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Supporting Information

Efficient Elimination of Chlorinated Organics on A Phosphoric Acid Modified CeO_2 Catalyst: A Hydrolytic Destruction Route

Xiaoxia Dai, Xinwei Wang, Samuel Pattisson, Yunhao Lu, David J. Morgan, Stuart H. Taylor, James H. Carter*, Graham J. Hutchings, Xiaole Weng*, Zhongbiao Wu

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Number of Figures: 4

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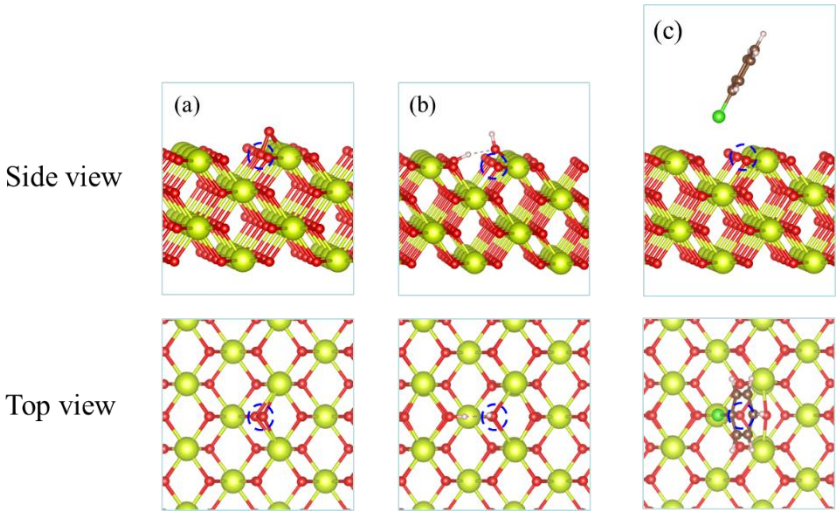


Figure S1. Optimized model of CeO_2 (110) with oxygen vacancy. The models were constructed by removing single oxygen atom from CeO_2(110) supercell to introduce oxygen vacancies. During geometry optimization, the atoms in the top two layers of CeO_2 slab were allowed to relax while atoms in the bottom two layers were fixed in their optimized bulk positions.

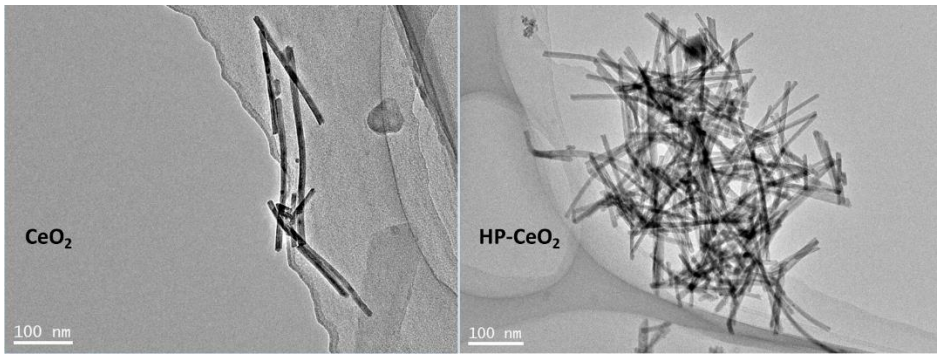


Figure S2. TEM images of CeO_2 and HP-CeO_2

Table S1. Physical properties of HP-CeO_2 and CeO_2

sample	p loading		surface area	lattice parameter	Ce^{3+}/Ce_{total} [a]
	(mmol g^{-1})	(nm^{-2})	(m^2 g^{-1})	(Å)	
CeO_2	0	0	96	5.411	29%
HP-CeO_2	0.21	1.18	108	5.413	26%

Note: (a) caculated from XPS results

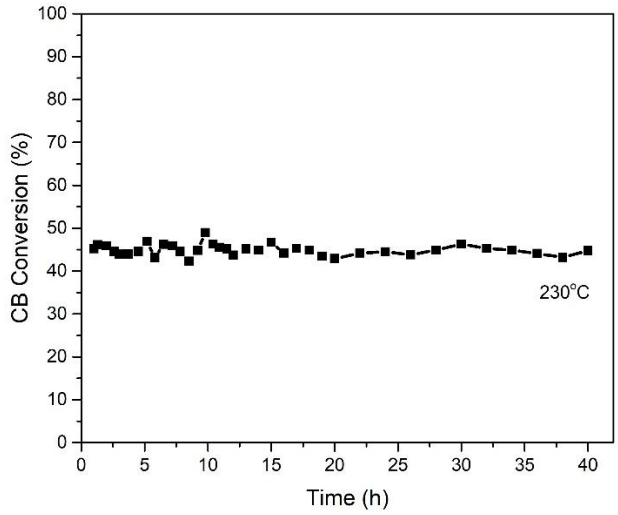


Figure S3. Stability test of CB oxidation over HP-CeO_2 at 230 °C. Reaction condition: GHSV at 10,000 mL/(g h), chlorobenzene at ca. 500 ppm, H_2O at 5000 ppm, N_2 flow rate at ca. 145 mL/min, O_2 flow rate at ca. 15 mL/min.

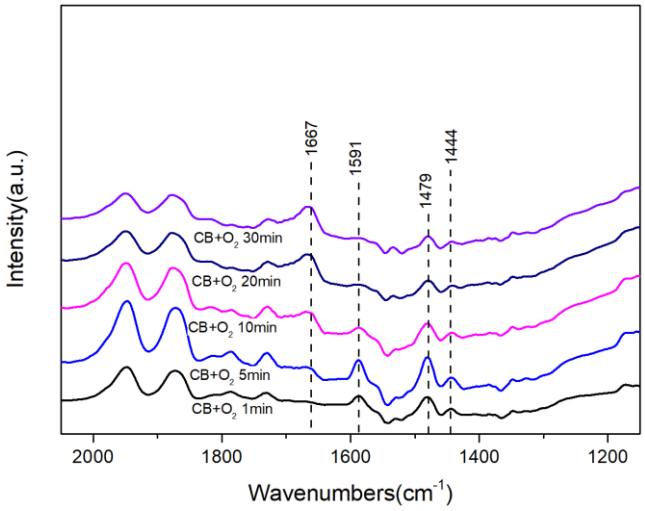


Figure S4. *in-situ* FTIR spectra of CB oxidation at 150 °C over CeO_2 catalyst in dry condition.

Table S2. Adsorption energies on various active sites

Species	Adsorption energy (eV)
O_2/O_{vac}	2.20
H_2O/O_{vac}	1.57
O_2+H_2O/O_{vac}	2.82
C_6H_5Cl/O_{vac}	0.39
$C_6H_5Cl+O_2/O_{vac}$	2.37

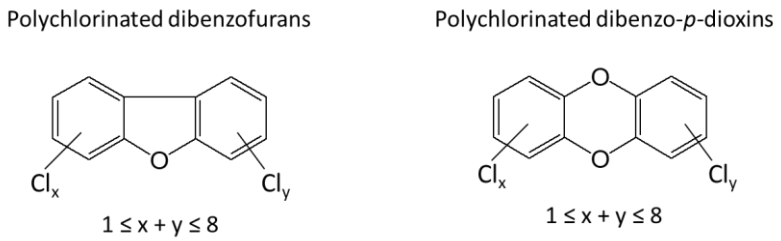
$C_6H_5Cl+H_2O/O_{vac}$	1.21
O_2/Ce	0.20
H_2O/Ce	0.62
O_2+H_2O/Ce	0.72
C_6H_5Cl/Ce	0.48
$C_6H_5Cl+H_2O$/Ce	1.81
O_2/P group	-1.59
H_2O/P group	0.63
O_2+H_2O/P group	-0.94
C_6H_5Cl/P group	0.50
$C_6H_5Cl+O_2$/P group	-0.56
$C_6H_5Cl+H_2O$/P group	2.77
HCl/P group	0.74
C_6H_5OH/P group	0.76

Table S3. Ingredients of 17 toxic dioxins in the off-gas of CeO_2 and HP-CeO_2 at 250 °C test with H_2O stream

Compound	Detection limit (pg)	TEF	CeO_2		HP-Ce	
			Cout (pg)	I-TEQ (ng/m^3)	Cout (pg)	I-TEQ (ng/m^3)
2378TCDD	0.5627	1	<0.5627	ND	<0.5627	ND
12378PeCDD	0.6234	0.5	<0.6234	ND	<0.6234	ND
123478HxCDD	0.6574	0.1	<0.6574	ND	<0.6574	ND

123678HxCDD	0.625	0.1	1.4879	0.00155	<0.625	ND
123789HxCDD	0.6931	0.1	<0.6931	ND	<0.6931	ND
1234678HpCDD	0.5632	0.01	6.2856	0.000655	<0.5632	ND
OCDD	0.7633	0.001	4.2767	4.45E-05	<0.7633	ND
2378TCDF	0.4675	0.1	0.9775	0.001018	<0.4675	ND
12378PeCDF	0.642	0.05	1.2645	0.000659	<0.642	ND
23478PeCDF	0.6132	0.5	1.04855	0.005461	<0.6132	ND
123478HxCDF	0.6015	0.1	2.3201	0.002417	<0.6015	ND
123678HxCDF	0.6329	0.1	2.5632	0.00267	<0.6329	ND
123789HxCDF	0.6512	0.1	0.57475	0.000599	<0.6512	ND
234678HxCDF	0.6877	0.1	2.3671	0.002466	<0.6877	ND
1234678HpCDF	0.7022	0.01	5.3266	0.000555	<0.7022	ND
1234789HpCDF	0.6934	0.01	<0.6934	ND	<0.6934	ND
OCDF	0.7142	0.001	3.3276	3.47E-05	<0.7142	ND
Total				0.01813		ND

Note: (1) CDD/CDF: chlorinated dibenzo-p-dioxin/dibenzofuran, structural formula represents as Fig S10 ; (2) ND: not detectable; (3) I-TEQ = Cout x TEF; (4) TEF: Toxic Equivalent Factors, toxic factors relative to the most toxic congener, 2,3,7,8-tetrachlorodibenzo-dioxin; (5) I-TEQ: International Toxicity Equivalence Quotient, the weighted value of the concentrations of 17 PCDD and PCDF congeners with chlorine in the 2, 3, 7 and 8 positions on the dibenzo skeleton, weighted according their Toxic Equivalent Factors (TEF) relative to the most toxic congener, 2,3,7,8-tetrachlorodibenzo-dioxin.



Structure diagrams of chlorinated dibenzo-p-dioxin/dibenzofuran