Supplementary Information

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

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Preparation of a ceria

**CeO\textsubscript{2}-ME-FA:** A methanol solution (3.5 mL) including Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O (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\textsubscript{2}-ME-AA, CeO\textsubscript{2}-ME-BA, CeO\textsubscript{2}-ME-PA:** CeO\textsubscript{2}-ME-AA, CeO\textsubscript{2}-ME-BA, and CeO\textsubscript{2}-ME-PA were prepared by similar process to CeO\textsubscript{2}-ME-FA by using 1.75 mmol of acetic acid, benzoic acid and phthalic acid as additives, respectively.

**CeO\textsubscript{2}-ME-EG, CeO\textsubscript{2}-ME-dEG, CeO\textsubscript{2}-ME-tEG:** CeO\textsubscript{2}-ME-EG, CeO\textsubscript{2}-ME-dEG, and CeO\textsubscript{2}-ME-tEG were prepared by similar process to CeO\textsubscript{2}-ME-FA by using 11.1 mmol of ethylene glycol, diethylene glycol and triethylene glycol as additives, respectively.

**CeO\textsubscript{2}-AN:** CeO\textsubscript{2}-AN was prepared by similar process to CeO\textsubscript{2}-ME-FA by using acetonitrile as a solvent without additive.

**CeO\textsubscript{2}-AN-EG, CeO\textsubscript{2}-ME-dEG:** CeO\textsubscript{2}-AN-EG and CeO\textsubscript{2}-ME-dEG were prepared by similar process to CeO\textsubscript{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$_2$. 

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\text{Benzyl Alcohol} \xrightarrow{([O])} \text{Benzaldehyde} \xrightarrow{\text{Benzylamine}} \text{N-Benzylideneaniline}
\]
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   | Solvent  | Additive          | Temperature (°C) |
|---------------|----------|-------------------|------------------|
| CeO2-ME-FA    | CH₃OH    | Formic acid       | 300              |
| CeO2-ME-AA    | CH₃OH    | Acetic acid       | 300              |
| CeO2-ME-BA    | CH₃OH    | Benzoic acid      | 300              |
| CeO2-ME-PA    | CH₃OH    | o-Phthalic acid   | 300              |
| CeO2-ME-EG    | CH₃OH    | Ethylene glycol   | 300              |
| CeO2-ME-dEG   | CH₃OH    | Diethylene glycol | 300              |
| CeO2-ME-tEG   | CH₃OH    | Triethylene glycol| 300              |
| CeO2-AN       | CH₃CN    | –                 | 300              |
| CeO2-AN-EG    | CH₃CN    | Ethylene glycol   | 300              |
| CeO2-AN-dEG   | CH₃CN    | Diethylene glycol | 300              |
| CeO2-AN-tEG   | CH₃CN    | Triethylene glycol| 300              |
| CeO2-AN7-W3-tEG | CH₃CN/H₂O=7/3 (v/v) | Triethylene glycol | 250<sup>b</sup> |
| CeO2-AN5-W5-tEG | CH₃CN/H₂O=5/5 (v/v) | Triethylene glycol | 250<sup>b</sup> |
| CeO2-W-tEG    | H₂O      | Triethylene glycol| 250<sup>b</sup> |

<sup>a</sup> 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. <sup>b</sup> 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 | Peak position (eV) |
|-------------|-------------------|
|             | v<sup>0</sup>  | v  | v'  | v'' | u<sup>0</sup> | u  | u'  | u'' | u''' |
| CeO<sub>2</sub>-AN-tEG | 883.4 | 883.6 | 887.0 | 890.4 | 899.8 | 901.8 | 902.0 | 905.4 | 908.8 | 918.2 |
| CeO<sub>2</sub>-AN7-W3-tEG | 882.6 | 883.3 | 886.2 | 889.8 | 899.1 | 901.0 | 901.7 | 904.6 | 908.2 | 917.5 |
| CeO<sub>2</sub>-AN5-W5-tEG | 882.0 | 882.8 | 885.6 | 889.3 | 898.7 | 900.4 | 901.2 | 904.0 | 907.7 | 917.1 |
| CeO<sub>2</sub>-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 |

<sup>a</sup> Short abbreviations tEG, AN, and W represent triethylene glycol, acetonitrile and water, respectively.

Table S3 Crystallite size and Ce<sup>3+</sup> concentration of ceria.

| Sample name<sup>a</sup> | CeO<sub>2</sub>-AN-tEG | CeO<sub>2</sub>-AN7-W3-tEG | CeO<sub>2</sub>-AN5-W5-tEG | CeO<sub>2</sub>-W-tEG | JRC-CEO-5 |
|-------------------------|------------------------|---------------------------|------------------------|---------------------|-----------|
| Crystallite size (nm)   | 3.3                    | 6.8                       | 10.2                   | 21.4                | 9.9       |
| Ce<sup>3+</sup> (at%)   | 57.4                   | 36.7                      | 36.3                   | 22.6                | 22.5      |
| Lattice parameter (nm)  | 0.544                  | 0.544                     | 0.543                  | 0.542               | 0.541     |

<sup>a</sup> Short abbreviations tEG, AN, and W represent triethylene glycol, acetonitrile and water, respectively.