Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Ce^{3+}-enriched Spherical Porous Ceria with an Enhanced Oxygen Storage Capacity

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Preparation of a ceria

CeO_2-ME-FA: A methanol solution (3.5 mL) including $Ce(NO_3)_3 \cdot 6H_2O$ (152 mg, 0.350 mmol) and formic acid (66.6 μL, 1.75 mmol) was transferred to an SUS316 batch-type reactor (10 mL volume). The reactor was heated up to 300 °C at a rate of 5.4 °C/min. The temperature was kept at 300 °C for 10 min, and then the reaction was quenched by placing the reactor into an ice-water bath. The obtained product was centrifuged, washed with methanol, and then dried under vacuum for overnight at room temperature to give a powder.

CeO_2-ME-AA, CeO_2-ME-BA, CeO_2-ME-PA: CeO_2-ME-AA, CeO_2-ME-BA, and CeO_2-ME-PA were prepared by similar process to CeO_2-ME-FA by using 1.75 mmol of acetic acid, benzoic acid and phthalic acid as additives, respectively.

CeO_2-ME-EG, CeO_2-ME-dEG, CeO_2-ME-tEG: CeO_2-ME-EG, CeO_2-ME-dEG, and CeO_2-ME-tEG were prepared by similar process to CeO_2-ME-FA by using 11.1 mmol of ethylene glycol, diethylene glycol and triethylene glycol as additives, respectively.

CeO_2-AN: CeO_2-AN was prepared by similar process to CeO_2-ME-FA by using acetonitrile as a solvent without additive.

CeO_2-AN-EG, CeO_2-ME-dEG: CeO_2-AN-EG and CeO_2-ME-dEG were prepared by similar process to CeO_2-ME-FA by using acetonitrile as a solvent with 11.1 mmol of ethylene glycol and diethylene glycol as additives, respectively.

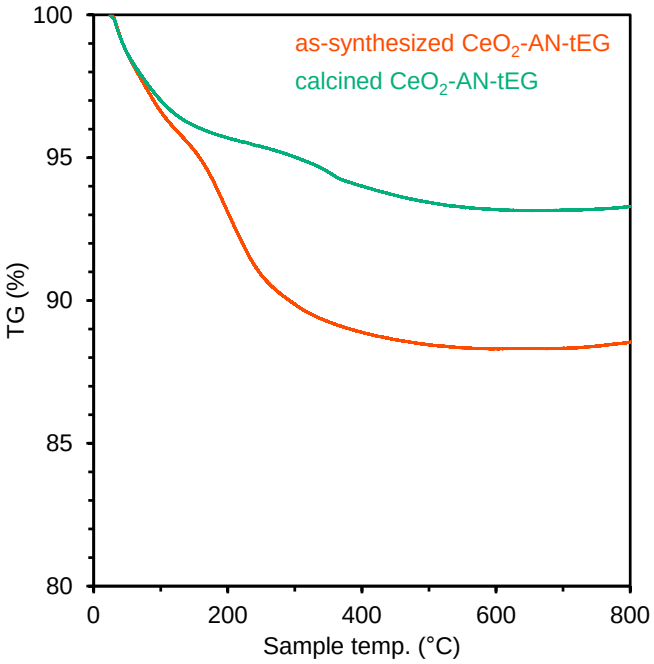

Fig. S1 TG profile of as-synthesized CeO_2-AN-tEG (red) and calcined CeO_2-AN-tEG (green). Both of them showed less than 2% weight loss after 300 °C.

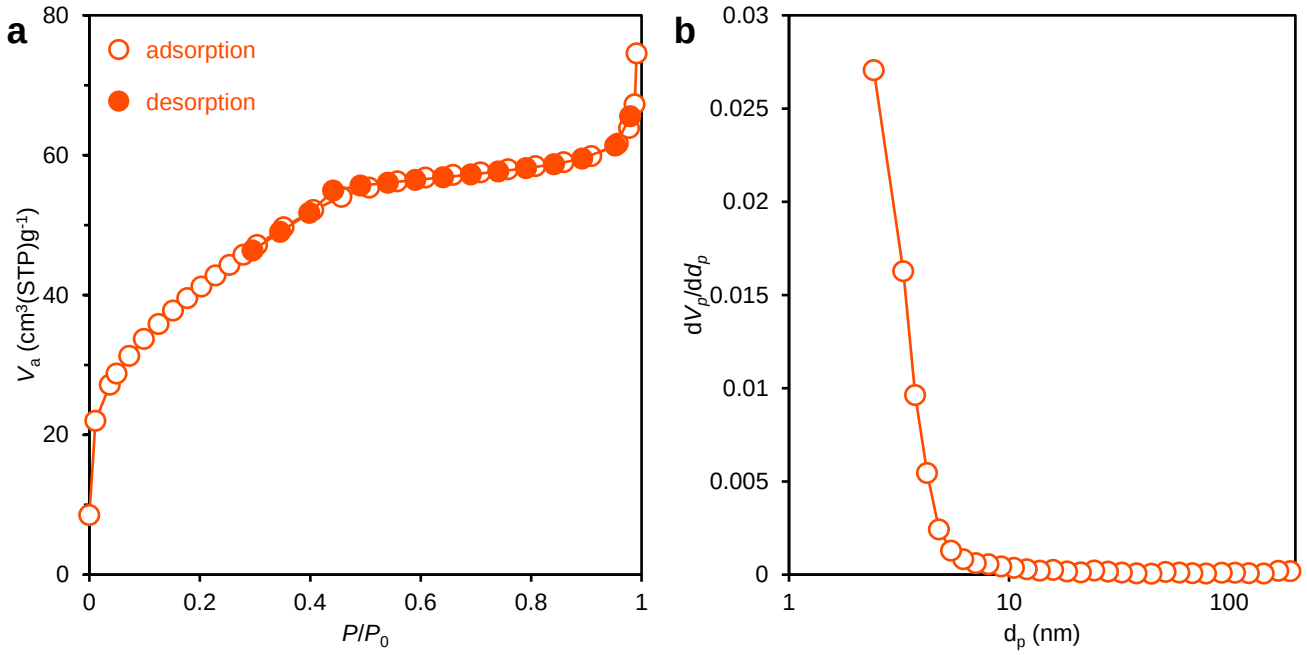

Fig. S2 N_2 adsorption/desorption measurements of CeO_2-AN-tEG. (a) Adsorption/desorption isotherm and (b) pore size distribution (BJH plot).

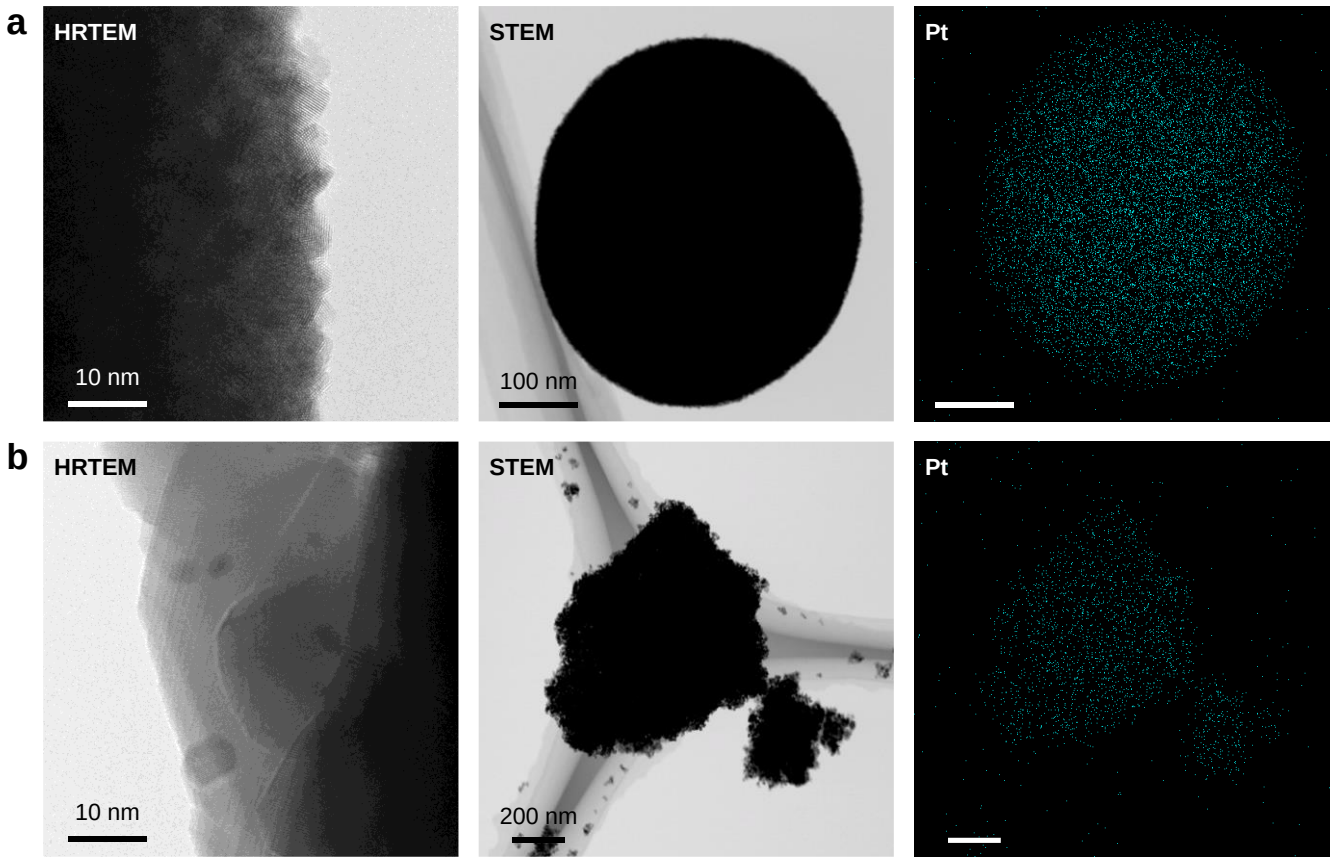

Fig. S3 Characterization of Pt-deposited CeO_2 catalyst. High resolution TEM images, STEM images and EDX mapping images of (a) Pt/CeO_2-AN-tEG and (b) Pt/JRC-CEO-5.

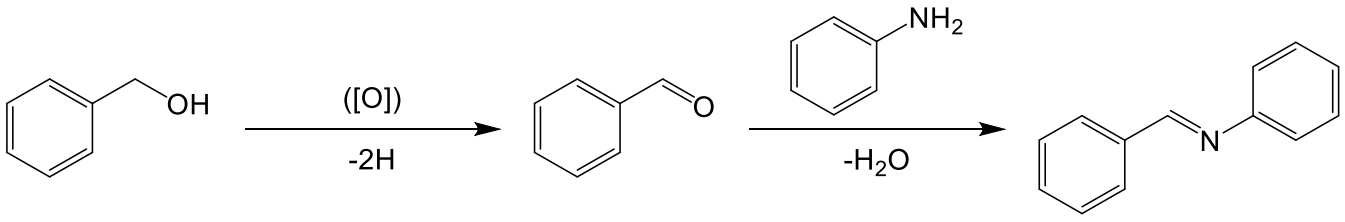

Fig. S4 Reaction path yielding *N*-benzylideneaniline from benzyl alcohol catalyzed by CeO_2.

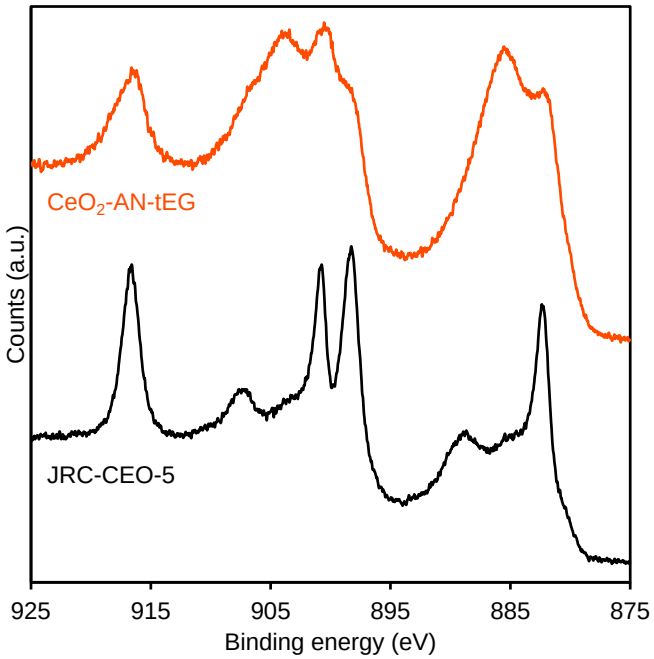

Fig. S5 Ce 3d HAXPES spectra of CeO_2-AN-tEG (red) and JRC-CEO-5 (black).

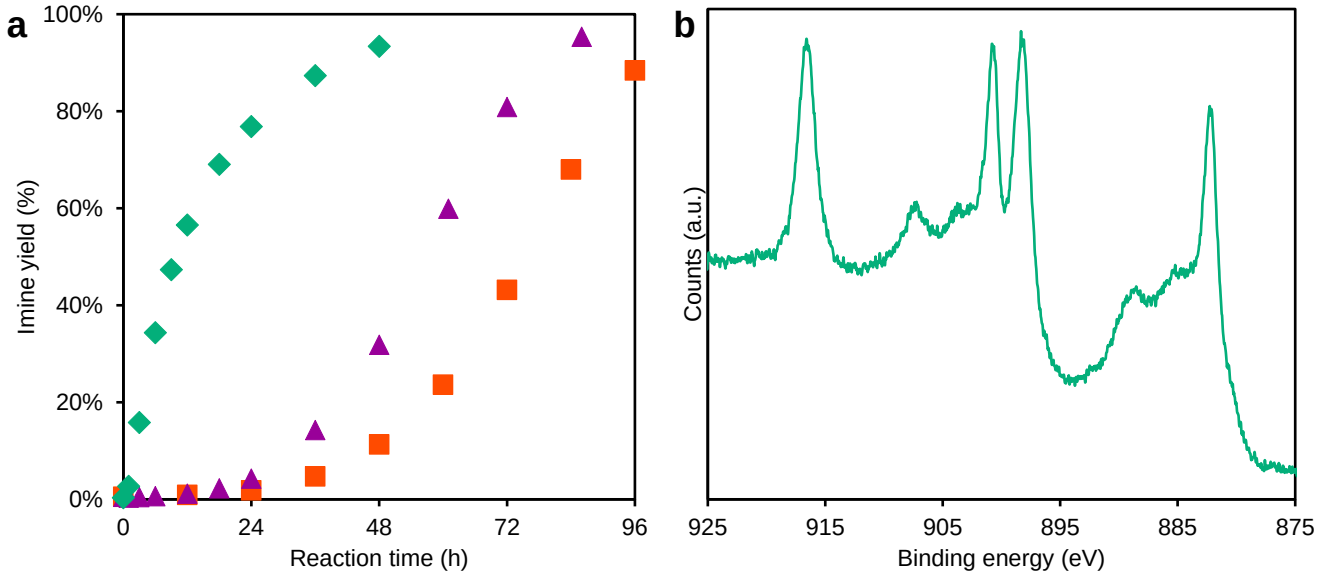

Fig. S6 Liquid phase oxidation reaction catalyzed by CeO_2. (a) Time course of imine yield with as-synthesized (red), calcined (green) and pretreated (violet) CeO_2-AN-tEG. Data on as-synthesized CeO_2-AN-tEG are same to those on CeO_2-AN-tEG showed in Fig. 3c. Calcination was performed at 300 °C for 1 h in air. (b) HAXPES spectrum of calcined CeO_2-AN-tEG at 300 °C for 1 h in air.

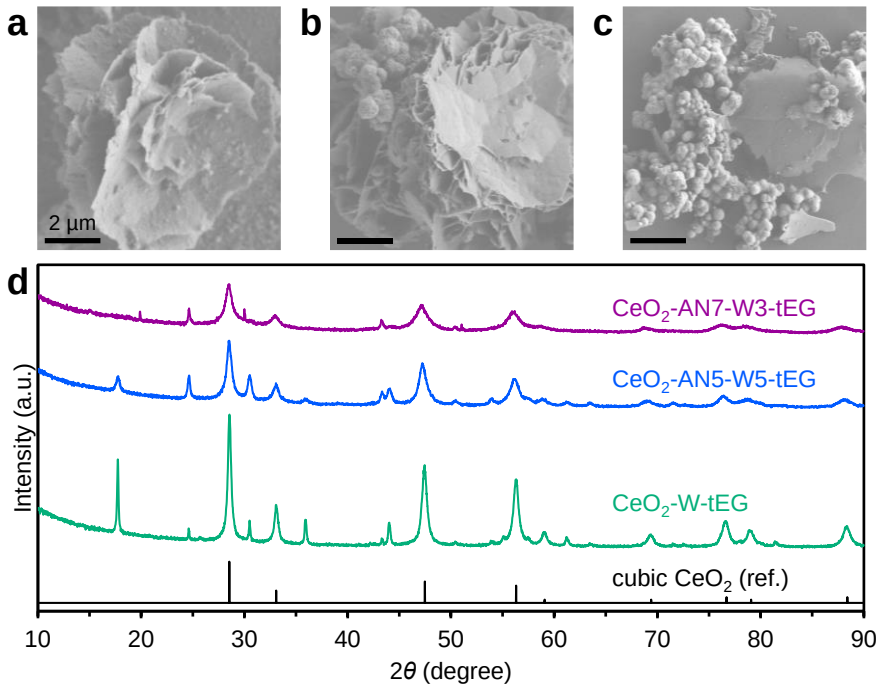

Fig. S7 SEM images of CeO_2, (a) CeO_2-AN7-W3-tEG, (b) CeO_2-AN5-W5-tEG and (c) CeO_2-W-tEG synthesized at 300 °C (scale bar: 2 µm). (d) XRD patterns of synthesized CeO_2, CeO_2-AN7-W3-tEG, CeO_2-AN5-W5-tEG and CeO_2-W-tEG. Black line represents reference XRD pattern of cubic CeO_2.

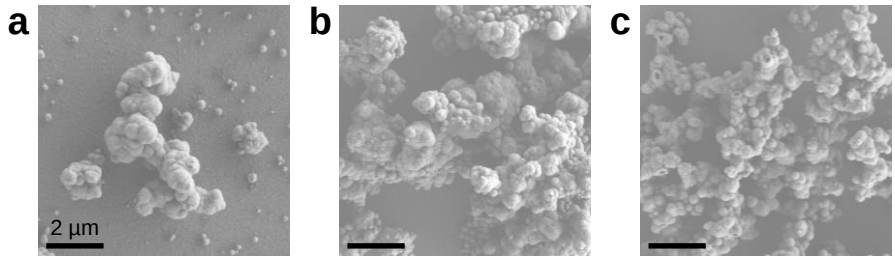

Fig. S8 SEM images of CeO_2, (a) CeO_2-AN7-W3-tEG, (b) CeO_2-AN5-W5-tEG and (c) CeO_2-W-tEG synthesized at 250 °C (scale bar: 2 µm).

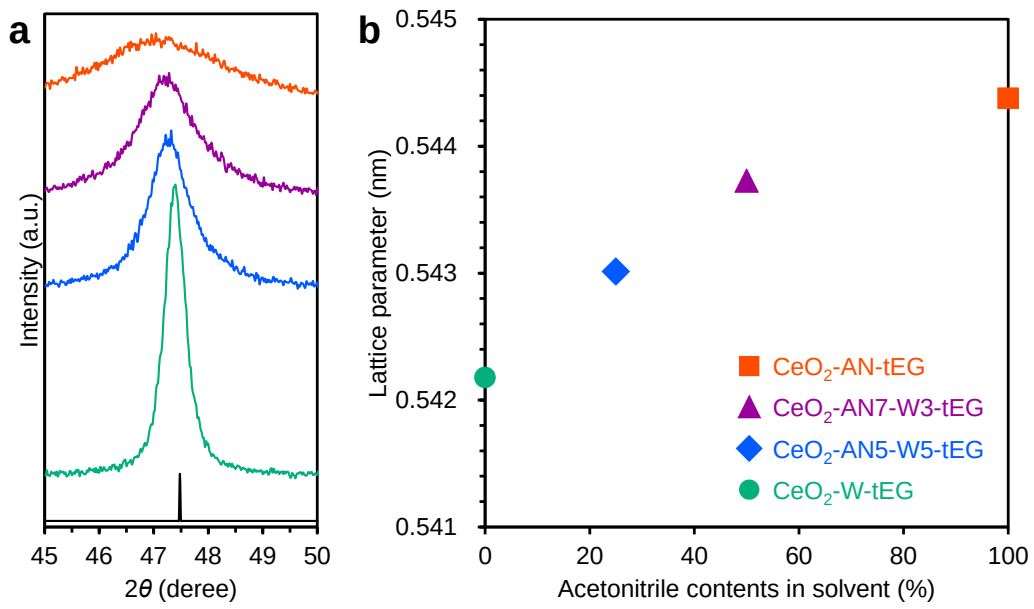

Fig. S9 XRD peak of (220) facet (a) and lattice parameter (b) of CeO_2 prepared in acetonitrile/water mixed solvents with different ratio. CeO_2-AN-tEG (red), CeO_2-AN7-W3-tEG (violet), CeO_2-AN5-W5-tEG (blue) and CeO_2-W-tEG (green). Black line represents reference XRD pattern of cubic CeO_2.

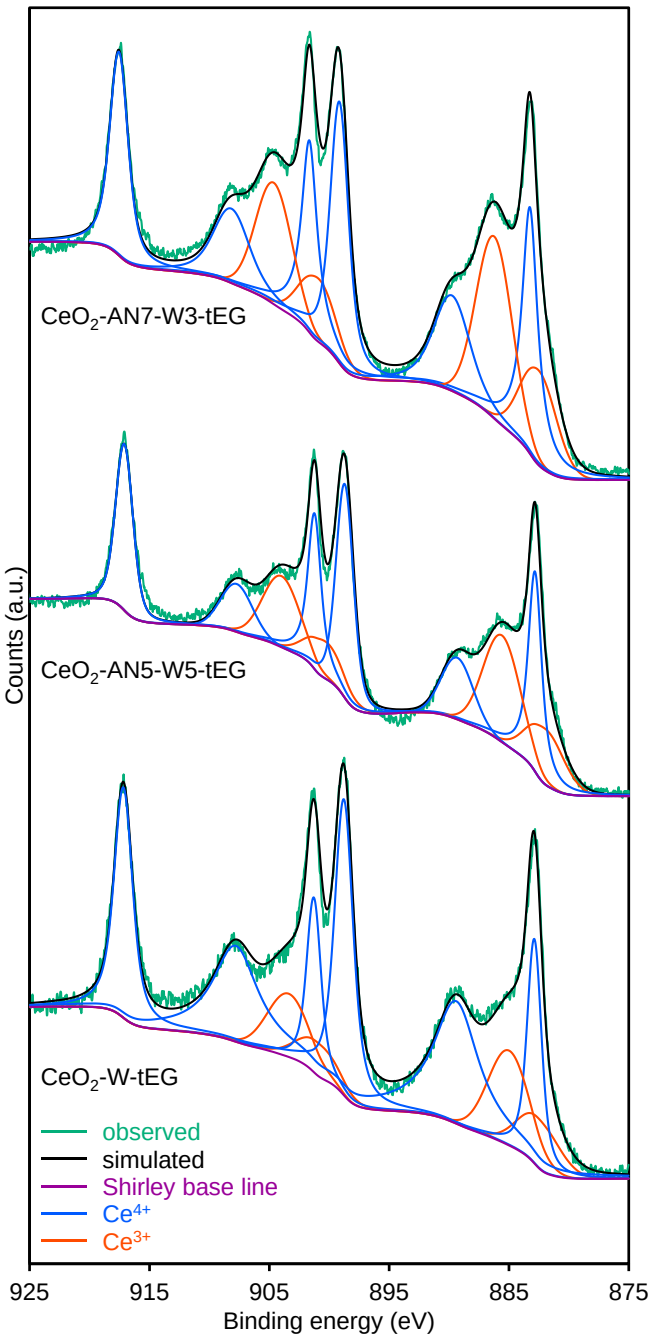

Fig. S10 Ce 3d HAXPES spectra and peak fitting curves of CeO_2-AN7-W3-tEG, CeO_2-AN5-W5-tEG and CeO_2-W-tEG. Observed (green), Shirley base line (violet), deconvolution peaks of Ce^{4+} (blue), deconvolution peaks of Ce^{3+} (red) and simulated curve (black).

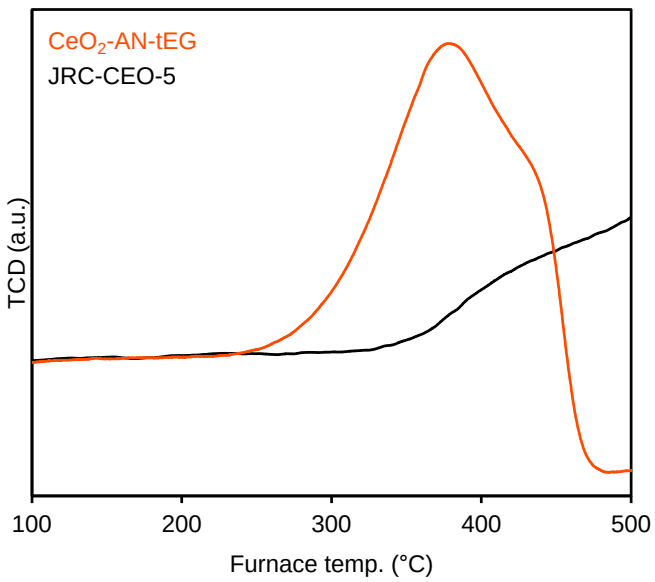

Fig. S11 H_2-TPR profiles of CeO_2-AN-tEG (red) and JRC-CEO-5 (black).

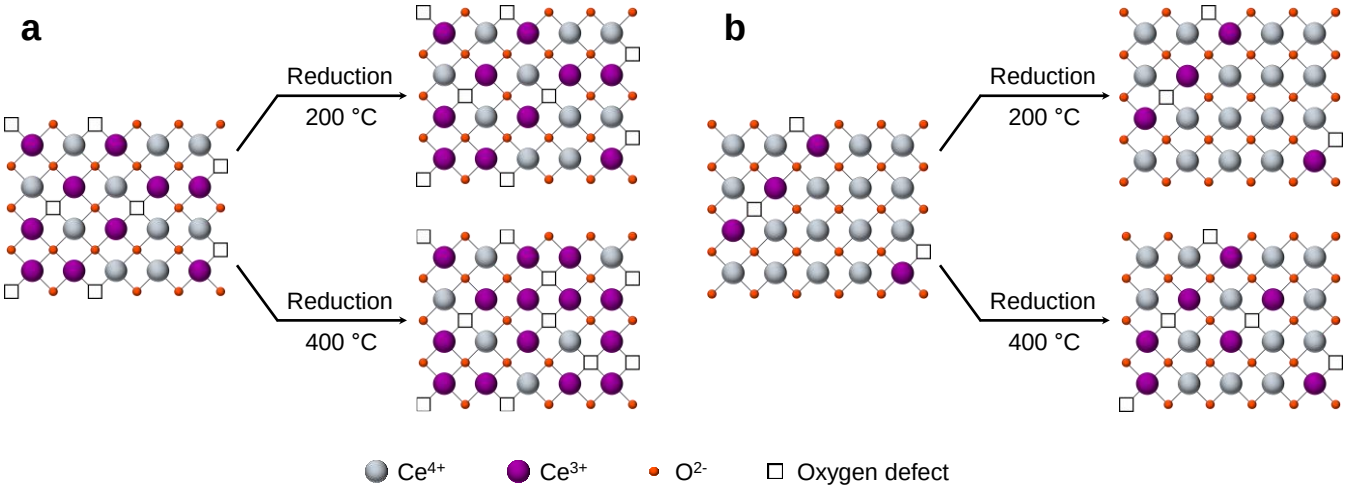

Fig. S12 Schematic diagram of CeO_2 reduction at 200 °C and 400 °C. (a) CeO_2-AN-tEG and (b) JRC-CEO-5. Ce^{4+} (gray circle) is partially reduced by H_2 to yield Ce^{3+} (violet circle). Then, new oxygen defects (square) are generated.

Table S1 Synthetic conditions of ceria porous spheres.

Sample name[a]	Solvent	Additive	Temperature (°C)
CeO_2-ME-FA	CH_3OH	Formic acid	300
CeO_2-ME-AA	CH_3OH	Acetic acid	300
CeO_2-ME-BA	CH_3OH	Benzoic acid	300
CeO_2-ME-PA	CH_3OH	*o*-Phthalic acid	300
CeO_2-ME-EG	CH_3OH	Ethylene glycol	300
CeO_2-ME-dEG	CH_3OH	Diethylene glycol	300
CeO_2-ME-tEG	CH_3OH	Triethylene glycol	300
CeO_2-AN	CH_3CN	–	300
CeO_2-AN-EG	CH_3CN	Ethylene glycol	300
CeO_2-AN-dEG	CH_3CN	Diethylene glycol	300
CeO_2-AN-tEG	CH_3CN	Triethylene glycol	300
CeO_2-AN7-W3-tEG	CH_3CN/H_2O=7/3 (*v*/*v*)	Triethylene glycol	250[b]
CeO_2-AN5-W5-tEG	CH_3CN/H_2O=5/5 (*v*/*v*)	Triethylene glycol	250[b]
CeO_2-W-tEG	H_2O	Triethylene glycol	250[b]

[a] Short abbreviations ME, FA, AA, BA, PA, EG, dEG, tEG, AN and W represent methanol, formic acid, acetic acid, benzoic acid, *o*-phthalic acid, ethylene glycol, diethylene glycol, triethylene glycol, acetonitrile and water, respectively. [b] Diffraction peaks ascribed to non-cubic ceria phase were recognized in the XRD patterns of product obtained at 300 °C (Fig. S7). Then, reaction temperature was lowered to 250 °C (Fig. S8).

Table S2 Peak positions of Ce3d HAXPES spectra.

Sample name[a]	Peak position (eV)									
	v^0	v	v'	v''	v'''	u^0	u	u'	u''	u'''
CeO_2-AN-tEG	883.4	883.6	887.0	890.4	899.8	901.8	902.0	905.4	908.8	918.2
CeO_2-AN7-W3-tEG	882.6	883.3	886.2	889.8	899.1	901.0	901.7	904.6	908.2	917.5
CeO_2-AN5-W5-tEG	882.0	882.8	885.6	889.3	898.7	900.4	901.2	904.0	907.7	917.1
CeO_2-W-tEG	882.6	882.9	885.0	889.4	898.8	901.0	901.3	903.4	907.8	917.2
JRC-CEO-5	882.2	882.8	885.1	889.3	898.7	900.6	901.2	903.5	907.7	917.1

[a] Short abbreviations tEG, AN, and W represent triethylene glycol, acetonitrile and water, respectively.

Table S3 Crystallite size and Ce^{3+} concentration of ceria.

Sample name[a]	CeO_2-AN-tEG	CeO_2-AN7-W3-tEG	CeO_2-AN5-W5-tEG	CeO_2-W-tEG	JRC-CEO-5
Crystallite size (nm)	3.3	6.8	10.2	21.4	9.9
Ce^{3+} (at%)	57.4	36.7	36.3	22.6	22.5
Lattice parameter (nm)	0.544	0.544	0.543	0.542	0.541

[a] Short abbreviations tEG, AN, and W represent triethylene glycol, acetonitrile and water, respectively.