Supporting information

Capping Experiments Reveal Multiple Surface Active Sites of CeO_2 and their Cooperative Catalysis

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General characterizations by pristine CeO_2

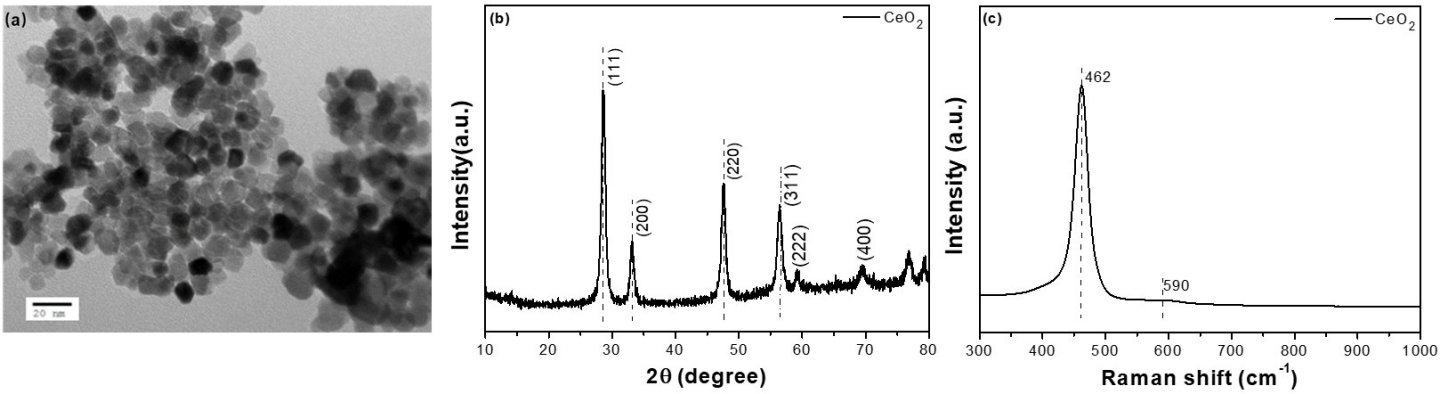


Figure S1. TEM (a), XRD (b), and Raman spectroscopy (c) of pristine CeO_2

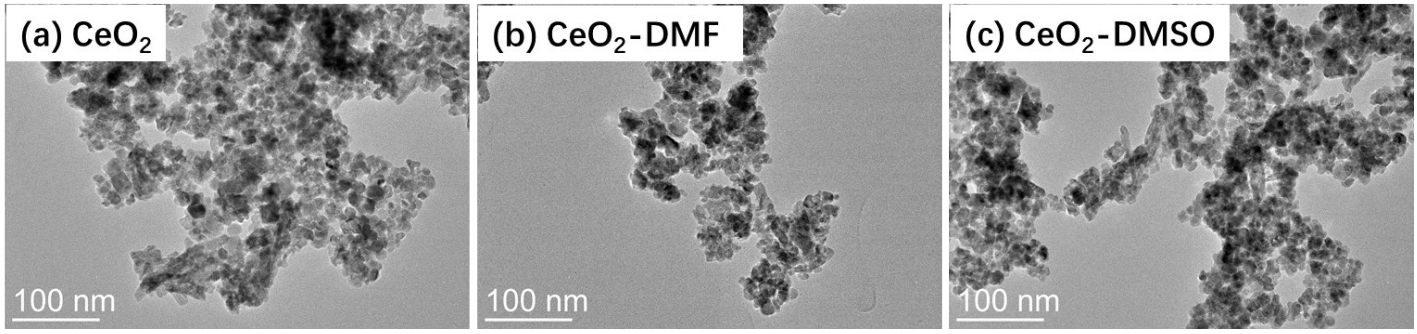


Figure S2. TEM of (a) pristine CeO_2, CeO_2-DMF (pristine CeO_2 treated in DMF), and CeO_2-DMSO (pristine CeO_2 treated in DMSO)

Treatment conditions: CeO_2 (100 mg), DMF or DMSO (2 mL), 60 °C for 12 h, in 0.1 MPa oxygen.

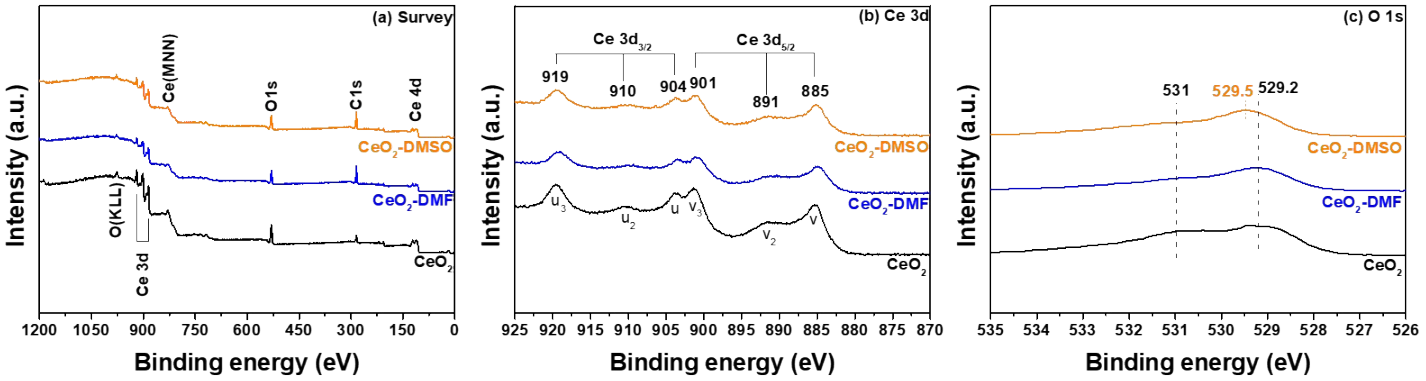


Figure S3. XPS of (a) pristine CeO_2, CeO_2-DMF (pristine CeO_2 treated in DMF), and CeO_2-DMSO (pristine CeO_2 treated in DMSO)

Treatment conditions: CeO_2 (100 mg), DMF or DMSO (2 mL), 60 °C for 12 h, in 0.1 MPa oxygen.

$$c\ (Ce^{3+}) = \frac{A_{v_0} + A_{v_2} + A_{u_0} + A_{u_2}}{A_{v_0} + A_{v_1} + A_{v_2} + A_{v_3} + A_{v_4} + A_{u_0} + A_{u_1} + A_{u_2} + A_{u_3}}$$

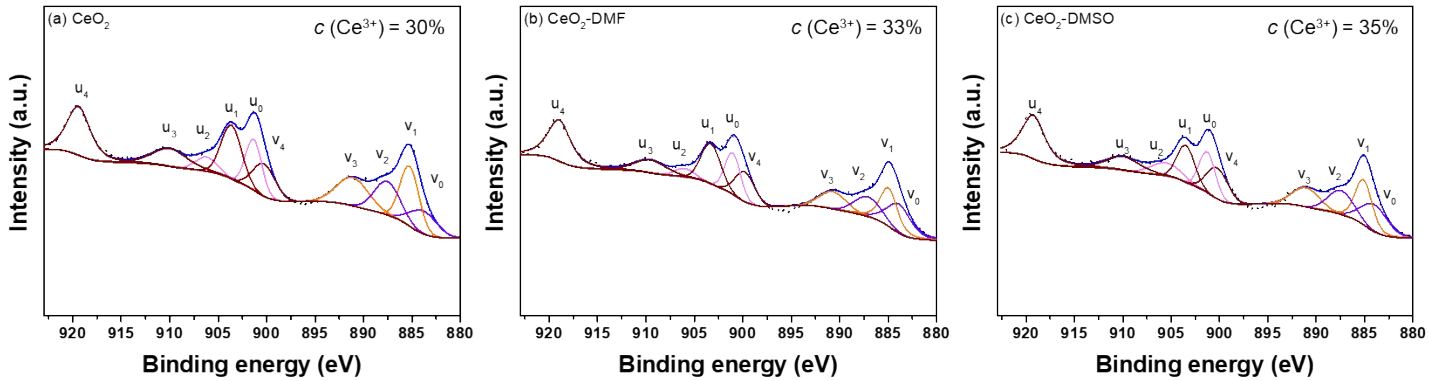


Figure S4. Decomposition of the Ce3d core level spectrum of (a) pristine CeO_2, CeO_2-DMF (pristine CeO_2 treated in DMF), and CeO_2-DMSO (pristine CeO_2 treated in DMSO)

The content of Ce^{3+} ions in these three samples were calculated based on the above equation.

Characterizations by Fourier transform IR (FTIR) spectroscopy

In order to obtain information about surface organic groups of CeO_2 treated with benzoic acid, FTIR spectra were collected on a Bruker Tensor 27 instrument equipped with a DLATGS detector using dry KBr as standard reference in the range of 4000–400 cm^{-1}. Samples were pressed into self-supporting wafers, which were measured as a KBr pellet.

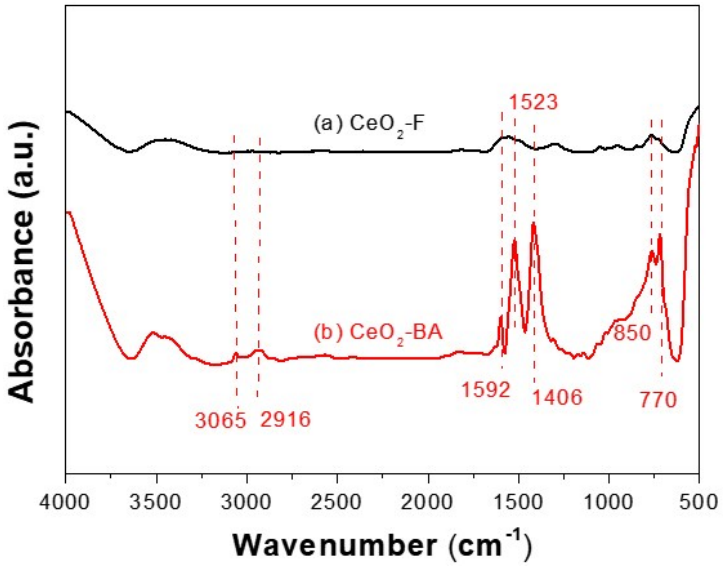


Figure S5. FT-IR spectra of fresh CeO_2 and CeO_2 treated with benzoic acid

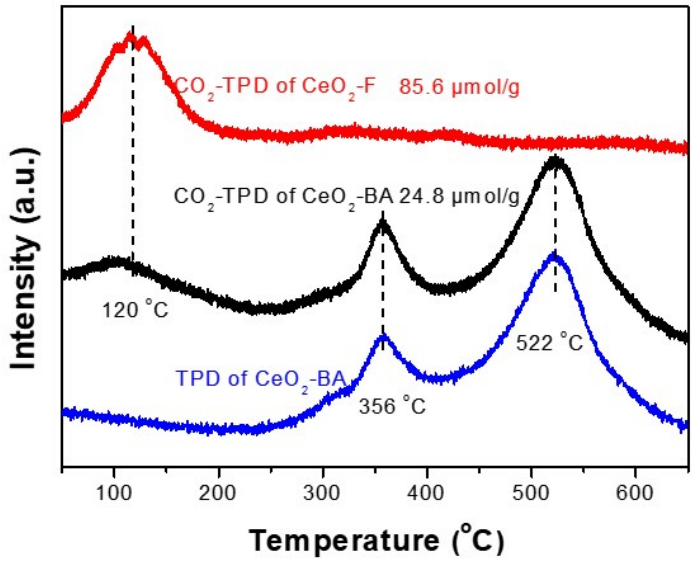
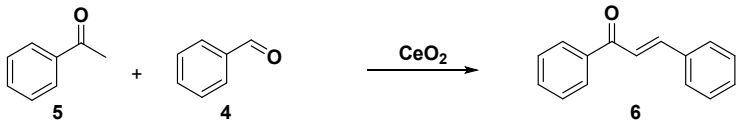


Figure S6. CO_2-TPD of fresh CeO_2 (CeO_2-F) and CeO_2 treated with benzoic acid (CeO_2-BA) and TPD of CeO_2-BA

Table S1. Aldol condensation of benzaldehyde with acetophenone over CeO_2 catalyst

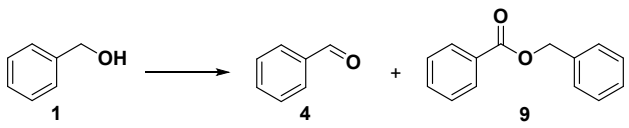


Entry	Catalyst	Reaction time (h)	Conv. (%) of **5**	Sel.(%) of **6**
1	Fresh CeO_2	1	1	0
2	Fresh CeO_2	3	4	0
3	Fresh CeO_2	5	7	0
4	Fresh CeO_2	7	13	55
5	CeO_2-BA[b]	1	< 1	N.D.
6	CeO_2-BA[b]	3	< 1	N.D.
7	CeO_2-BA[b]	5	< 1	N.D.
8	CeO_2-BA[b]	7	< 1	N.D.

Reaction conditions: **5** (0.5 mmol), **4** (0.75 mmol), catalyst (100 mg), *p*-xylene (2 mL), 150 °C, under Ar. [a] The conversions and selectivities based on acetophenone consumption were determined by GC. [b] The CeO_2-BA was fresh CeO_2 treated by benzoic acid in O_2 and then centrifugation, washed with ethanol for three times, and dried at 100 °C. N.D. = No detection.

The fresh CeO_2 gave 10% conversion of acetophenone for the Aldol reaction (Table S1, entry 1). However, Aldol reaction did not occur over the CeO_2 treated with benzoic acid (denoted as CeO_2-BA) (Table S1, entry 2).

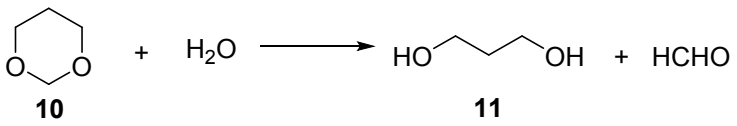
Table S2. Oxidation of benzyl alcohol over CeO_2 catalyst



Entry	Catalyst	Reaction time (h)	Conv.(%) of **1**[a]	Sel.(%) of **4**	Sel.(%) of **9**
1	Fresh CeO_2	1	8	53	47
2	Fresh CeO_2	3	11	71	29
3	Fresh CeO_2	5	16	65	35
4	Fresh CeO_2	7	39	35	65
5	CeO_2-BA[b]	1	8	55	45
6	CeO_2-BA[b]	3	10	8	92
7	CeO_2-BA[b]	5	15	29	71
8	CeO_2-BA[b]	7	37	29	71

Reaction conditions: **1** (0.75 mmol), catalyst (100 mg), *p*-xylene (2 mL), 150 °C, 1 atm air. [a] The conversions and selectivities based on benzyl alcohol consumption were determined by GC. [b] The CeO_2-BA was fresh CeO_2 treated by benzoic acid in O_2 and then centrifugation, washed with ethanol for three times, and dried at 100 °C.

Table S3. Hydrolysis of 1,3-dioxane over CeO_2 catalyst



10 **11**

Entry	Catalyst	Reaction time (h)	Conv.(%) of **10**[a]	Sel.(%) of **11**
1	Fresh CeO_2	4	1	>99
2	Fresh CeO_2	6	10	>99
3	Fresh CeO_2	8	39	>99
4	Fresh CeO_2	10	87	>99
5	CeO_2-BA[b]	4	1	>99
6	CeO_2-BA[b]	6	16	>99
7	CeO_2-BA[b]	8	38	>99
8	CeO_2-BA[b]	10	85	>99

Reaction conditions: **10** (1.5 mmol), catalyst (100 mg), H_2O (2 mL), 150 °C. [a] The conversions and selectivities based on **10** consumptions were determined by GC. [b] The CeO_2-BA was fresh CeO_2 treated by benzoic acid in O_2 and then centrifugation, washed with ethanol for three times, and dried at 100 °C.