Ce^{3+}	NH ₃ -DRIFTS
CeO ₂	1.86	1.79	1.06
Ce _{0.7} Zr _{0.3} O ₂	2.26	1.38	0.66
S-Ce _{0.7} Zr _{0.3} O ₂	3.10	1.63	1.57

^a A_B was the total area of the peaks corresponding to the Brønsted acid in the spectra of NH₃-DRIFTS;

^b A_L was the total area of the peaks corresponding to the Lewis acid in the spectra of NH₃-DRIFTS.