Supporting Information

Effect of Oxygen Storage Materials on the Performance of Pt-based Three-Way Catalysts

Gang Wang,[†] Yuan Jing,[†] Kah Wei Ting,[†] Zen Maeno,[†] Xiaorui Zhang,[§] Shuhei Nagaoka,*[§] Ken-ichi Shimizu[†,‡], and Takashi Toyao*[†,‡]

[†] Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan

[§] Johnson Matthey Japan G.K., 5123-3, Kitsuregawa, Sakura, Tochigi 329-1412, Japan

[‡] Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Katsura, Kyoto 615-8520, Japan

*Corresponding authors:

Takashi Toyao and Shuhei Nagaoka

E-mail: toyao@cat.hokudai.ac.jp; Shuhei.Nagaoka@mattheyasia.com

Supplementary Results

Table S1. Composition of the simulated exhaust gas mixtures for light-off tests.

λ	CO /%	C_3H_6 /ppm	H_2 /%	NO /ppm	O_2 /%	CO_2 /%	H_2O /%	N_2
0.95	2.40	420	0.80	1000	0.60	15	10	balance
1.00	0.60	420	0.20	1000	0.60	15	10	balance
1.05	0.60	420	0.20	1000	1.65	15	10	balance

Table S2. Composition of the simulated exhaust gas mixtures for λ sweep tests.

λ	CO /%	C_3H_6 /ppm	H_2 /%	NO /ppm	O_2 /%	CO_2 /%	H_2O /%	N_2
0.95	2.11	420	0.70	500	0.50	14	10	balance
0.96	1.76	420	0.59	500	0.50	14	10	balance
0.97	1.40	420	0.49	500	0.50	14	10	balance
0.98	1.07	420	0.38	500	0.50	14	10	balance
0.99	0.78	420	0.28	500	0.50	14	10	balance
1.00	0.50	420	0.17	500	0.50	14	10	balance
1.01	0.50	420	0.17	500	0.72	14	10	balance
1.02	0.50	420	0.17	500	0.92	14	10	balance
1.03	0.50	420	0.17	500	1.10	14	10	balance
1.04	0.50	420	0.17	500	1.30	14	10	balance
1.05	0.50	420	0.17	500	1.54	14	10	balance

Table S3. Composition of the simulated exhaust gas mixtures for λ switching tests.

λ	CO /%	C_3H_6 /ppm	H_2 /%	NO /ppm	O_2 /%	CO_2 /%	H_2O /%	N_2
0.95	2.40	420	0.80	1000	0.60	15	10	balance
1.05	0.60	420	0.20	1000	1.65	15	10	balance

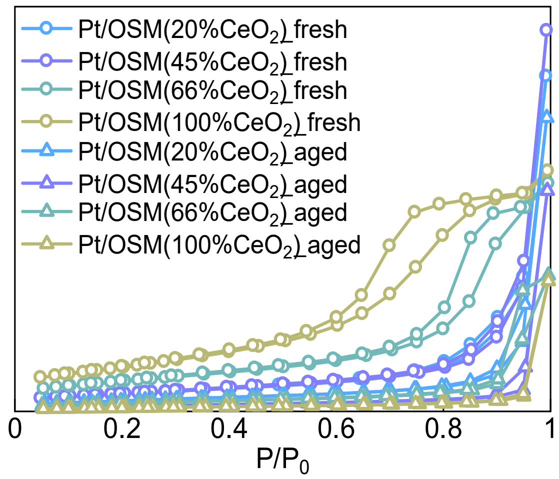

Figure S1. Isothermal N_2 adsorption and desorption curves of fresh and aged Pt/OSMs having different ceria content.

Table S4. Textual properties of Pt/OSMs having different ceria content.

Catalyst	S_{BET}[a] /m^2 g^{-1}	Pt particle size[b] /nm	Pt particle size[c] /nm
Pt/OSM(20%CeO_2)_fresh	58	4.0	3.0
Pt/OSM(45%CeO_2)_fresh	57	3.9	2.8
Pt/OSM(66%CeO_2)_fresh	99	3.2	2.2
Pt/OSM(100%CeO_2)_fresh	146	2.3	2.1
Pt/OSM(20%CeO_2)_aged	36	-	8.9
Pt/OSM(45%CeO_2)_aged	18	-	9.0
Pt/OSM(66%CeO_2)_aged	27	-	8.7
Pt/OSM(100%CeO_2)_aged	12	-	9.2

[a] Determined by N_2 adsorption, [b] Estimated by CO adsorption at -70 °C, [c] Estimated by HAADF-STEM

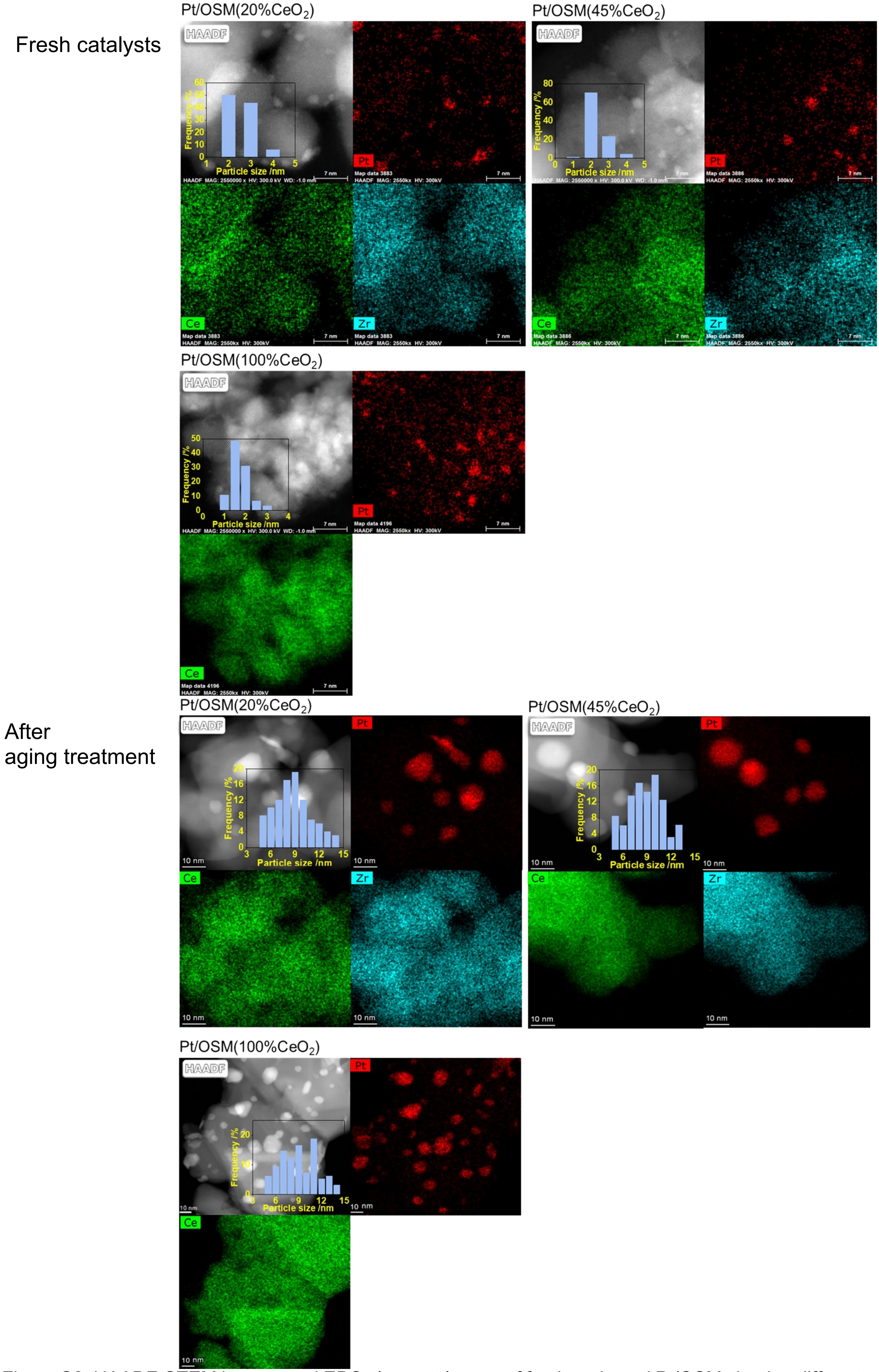

Figure S2. HAADF-STEM images and EDS elemental maps of fresh and aged Pt/OSMs having different ceria content.

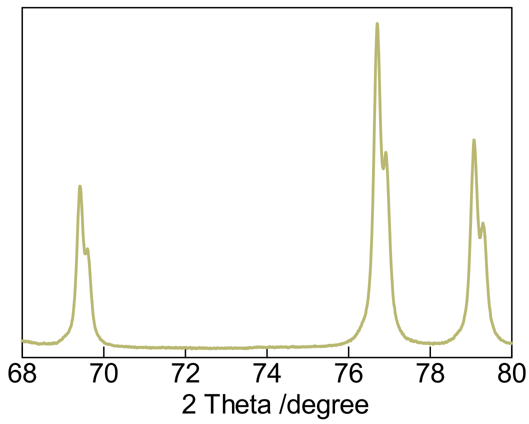

Figure S3. Close-up of XRD pattern of aged Pt/OSM(100%CeO_2) for the peak splitting.

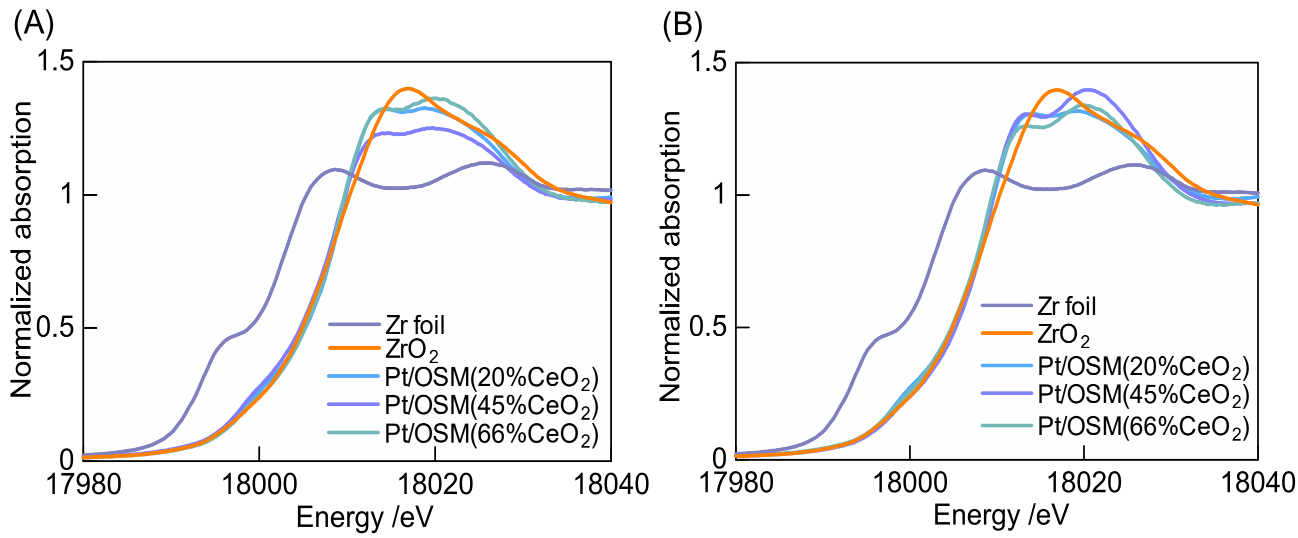

Figure S4. Zr K-edge XANES spectra of (A) fresh and (B) aged Pt/OSMs (27.1 mg for Pt/OSM(20%CeO_2), 44.7 mg for Pt/OSM(45%CeO_2), and 82.0 mg for Pt/OSM(66%CeO_2)) having different ceria content.

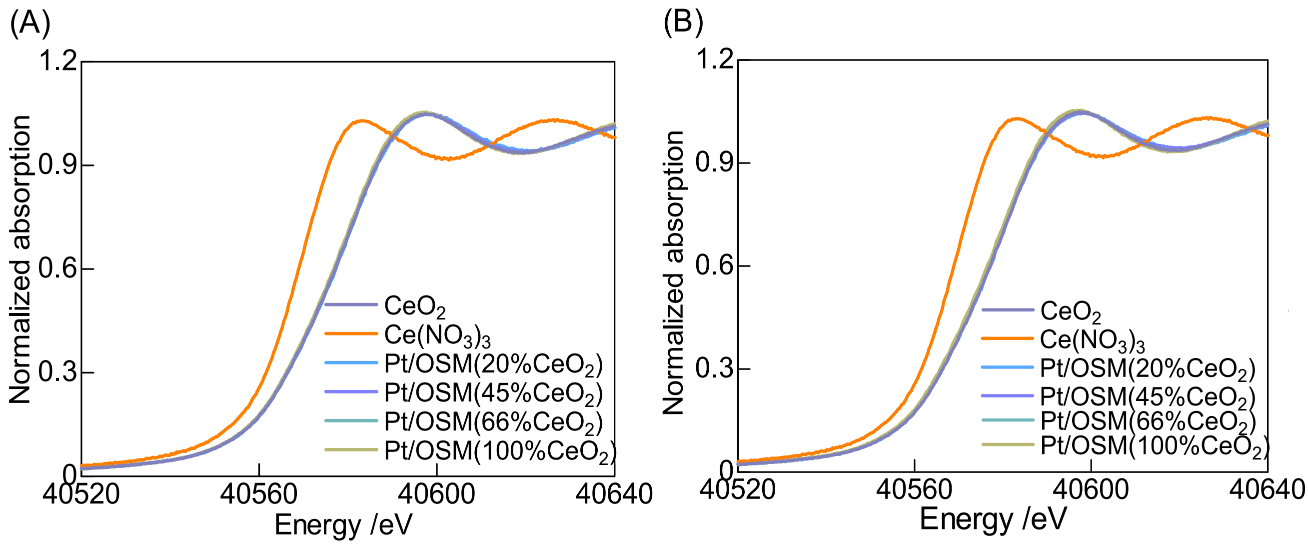

Figure S5. Ce K-edge XANES spectra of (A) fresh and (B) aged Pt/OSMs (110 mg for Pt/OSM(20%CeO_2), 47.0 mg for Pt/OSM(45%CeO_2), 33.0 mg for Pt/OSM(66%CeO_2), and 22.0 mg for Pt/OSM(100%CeO_2) having different ceria content.

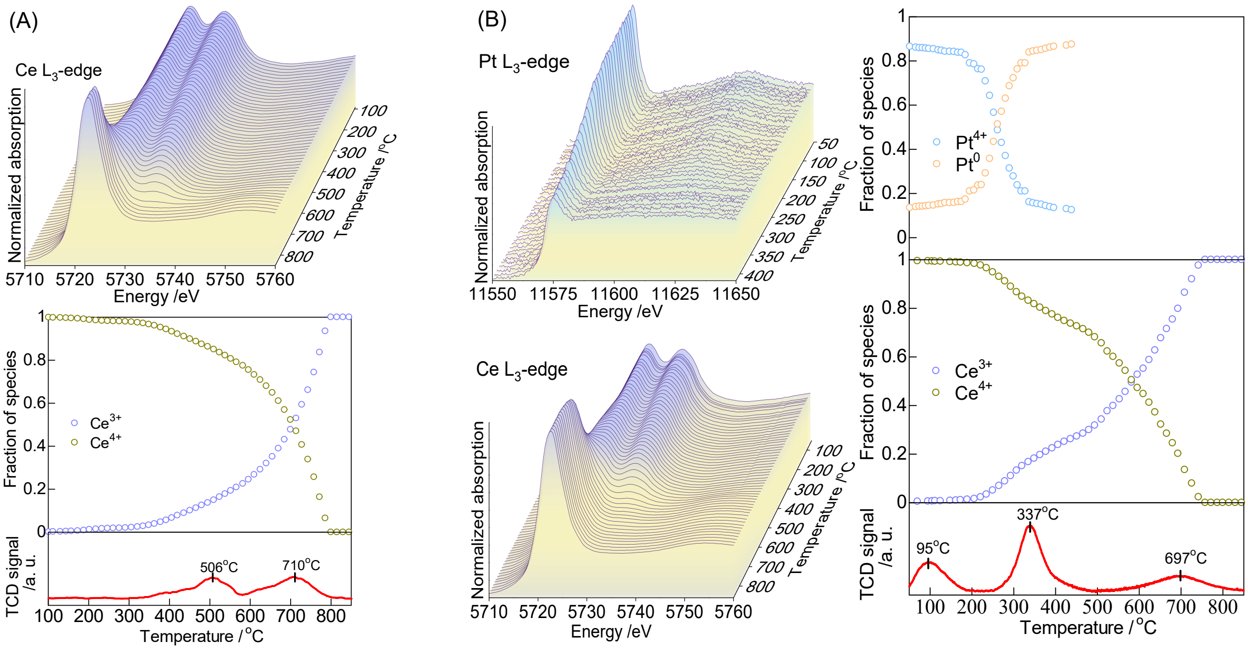

Figure S6. *In situ* Ce and Pt L_3-edge XAS during H_2-TPR of (A) OSM(100%CeO_2) (1.3 mg sample mixed with 20.4 mg BN) and (B) PtO_2/OSM(100%CeO_2) (Sample weight = 1.3 mg with 20.4 mg of BN for Ce L_3-edge and 17.3 mg with 12.8 mg of BN for Pt L_3-edge examination) conducted under H_2 flow (1000 mL/min) at the heating rate of 15 °C/min using CeO_2 and $Ce(NO_3)_3$, and Pt foil and PtO_2 as references for linear combination fitting analysis.

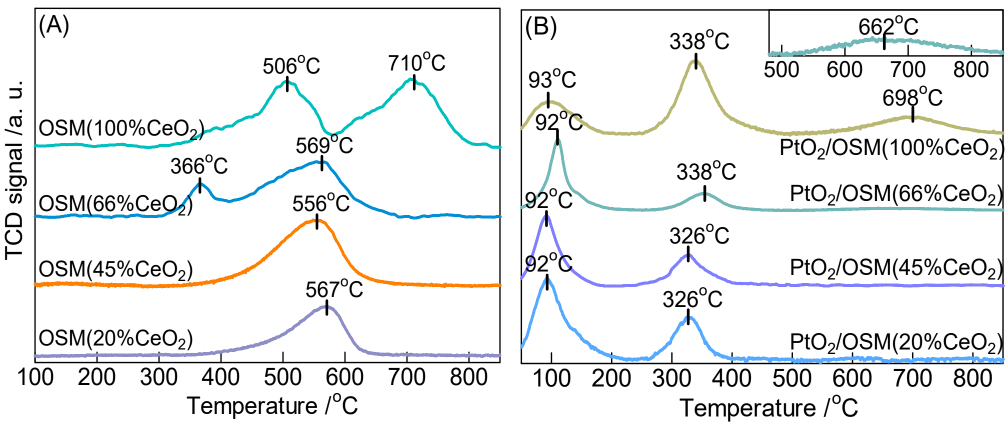

Figure S7. H_2-TPR profiles of (A) OSM supports and (B) PtO_2/OSMs having different ceria content.

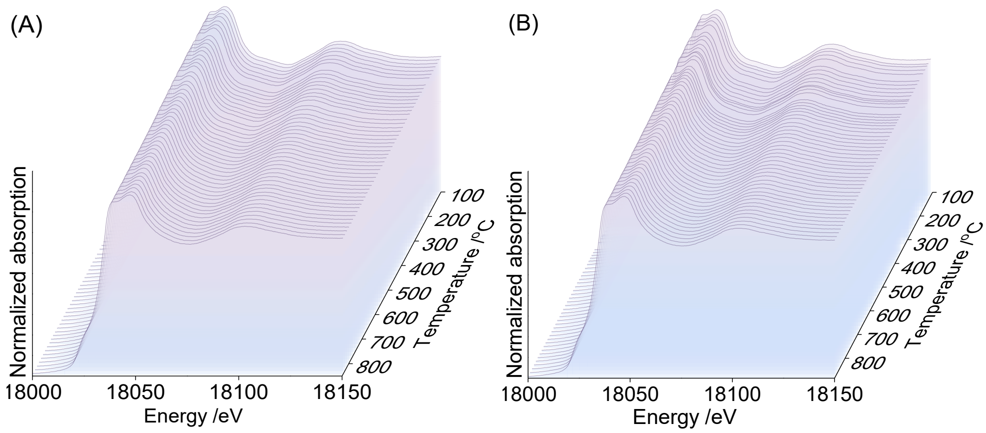

Figure S8. *In situ* Zr K-edge XANES spectra recorded during H_2-TPR of (A) OSM(66%CeO_2) (Sample weight = 18.7 mg with 12.8 mg of BN) and (B) PtO_2/OSM(66%CeO_2) (Sample weight = 19.3 mg sample with 12.8 mg of BN) conducted under H_2 flow (1000 mL/min) using Zr foil and ZrO_2 as reference.

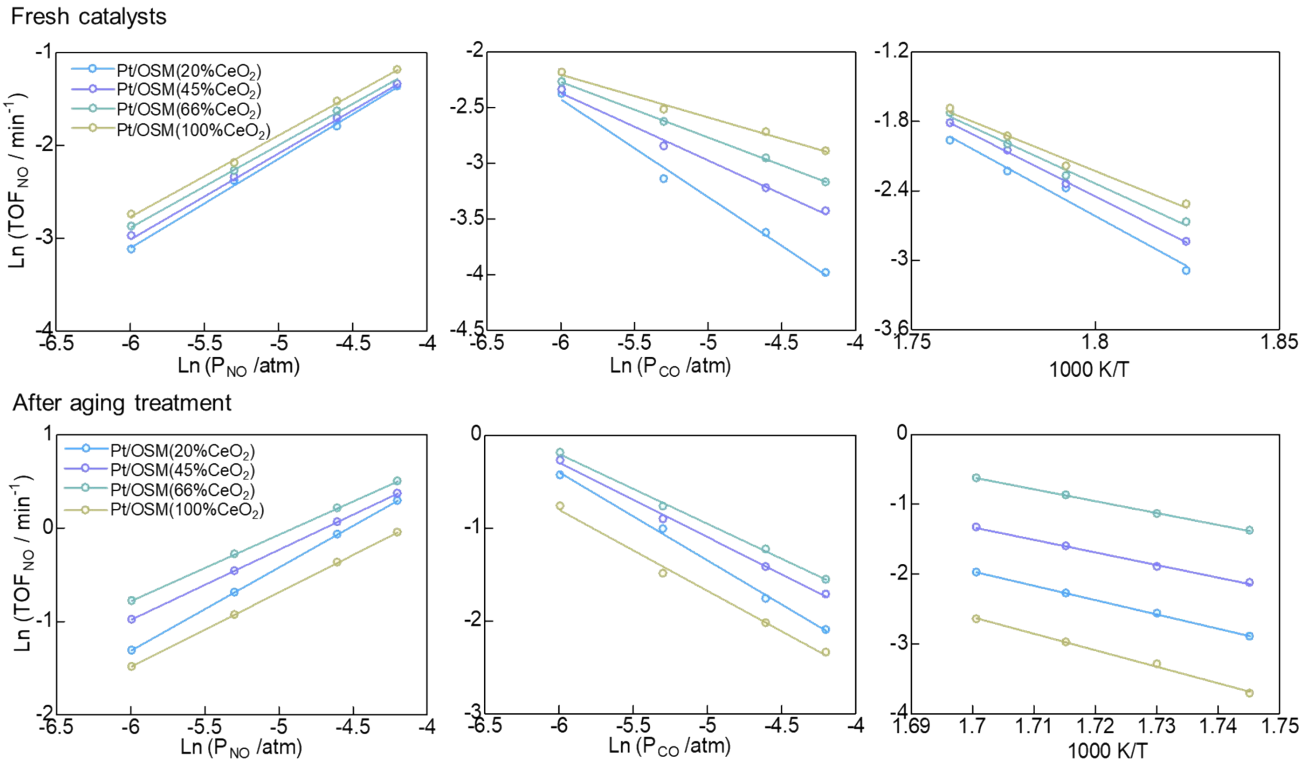

Figure S9. Apparent kinetic studies on NO–CO reactions over fresh and aged powdered Pt/OSMs (20 mg) having different ceria content at the reaction condition of 0.25-1.5% NO (0.5% for Arrhenius plot test), 0.5-2.0% CO (0.5% for Arrhenius plot test) in He flow (80 mL/min), 285 °C and 320 °C for reaction order measurement on fresh and aged catalysts, while 275-295 °C and 300-315 °C for Arrhenius plot examination on corresponding samples.

Table S5. Kinetic informatics of reaction order and activation barrier.

Catalyst	Reaction order of NO	Reaction order of CO	Activation barrier ($kJ\ mol^{-1}$)
Pt/OSM(20%CeO_2)_fresh	0.96	-1.15	144
Pt/OSM(45%CeO_2)_fresh	0.91	-0.75	133
Pt/OSM(66%CeO_2)_fresh	0.89	-0.65	121
Pt/OSM(100%CeO_2)_fresh	0.87	-0.50	106
Pt/OSM(20%CeO_2)_aged	1.37	-1.88	170
Pt/OSM(45%CeO_2)_aged	1.15	-1.60	150
Pt/OSM(66%CeO_2)_aged	1.07	-1.50	141
Pt/OSM(100%CeO_2)_aged	1.21	-1.70	193

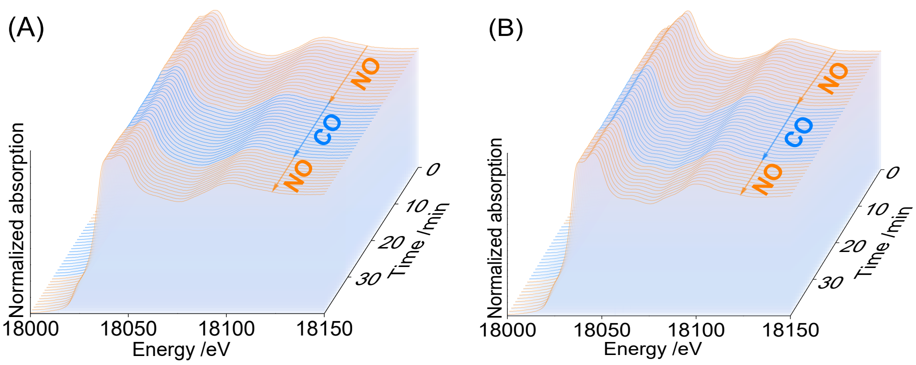

Figure S10. *In situ* Zr K-edge XAS measurements during NO–CO reactions on (A) fresh and (B) aged Pt/OSM(66%CeO_2) (Sample weight = 19.3 mg with 12.8 mg of BN) in a switched flow of 0.5% NO/He and 0.5% CO/He (1000 mL/min) at 200 °C after H_2 reduction at 400 °C, using Zr foil and ZrO_2 as references.

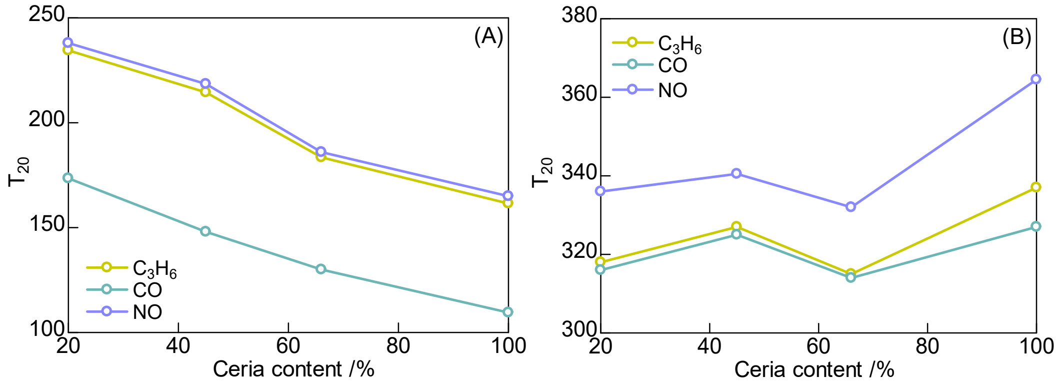

Figure S11. Effect of ceria content on T_{20} behavior over (A) fresh and (B) aged Pt/OSMs having different ceria content for the TWC light-off performance tests over fresh and aged Pt/OSM-coated honeycomb catalysts (Figure 9) under a switched flow of CO (2.4-0.6%), C_3H_6 (420 ppm), H_2 (0.8-0.2%), NO (1000 ppm), O_2 (0.6-1.65%), CO_2 (15%), and H_2O (10%) (with the balance being composed of N_2) with the lambda perturbation set at 1 Hz changing from 0.95 (rich) to 1.05 (lean) at a heating rate of 25 °C/min and SV = 100,000 h^{-1}.

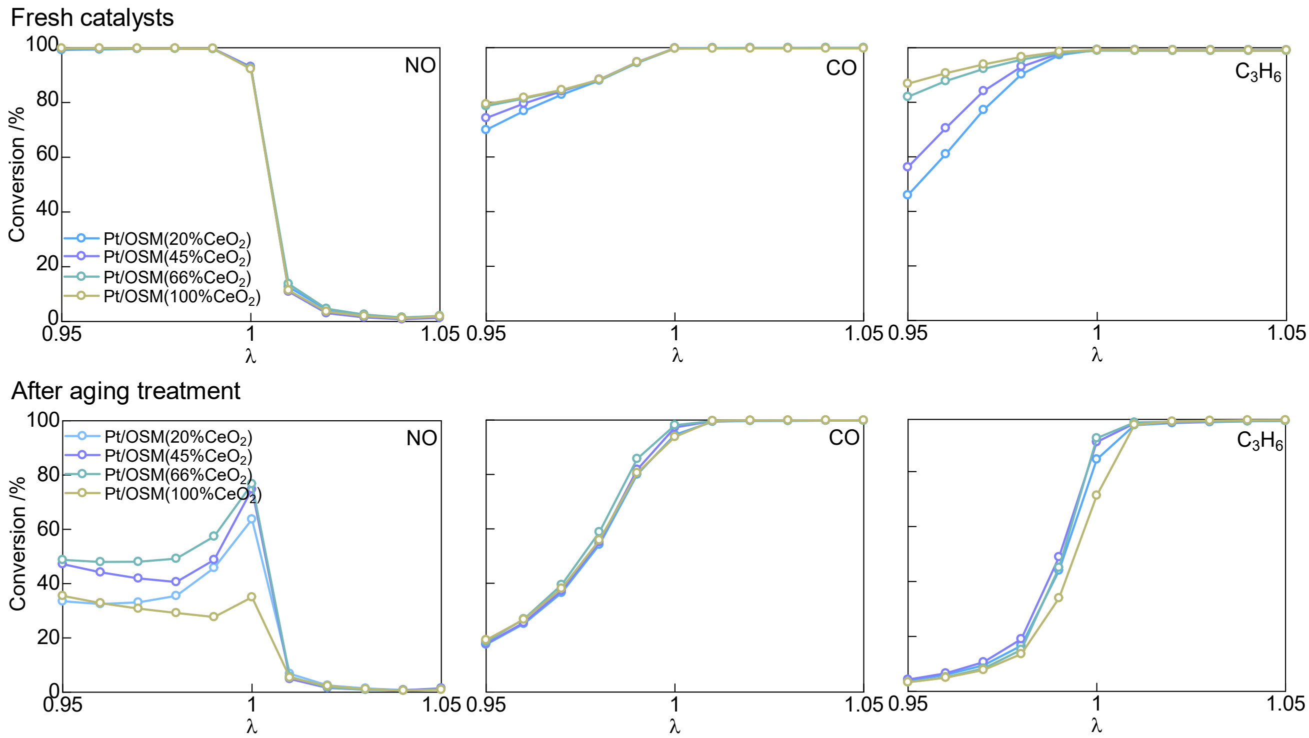

Figure S12. Effect of OSMs on TWC lambda-sweep performance over fresh and aged Pt/OSM-coated honeycomb catalysts under a switched flow of CO (2.4-0.6%), C_3H_6 (420 ppm), H_2 (0.8-0.2%), NO (1000 ppm), O_2 (0.6-1.65%), CO_2 (15%), and H_2O (10%) (with the balance being composed of N_2) with the lambda perturbation interval set at 60 s and changing from 0.95 (rich) to 1.05 (lean) through steps of 0.01 at 400 °C and SV = 100,000 h^{-1}.

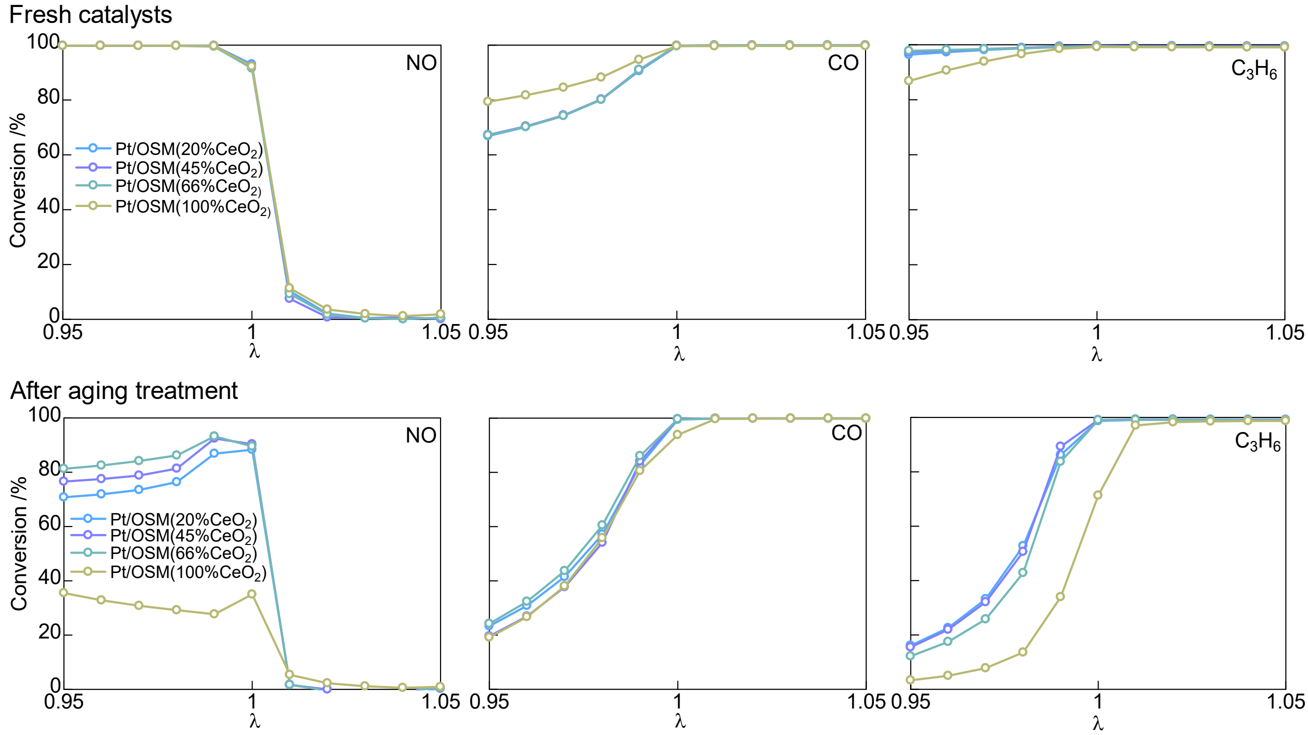

Figure S13. Effect of OSMs on TWC lambda-sweep performance over fresh and aged Pt/OSM-coated honeycomb catalysts under a switched flow of CO (2.4-0.6%), C_3H_6 (420 ppm), H_2 (0.8-0.2%), NO (1000 ppm), O_2 (0.6-1.65%), CO_2 (15%), and H_2O (10%) (with the balance being composed of N_2) with the lambda perturbation interval set at 60 s and changing from 0.95 (rich) to 1.05 (lean) through steps of 0.01 at 500 °C and SV = 100,000 h^{-1}.