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1 **Efficient Elimination of Chlorinated Organics on A**
2 **Phosphoric Acid Modified CeO₂ Catalyst: A Hydrolytic**
3 **Destruction Route**

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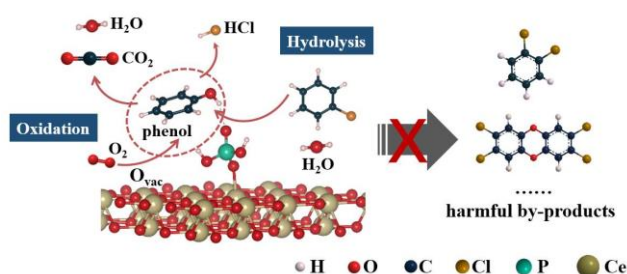
18 **Abstract**

19 The development of efficient technologies to prevent the emission of hazardous
20 chlorinated organics from industrial sources without forming harmful by-products, such
21 as dioxins, is a major challenge in environmental chemistry. Herein, we report a new
22 hydrolytic destruction route for efficient chlorinated organics elimination and
23 demonstrate that phosphoric acid modified CeO₂ (HP-CeO₂) can decompose
24 chlorobenzene (CB) without forming polychlorinated congeners under the industry-
25 relevant reaction conditions. The active site and reaction pathway were investigated,
26 and it was found that surface phosphate groups initially react with CB and water to form
27 phenol and HCl, followed by deep oxidation. The high on-stream stability of the
28 catalyst was due to the efficient generation of HCl, which removes Cl from the catalyst
29 surface and ensures O₂ activation and therefore deep oxidation of the hydrocarbons.

30 Subsequent density functional theory (DFT) calculations revealed a distinctly
31 decreased formation energy of an oxygen vacancy at nearest (V_{O-1}) and next-nearest
32 (V_{O-2}) surface sites to the bonded phosphate groups, which likely contributes to the high
33 rate of oxidation observed over the catalyst. Significantly, no dioxins, which are
34 frequently formed in the conventional oxidation route, were observed. This work not
35 only reports an efficient route and corresponding phosphate active site for chlorinated
36 organics elimination, but also illustrates that rational design of reaction route can solve
37 some of the most important challenges in environmental catalysis.

38 **Keywords:** Chlorinated organics, Phosphate, Hydrolysis destruction, CeO_2 , Dioxin

39 TOC/Abstract Art



40

41 1. INTRODUCTION

42 Chlorinated organics have widespread industrial applications in the manufacture
43 of polyvinyl chloride, pharmaceuticals, herbicides and fungicides ^{1,2}. Certain quantities
44 are also present in the flue gas of municipal solid waste incineration and metal smelting
45 and refining processes ^{3,4}. Such chlorinated compounds are listed by the United States
46 Environmental Protection Agency as environmental priority control pollutants due to
47 their inherent bioaccumulation and potential carcinogenicity ⁵. Therefore, the
48 destruction of these compounds prior to emission is of the utmost importance. In
49 particular, polychlorinated dibenzofurans, biphenyls and hexachlorobenzenes are
50 classified as Persistent Organic Pollutants (POPs) by the Stockholm Convention. These
51 POPs, together with other polychlorinated congeners, are formed as by-products in
52 combustion processes *via* the condensation of chlorinated hydrocarbons, chlorophenols
53 or chlorobenzenes (CBs) in a series of reactions (e.g. Ullmann reaction ⁶) ⁷. These
54 condensation reactions occur especially at 250-450 °C ⁷ on the surface of fly ash ⁸ and
55 industrial catalysts ^{9,10}.

56 The development of stable and selective catalysts for the destruction of chlorinated
57 organics is an active research field of global importance. Commercially viable catalysts
58 must directly oxidize the chlorinated compounds into harmless products without
59 forming polychlorinated side-products. However, the electronegativity of chlorine
60 makes it preferentially adsorb on electrophilic surface sites, e.g. noble metals, oxygen
61 vacancies, Brønsted and Lewis acid sites. This leads to the accumulation of chlorine on
62 the surface and the inhibition of sufficient oxidation. The accumulated chlorine
63 ultimately leads to catalyst chlorination and promotes the formation of harmful
64 polychlorinated by-products, such as dioxins. Condensation reactions can be minimized
65 by operating below 250 °C and so a commercially-viable catalyst should be active in
66 this temperature range.

67 Previously, U_3O_8 ¹¹ and VO_x based catalysts^{12, 13} were shown to be efficient for
68 catalytic destruction of chloroaromatics from industrial exhausts, though both are
69 hazardous materials themselves. Inspired by the Deacon Reaction technology ($4HCl +$
70 $O_2 \rightarrow 2Cl_2 + 2H_2O$)¹⁴, Dai *et al.* have synthesized a RuO_x - TiO_2 - CeO_2 catalyst capable
71 of converting surface-bound Cl to Cl_2 ¹⁵. However, Ru is costly and the activation
72 barrier of Cl recombination on RuO_x has been calculated to be 228 kJ/mol¹⁶, which
73 renders the catalyst inactive at low temperatures. In particular, these catalysts all
74 produce polychlorinated congeners, including dioxin-like by-products^{10, 17, 18}. In
75 addition to direct catalytic oxidation, a hydrolysis route has been considered to be
76 promising for chlorinated organics elimination^{19, 20}. This process is efficient at
77 dechlorinating hydrocarbons and removing chlorine from the catalyst surface, but low-
78 temperature catalysts have not yet been reported.

79 The Gulf Research & Development Company published a patent in 1973 that states
80 rare earth (RE) metal phosphates can hydrolytically dechlorinate aryl halides into the
81 corresponding ring-hydroxylated aryl compounds and HCl⁴. Weckhuysen and co-
82 workers subsequently reported RE oxides, including La_2O_3 , Pr_2O_3 , Nd_2O_3 and CeO_2 ,
83 were active in the hydrolytic destruction of CCl_4 ²¹⁻²⁵. However, based on theoretical
84 investigations²¹, the energy required for the dissociative adsorption of CCl_4 on the most
85 active La_2O_3 was about 192 kJ/mol and that for the hydrolytic regeneration was about

86 180 kJ/mol. Such high energy barriers render the RE catalysts inactive below 300 °C,
87 so are not intrinsically active enough to be of commercial interest.

88 In our previous work, we showed that phosphoric acid treatment is an effective
89 way to etch and modify lanthanide oxides, which provided hydrolytic reactivity in the
90 catalyst ²⁶. Dai *et al.* recently modified CeO₂ nanosheets using an organophosphate
91 precursor, but did not describe any hydrolysis function in this catalyst ^{27, 28}. Herein we
92 explored that phosphoric acid modified CeO₂ nanorods are highly active and stable
93 catalysts for the hydrolytic destruction of chlorobenzene, a model chlorinated organic
94 molecule. Subsequent density functional theory (DFT) calculations and catalyst
95 characterization revealed the origin of the observed activity and a reaction pathway was
96 proposed.

97 **2. EXPERIMENTAL SECTION**

98 **2.1 Catalyst Synthesis**

99 CeO₂ nanorods were synthesized according to previous work ²⁹⁻³¹. The process
100 was as follows: Ce(NO₃)₃·6H₂O (1.736 g) and NaOH (19.2 g) were dissolved in 10 and
101 70 mL of deionized water, respectively. The two solutions were then combined and
102 continuously stirred for 30 min. Then the mixed solution was transferred to a Teflon-
103 lined stainless steel autoclave and hydrothermally treated at 100 °C for 24 h to form the
104 CeO₂ nanorods. The formed solids were recovered by centrifugation and washed with
105 deionized water and ethanol several times, followed by drying at 100 °C for 8 h.

106 Phosphate-functionalized CeO₂ (hereafter denoted as HP-CeO₂) was prepared
107 using a wet impregnation method. CeO₂ nanorods were initially washed with ethanol
108 to introduce surface hydroxyl groups ³², and enhance the anchoring of phosphate groups
109 on the CeO₂ surface. CeO₂ nanorods (1.0 g) and an aqueous solution of H₃PO₄ (0.1 M,
110 25 mL) were mixed at 25 °C and stirred for 1 h. The mixture was then washed with
111 deionized water (2 L) several times until the pH reached *ca.* 7, followed by drying at
112 100 °C overnight.

113 **2.2 Catalytic activity and by-product analyses**

114 Catalytic activity was measured in a fixed-bed reactor, in which 1.0 g of catalyst
115 was loaded into an 8 mm reactor tube and secured in place between plugs of silica wool.
116 The reaction feed consisted of 500 or 200 ppm chlorobenzene, 145 mL/min N₂, 15

117 mL/min O₂ with a gas hourly space velocity (GHSV) at 10000 h⁻¹. The reaction
118 temperature was controlled using a thermocouple placed in the center of the catalyst
119 bed. Catalysts were evaluated over the range 150-250 °C. All catalysts were sieved to
120 40-60 mesh and pre-treated at 300 °C for 1 h in the flow of He before each
121 measurement. The concentration of chlorobenzene, along with CO₂ and CO production,
122 were analyzed on-line using a gas chromatograph (GC, Agilent 6890, America)
123 equipped with a flame ionization detector (FID) preceded by a methanizer, and an
124 electron capture detector (ECD). Experiments with 0.5 vol.% H₂O (CB/H₂O = 1/10)
125 were carried out by feeding a N₂ flow (15 mL/min) through a water saturator at a fixed
126 temperature to achieve a partial pressure of approximately 0.5 vol.%. The water
127 container was kept at 30 °C and the transfer line was set as short as possible so as to
128 prevent condensation.

129 The concentration of Cl⁻ from HCl was measured using an ion chromatograph
130 instrument (Shimadzu LC-20A, Japan) equipped with a Shim-pack IC-A3 adsorption
131 column. In a lab-scale measurement, the establishment of Cl balance during the
132 catalytic oxidation of chloroaromatics is very difficult. The generated HCl
133 preferentially adsorbs on the stainless steel lines of the reactor and leads to very few
134 HCl in the effluent gases. As such, measurements on the HCl production usually require
135 an enrichment process where a 0.0125 mol/L NaOH solution was used to adsorb the
136 HCl for a defined time period of 30 min. The quantitative measurements (even ignoring
137 the error) could only reveal the trend in HCl production for each catalyst.

138 The quantitative identification of gaseous by-products was achieved with a
139 calibrated GC/MS system. The gaseous by-products were sampled from the off-gases
140 in a gas sampling bag (Teflon®FEP, 1 L volume). The sample was the injected by an
141 autosampler (ENTECH 7016), and pre-concentrated according to the EPA method TO-
142 15 (US EPA, 1999) using a pre-concentrator (ENTECH 7200). After the sample gas
143 (400 mL) was pre-concentrated on the trap, the trap was heated and the VOCs were
144 thermally desorbed and refocused on a cold trap. This trap was further heated and the
145 VOCs were thermally desorbed again onto the head of the capillary column. Then, the
146 oven temperature (programmed) increased and the VOCs began to elute and were
147 analyzed by the GC/MS system (Agilent 6890N GC equipped with Agilent 5977B MS)
148 with a DB-624 (60 m × 0.25 mm × 1.4 μm, 6% cyanopropyl-phenyl / 94%

149 dimethylpolysiloxane, Agilent Technologies, USA) capillary column. The GC oven
150 temperature was initially held at 35 °C for 3 min, then increased to 140 °C at the rate
151 of 6 °C/min, finally increased to 220 °C at the rate of 10 °C/min and held at 220 °C for
152 3 min (whereas held at 220 °C for 2 min for post-operation). The mass spectrometer
153 was operated in the electron impact ionization mode using selected ion monitoring
154 (SIM). The ion source temperature was set at 230 °C.

155 The surficial semi-volatiles organic residual on the catalyst surface were extracted
156 using dichloromethane, where 5 mL dichloromethane and 1 g catalyst were mixed in a
157 glass bottle and ultrasonically oscillated in an ice-bath for 30 min. The above process
158 (mixing, oscillation and extraction) was repeated once. The extracted liquid was then
159 transferred into a test-tube and concentrated to 0.5 mL using a nitrogen blower. The
160 liquid was filtered and eventually 0.5 µL of the filtrate were splitless injected into a
161 GC/MS system (the same as used in the qualitative identification) for analyses.

162 In dioxin measurements, the off-gas from CB oxidation was collected by
163 absorption in a 100 mL toluene for 10 h. The total extract was then concentrated to
164 about 1 mL by rotary evaporation and exchanged by 10 mL hexane for further pre-
165 treatment. Both pre-treatment and determination of PCDD/F were conducted according
166 to EPA method 1613 (US EPA, 1994). Sample clean-up involved percolation through
167 a multi-silica gel column and a basic-alumina column. Then, the eluate again was
168 concentrated, while being blown by nitrogen to approximately 20 µL. Finally, the
169 cleaned solution was spiked with known amounts of a Method 1613 standard solution.
170 The recovery efficiency of each internal standard was established at between 60% and
171 115%, conforming to the required 40–130%. All analyses were performed by
172 HRGC/HRMS on a 6890 Series gas chromatograph (Agilent, USA) and coupled to a
173 JMS-800D mass spectrometer (JEOL, Japan). A DB-5MS (60 m × 0.25 mm I.D., 0.25m
174 film thickness) capillary column was used for separation of the PCDD/F congeners.
175 The GC temperature program was optimized as follows: splitless injection of 2 µL at
176 150 °C, initial oven temperature of 150 °C for 1 min, then increased at 25 °C/min to
177 190 °C, finally increased at 3 °C/min to 280 °C and held for 20 min. Helium was used
178 as the carrier gas. The mass spectrometer was operated in the electron impact ionization
179 mode using selected ion monitoring (SIM). Electron energy was set to 38 eV. Source
180 temperature was 280 °C. The mass system was tuned to a minimum resolution of 10,000

181 (10% valley) using perfluorokerosene (PFK) as lock mass. The detailed quantitative
182 determination of PCDD/Fs was referred to US EPA method 1613.

183 **2.3 Catalyst Characterization**

184 P loading was analyzed using a Perkin Elmer Optima 2100 DV Inductively
185 Coupled Plasma Optical Emission Spectrometer (ICP-OES). The sample (*ca.* 10 mg)
186 was digested in 5 mL of 4 M HCl, 1 mL concentrated HNO₃, and 2 mL of 30 v/v%
187 H₂O₂, then sonicated for ten minutes, and placed into a 50 °C water bath for 12 h.
188 Thereafter, the sample was diluted to 10 mL of total solution.

189 Transmission electron microscopy (TEM) was carried out to monitor the structural
190 changes of CeO₂ using a FEI TECNAI G2 20 XTwin HRTEM working at an
191 accelerating voltage of 200 kV. The samples for TEM measurements were drop-casted
192 onto carbon coated copper grids from an ethanol suspension.

193 *In situ* FTIR was conducted by using a Nicolet 6700 FTIR spectrometer equipped
194 with a MCT detector. The FTIR cell (Harrick) had CaF₂ windows allowing the catalyst
195 to be heated to 400 °C at atmospheric pressure. In each measurement, the catalyst was
196 pretreated in a flow of He (99.99%, 30 mL/min) at the temperature of 350 °C for 1 h
197 and then allowed to cool to room temperature. The background spectrum, recorded
198 under flowing He, was subtracted from the sample spectrum. For H₂O adsorption
199 measurements, the H₂O was introduced by saturating the N₂ carrier gas through a
200 Dreschel Bottle containing deionized H₂O (N₂ was pre-dehydrated using molecular
201 sieve). For FTIR studies of CB oxidation, 200 ppm of CB, O₂ (10 vol.%), 2000 ppm
202 H₂O (injected using a micro injection pump) and the N₂ carrier gas were introduced at
203 150 °C for 30 min. In NH₃-IR, the N₂ carrier gas with 5 vol.% NH₃ was purged through
204 the catalyst at 150 °C for 30 min. The spectra (average of 64 scans at 4 cm⁻¹ resolution)
205 were simultaneously recorded at different times in each run. The final differential
206 sample spectra were calculated by applying the Kubelka–Munk function.

207 X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra-
208 DLD photoelectron spectrometer, using monochromatic Al K α radiation at 144 W (12
209 mA \times 12 kV) power. High resolution and survey scans were performed at pass energies
210 of 40 and 160 eV respectively. Magnetically confined charge compensation was used
211 to minimize sample charging and the resulting spectra were calibrated to the C(1s) line
212 at 284.8 eV.

213 Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-
214 2500 powder diffractometer with Cu K α radiation source (operated at 40 kV and 40
215 mA, wavelength 0.15418 nm), the data were collected over the 2θ range from 10° to
216 80° .

217 O₂ temperature programmed desorption (O₂-TPD) was carried out on a custom-
218 built apparatus (TP-5089, Tianjin Xianquan Co., Ltd., China), connected to a mass
219 spectrometer (HIDEN QGA, UK). 100 mg of catalyst was first pretreated in a 5 %
220 O₂/He gas flow at 350 °C for 1 h and then cooled to room temperature. After purging
221 pure He for 1 h, the catalyst was heated to 800 °C at the rate of 10 °C/min. The signals
222 of desorbed O₂ was recorded using a MS.

223 NH₃ temperature programmed desorption (NH₃-TPD) was carried out on a
224 custom-built apparatus (TP-5089, Tianjin Xianquan Co., Ltd., China), connected to a
225 mass spectrometer (HIDEN QGA, UK). 100 mg of catalyst was first pretreated in a He
226 gas flow at 350 °C for 1 h and then cooled to room temperature. Afterwards, a flow of
227 6 % NH₃/He was introduced for 30 min. Then the gas flow was switched back to pure
228 He for 30 min. The catalyst was reheated to 600 °C at the rate of 10 °C/min. The signals
229 of desorbed NH₃ was recorded using a MS.

230 **2.4 DFT calculations**

231 All the first-principles calculations were based on Hubbard-corrected density-
232 functional theory (DFT+U) with $U = 5.0$ eV for Ce using the Vienna *ab initio*
233 simulation package (VASP). The Perdew-Burke-Ernzerhof generalized gradient
234 approximation (PBE-GGA) exchange-correlation potential was used, and ionic
235 potentials were treated by the projector-augmented wave (PAW) pseudopotential
236 method. The kinetic energy cutoff was set to 400 eV. The Brillouin zone integration
237 was performed with a single gamma point for geometric optimization. The convergence
238 criteria for the electronic energy and the geometry relaxation were set to 10^{-4} eV and
239 0.03 eV/Å, respectively. A vacuum layer of at least 15 Å thick was added in the slab
240 cell along the direction perpendicular to the surface in order to avoid the artificial
241 interactions between the model and its periodic images. The CeO₂(110) surface was
242 modeled with a supercell (4×3) approach by periodically repeated slabs. Optimized
243 model of CeO₂ were constructed by removing single oxygen atom from CeO₂ supercell
244 to introduce oxygen vacancies (**Figure S1**). During geometry optimization, the atoms

245 in the top two layers of CeO₂ slab were allowed to relax while atoms in the bottom two
 246 layers were fixed in their optimized bulk positions. The model of HP-CeO₂ was
 247 constructed by a phosphate group adsorbed on the CeO₂ surface (indicated as
 248 H₂PO₄/CeO₂), with corresponding molecule adsorbed on the phosphate group. During
 249 geometry optimization, the atoms in the two layers of CeO₂ slab were fixed in their
 250 optimized surface positions.

251 The adsorption energy (E_{ad}) of molecular adsorbates on the substrate was
 252 calculated as:

$$253 \quad E_{ad} = E_{sub} + E_{mol} - E_{tot}$$

254 where E_{sub} , E_{mol} and E_{tot} are the total energies of optimized clean substrates, molecular
 255 adsorbates in the gas phase and substrates with molecular adsorbates, respectively.

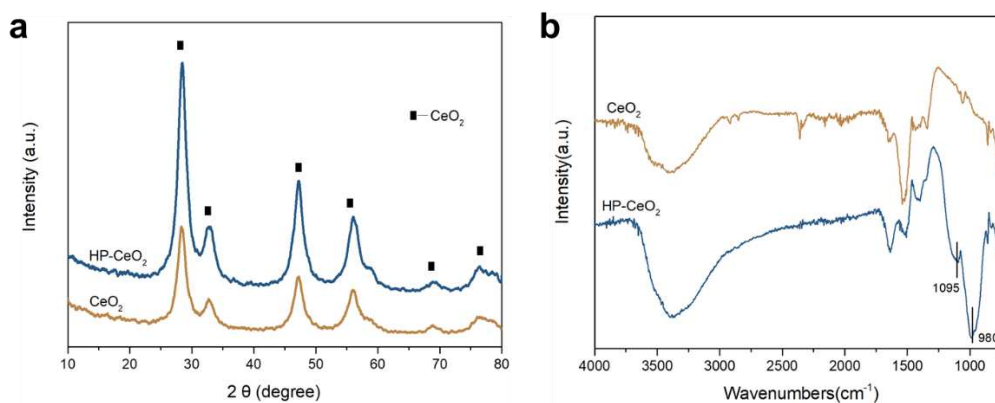
256 The formation energy of an oxygen vacancy (E_v) was calculated by:

$$257 \quad E_v = E_{vac} + \frac{1}{2} E_{O_2} - E_{tot}$$

258 where E_{vac} and E_{tot} are the total energies of the model with and without an oxygen
 259 vacancy on the CeO₂ surface. And E_{O_2} is the total energy of an oxygen molecule in the
 260 gas phase. A positive value for E_v means that energy is needed to create an oxygen
 261 vacancy.

262 3. RESULTS AND DISCUSSIONS

263 3.1 Phase Identification

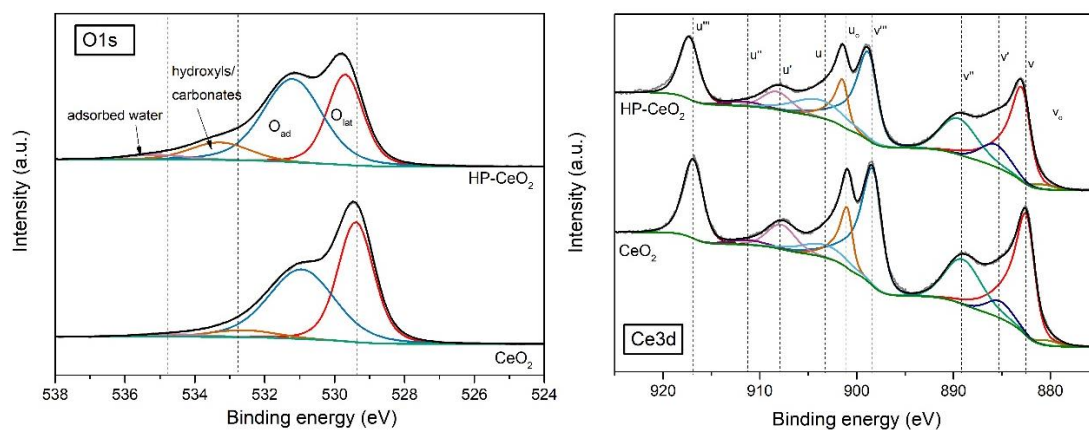


264
 265 **Figure 1.** (a) X-ray powder diffraction patterns and (b) IR spectra of CeO₂ and HP-CeO₂ catalysts

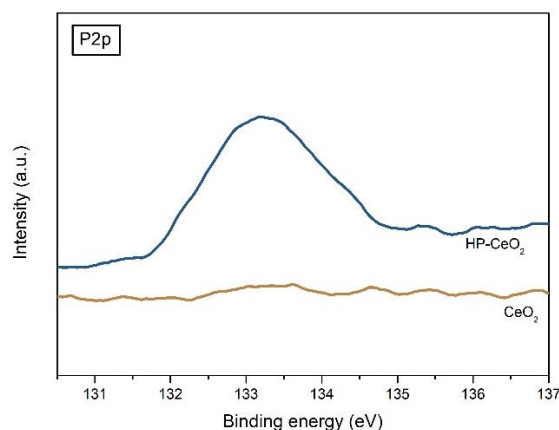
266 As identified by XRD analyses (**Figure 1**), both CeO₂ and HP-CeO₂ catalysts
 267 could be indexed to the face-centered cubic fluorite structure with space group Fm-3m
 268 (JCPDS 34-0394), and no evidence of phosphate-related structures and bulk CePO₄ was

269 observed. According to ICP-OES results, the loading of P in the HP-CeO₂ was
 270 measured at approximately 6.64 g/kg_{catalyst} (0.6 wt%). This corresponds to
 271 approximately 1.18 P-atoms per nm² of catalyst and essentially represents a surface
 272 unsaturation as the theoretical quantity of Ce atoms on preferentially exposed (110)
 273 surface in CeO₂ nanorod^{30, 33} is approximately 19.4 Ce-atoms per nm²³⁴. Obviously,
 274 bulk phosphate (M_xPO₄) would be not generated in the HP-CeO₂ as it only forms under
 275 sufficiently high P loading³². TEM (**Figure S2**) and surface area analyses (**Table S1**)
 276 suggested the modification with H₃PO₄ did not distinctly change the crystal
 277 morphology and surface area of CeO₂ nanorods.

278 To confirm the successful anchoring of phosphate groups, FTIR was carried out
 279 and the spectra are shown in **Figure 1(b)**. In comparison with CeO₂, HP-CeO₂ exhibited
 280 two additional bands. The bands located at 980 and 1095 cm⁻¹ were assigned to
 281 symmetric stretching $\nu_s(\text{P-O})$ and asymmetric stretching $\nu_{as}(\text{P-O})$ of PO₄ entities,
 282 respectively^{35, 36}, confirming the immobilization of phosphate groups on the CeO₂
 283 surface. No characteristic bands for P-O-P species ($\nu_s = 759\text{-}767$ cm⁻¹ and $\nu_{as} = 925\text{-}$
 284 934 cm⁻¹³⁷) were observed, which indicated that the phosphate species is present as an
 285 orthophosphate rather than a pyrophosphate. A broad band at 3000 - 3650 cm⁻¹ was
 286 observed in the CeO₂ and HP-CeO₂. This could originate from the hydroxyl groups
 287 associated to Ce³⁺ sites³⁸ or the P-OH groups³².



288



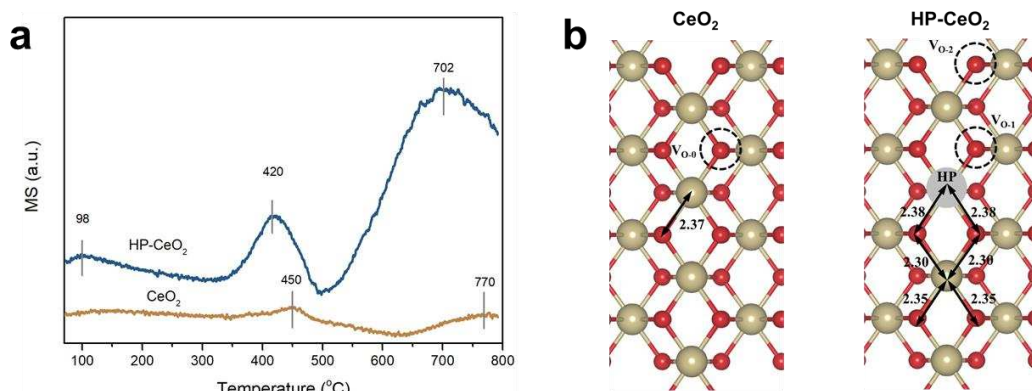
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290 **Figure 2.** Ce3d, O1s and P2p XPS spectra of CeO₂ and HP-CeO₂ catalysts

291 The chemical nature and composition of surface species of CeO₂ and HP-CeO₂
 292 were probed *via* XPS analyses (see **Figure 2**), which revealed CeO₂ with four O 1s XPS
 293 peaks centered at 529.7, 531.2, 533.3, 535.2 eV, corresponding to lattice oxygen of the
 294 ceria, oxygen defect sites, hydroxyl or carbonate groups and adsorbed molecular water,
 295 respectively^{39, 40}. The Ce 3d spectrum revealed characteristic u₀, u', v₀, v' signals for
 296 Ce³⁺ and u''', u'', u, v''', v'', v peaks for Ce⁴⁺³⁰. It should be noted the presence of
 297 molecular water is, understandably, contentious given the samples are analyzed under
 298 vacuum where the water would be expected to be lost. We believe a more plausible
 299 explanation for this signal is due to changes in the background and peak broadening
 300 due to a greater defect density as implied by the Ce(IV)/Ce(III) ratio in the Ce(3d)
 301 spectra (**Table S1**).

302 HP-CeO₂ exhibited similar oxygen species, but the concentration of each species
 303 was different. In particular, the O species at 533 eV was much more pronounced than
 304 in CeO₂. This species has previously been assigned to P-OH and M-O-P species⁴¹ and
 305 indicates the presence of phosphates at the surface. Additionally, the oxygen vacancy
 306 species at 531 eV was also more prominent in HP-CeO₂, especially when compared to
 307 the Ce-O lattice species at 529 eV. This suggested that the presence of phosphate groups
 308 on the surface promotes oxygen vacancy formation, although M-OH species are also
 309 found in this region. The P 2p XPS spectrum only revealed one peak, centered around
 310 133.2 eV, further confirming phosphate species is present on the catalyst surface.

311 **3.2 Redox and acidic properties analyses**

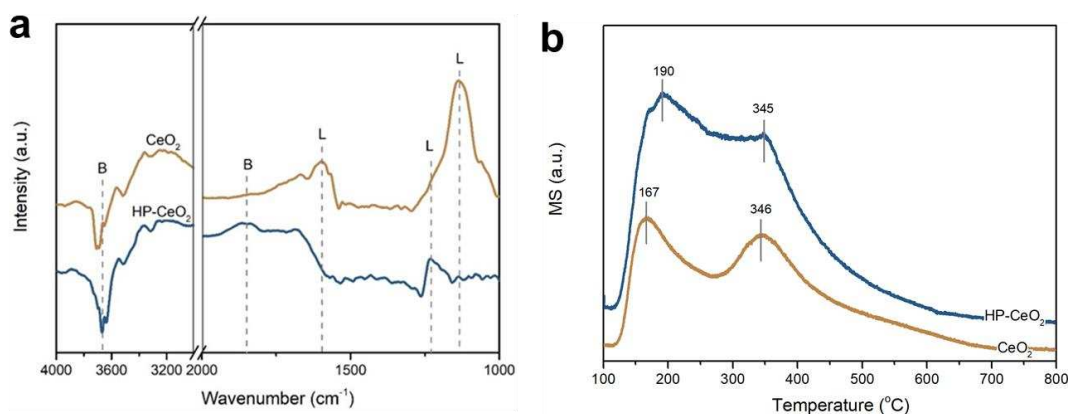


312

313 **Figure 3.** (a) O₂-TPD, (b) DFT calculations profiles of CeO₂ and HP-CeO₂ catalysts. Atoms with
 314 red and yellow colors represent oxygen and cerium atoms, respectively.

315 To gain an insight into the redox properties of CeO₂ and HP-CeO₂, O₂-TPD was
 316 conducted. In general, the desorbed oxygen species can be categorized into
 317 chemisorbed oxygen species (α -O) at 100-300 °C, superficial lattice oxygen (α' -O,
 318 including the nonstoichiometric oxygen α'' -O) at 300-600 °C and bulk lattice oxygen
 319 (β -O) above 600 °C²⁶. As depicted in **Figure 3(a)**, CeO₂ exhibited two main desorption
 320 peaks with maxima at 450 °C and 770 °C. The former peak was assigned to the
 321 superficial lattice oxygen generated from grain boundaries and dislocations, and the
 322 latter was related to the bulk oxygen desorbed *via* vacancy migration inwards with the
 323 increase of temperature^{30, 39}. For HP-CeO₂, the oxygen desorption peaks both
 324 strengthened and shifted to a lower temperature range, and a new peak located at 98 °C
 325 appeared, which corresponded to oxygen chemisorbed on the surface of oxygen
 326 vacancies (α -O)⁴². In comparison with CeO₂, HP-CeO₂ exhibited enriched α' -O and β -
 327 O species and extra α -O species, revealing an enhanced oxidation ability by acid
 328 modification.

329 In order to elucidate the cause for such an enhancement, DFT calculations were
 330 carried out. According to DFT calculations (**Figure. 3(b)**), after the deposition of the
 331 phosphate, the formation energy of a CeO₂ oxygen vacancy at nearest (V_{O-1}) and next-
 332 nearest (V_{O-2}) sites to the phosphate groups was only 0.46 eV and 0.77 eV, respectively,
 333 whereas for stoichiometric CeO₂, this energy was 2.11 eV. This result is consistent with
 334 the XPS O1s analyses (**Figure. 2(a)**), and explained why the HP-CeO₂ exhibited labile
 335 active oxygen species in the catalyst.



336

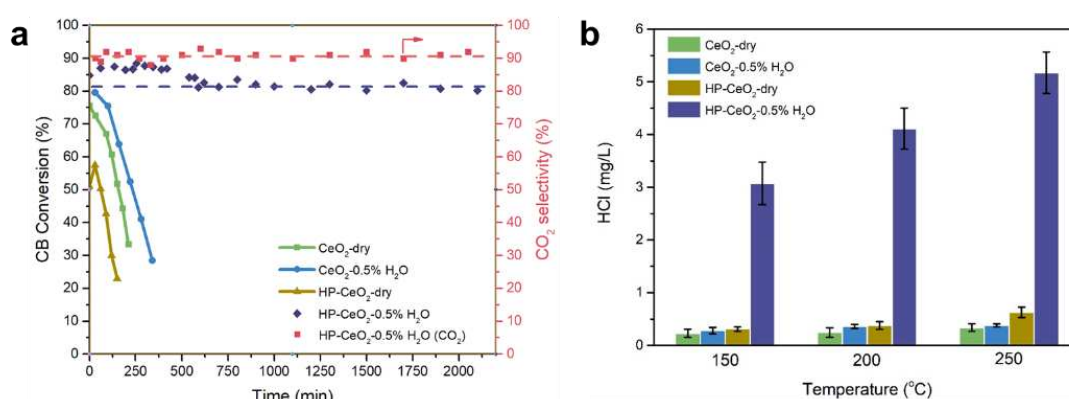
337 **Figure 4.** (a) NH₃-IR and (b) NH₃-TPD profiles of CeO₂ and HP-CeO₂ catalysts

338 The acidic properties of CeO₂ and HP-CeO₂ were evaluated using NH₃-IR and
 339 NH₃-TPD. As shown in **Figure 4(a)**, for the CeO₂, an intense band at 1135 cm⁻¹ and a
 340 weaker one at 1595 cm⁻¹ were observed. Both bands were assigned to adsorbed NH₃ on
 341 Lewis acid sites⁴³. The negative band located at 3680 cm⁻¹ could be assigned to the OH
 342 stretch of Brønsted acid sites due to the interaction of surface hydroxyls with NH₃^{44,45}.
 343 HP-CeO₂ exhibited two additional bands at 1235 cm⁻¹ and 1850 cm⁻¹, while the features
 344 at 1135 and 1595 cm⁻¹ disappeared. The band at 1235 cm⁻¹ was related to Lewis acid
 345 sites while 1850 cm⁻¹ was associated with Brønsted acid sites⁴³. The negative band at
 346 3680 cm⁻¹ was more intense in HP-CeO₂ than that in the CeO₂. These data suggested
 347 that acid modification resulted in an enhancement of Brønsted acid sites at the expense
 348 of Lewis acid sites. The concentration of acid sites was measured using NH₃-TPD. As
 349 shown in **Figure 4(b)**, HP-CeO₂ exhibited two more intense NH₃ desorption peaks at
 350 190 °C and 345 °C, which corresponded to weak acid sites that originated from the
 351 desorption of NH₃ adsorbed on Ce^{4+/3+} and surface acidic hydroxyl groups (mainly
 352 originated from phosphate groups)²⁷. The acid site density of CeO₂ was measured at
 353 0.205 mmol/g, which was two-fold lower than that of HP- CeO₂ (0.523 mmol/g).

354 3.3 Catalytic activity measurements

355 **Figure 5 (a)** illustrated the stability tests of CB catalytic oxidation over CeO₂ and
 356 HP-CeO₂ catalysts under the dry and humid conditions. It was noted that, in dry
 357 conditions, both HP-CeO₂ and CeO₂ were initially active but rapidly deactivated at 250
 358 °C; the CB conversion rate both decreased to less than 30% after 200 min. In
 359 comparison, the introduction of excessive H₂O vapor (CB/H₂O = 1/10) yielded a stable
 360 CB conversion for HP-CeO₂. Approximately 90% CO₂ selectivity was obtained in the
 361 catalyst. Such a high stability was confirmed by lowering the conversion to

362 approximately 40% (by dropping the reaction temperature to 230 °C). At this
 363 temperature, the conversion of CB was unchanged after 40 h on-stream (**Figure. S3**).
 364 **Figure 5(b)** illustrated the HCl production in the off-gas at different temperatures.
 365 Although a full Cl balance was not possible to calculate due to the high affinity of HCl
 366 for the inside of the stainless steel reactor, the HCl production over HP-CeO₂ was nearly
 367 ten-fold higher when water vapor was present; this was also the case at reaction
 368 temperatures of 150 and 200 °C. These findings strongly suggested that the presence of
 369 water facilitates chlorine desorption (as HCl), thus greatly enhancing the stability by
 370 replenishing active sites. The accumulation of chlorine on the catalyst surface after
 371 reaction was also measured using ion chromatography. It was noted that under the dry
 372 condition, 8.25 g/kg_{catalyst} and 10.36 g/kg_{catalyst} for HP-CeO₂ and CeO₂, respectively, of
 373 chlorine was present in the post-reaction samples, while in the presence of water vapor,
 374 the residual 7.56 g/kg_{catalyst} of chlorine was measured for CeO₂, but only 2.36 g/kg_{catalyst}
 375 for HP-CeO₂. Additionally, the content of P after stability measurement at 250 °C was
 376 also measured, and the results showed the P content was decreased by 5.9%, suggesting
 377 that significant P were retained after tests.

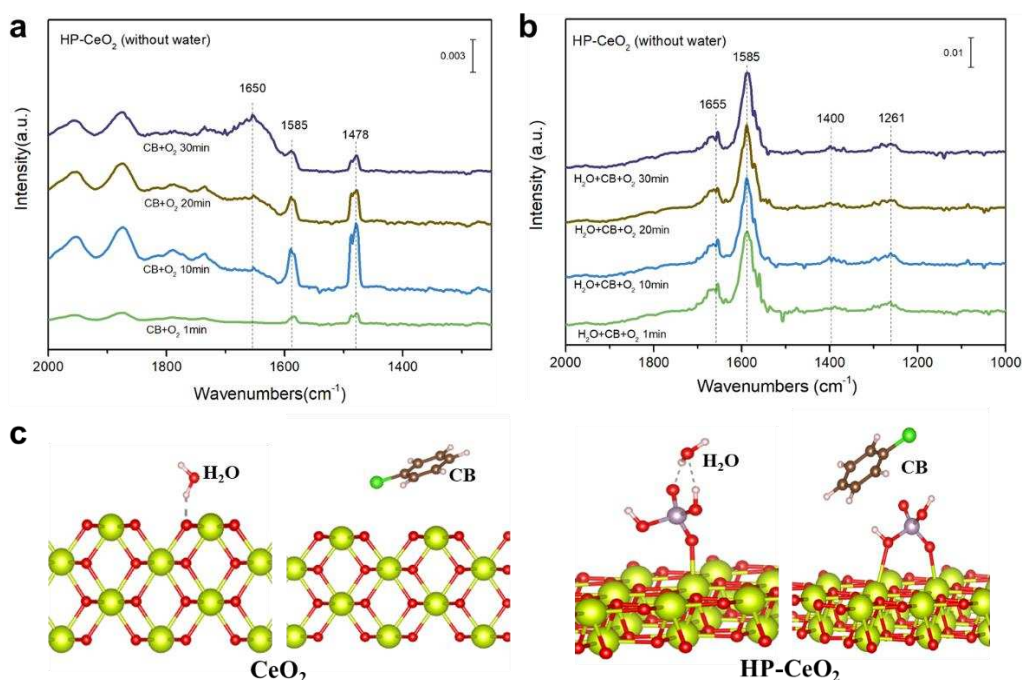


378
 379 **Figure 5. (a)** Stability measurements of CeO₂ and HP-CeO₂ catalysts with and without water vapor
 380 at 250 °C; **(b)** HCl productions of CeO₂ and HP-CeO₂ catalysts with and without water vapor at 250
 381 °C. Reaction conditions: GHSV = 10,000 mL/(g h), 500 ppm chlorobenzene, 0.5 % H₂O, N₂ flow
 382 rate = ca. 145 mL/min, O₂ flow rate = ca. 15 mL/min.

383 3.4 *in-situ* FT-IR analyses

384 To gain an insight into the reaction mechanism, *in-situ* FTIR analyses were
 385 conducted. **Figure 6(a)** showed the spectra collected at 150 °C under the dry stream of
 386 CB and O₂ over HP-CeO₂. The bands at 1585 and 1478 cm⁻¹ are assigned to the C=C
 387 degenerate stretching vibrations of the aromatic ring⁴⁶. The bands at 2000-1700 cm⁻¹

388 were associated with harmonics (combinations and overtones) of out-of-plane C-H
 389 deformation modes⁴⁷, with side-on adsorption geometry, and originate from the π -type
 390 aromatic clouds on electron-withdrawing centers of the metal oxides⁴⁸. It was noted
 391 that these characteristic bands for CB adsorption increased in the first 10 min and then
 392 gradually decreased. In general, CB adsorption on the CeO₂ surface could be through a
 393 π -complex between surface Ce⁴⁺ and aromatic ring⁴⁹. Such a complex is formed both
 394 on dehydroxylated and fully hydroxylated surface via either the Ce⁴⁺... π -electron
 395 interaction or dual-site interaction (OH... π -electron and OH...Cl). In this work, since
 396 the CeO₂ nanorods were washed by ethanol, initially, the abundant surface hydroxyls
 397 would provide sufficient sites for dual-site CB adsorption, resulting in the formation of
 398 phenolate species. Over time, these hydroxyls were gradually consumed and the
 399 phenolates were oxidized. A broad band centered at 1650 cm⁻¹ started to grow and
 400 dominated after 30 min. This band was assigned to vibrations of CB adsorbed on the
 401 surface oxygen vacancies⁵⁰, indicating that CB adsorption on the oxygen vacancies
 402 began to dominate the process after the hydroxyls had been fully consumed. The CeO₂
 403 catalyst revealed similar FTIR spectra to HP-CeO₂ (**Figure S4**), suggesting that without
 404 H₂O, the adsorption of CB on these two catalysts were analogous, which is consistent
 405 with their activity measurements (**Figure 5**).

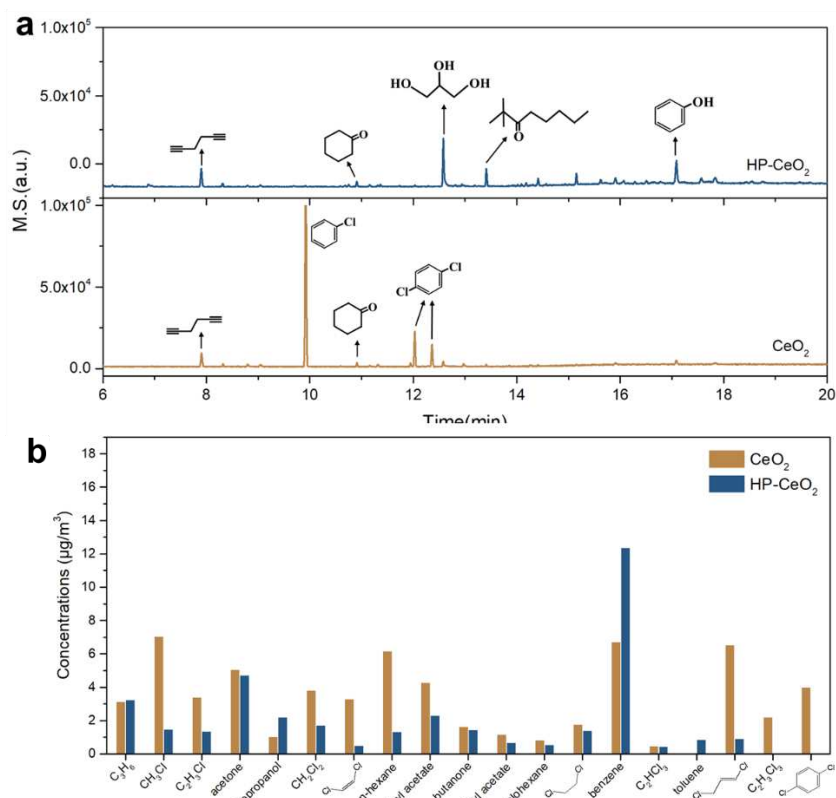


406
 407 **Figure 6.** *in-situ* FTIR spectra of CB oxidation over HP-CeO₂ at 150 °C (a) without or (b) with
 408 H₂O; (c) optimized models of adsorbed H₂O and C₆H₅Cl molecule at CeO₂ and HP-CeO₂ surfaces.

409 **Figure 6(b)** illustrates the spectra collected from CB oxidation with the addition
410 of water vapour. It was noted that the peak located at 1585 cm^{-1} dominated the spectra,
411 suggesting that the CB was only adsorbed via the π -type interaction with surface
412 hydroxyl groups. Furthermore, the harmonics in the range of $2000\text{-}1700\text{ cm}^{-1}$ were not
413 observed, which indicated that in the presence of H_2O , the CB did not adsorb on the
414 surface oxygen vacancies. According to DFT calculations (**Figure 6(c)** and **Table S2**),
415 the co-adsorption energy of CB and O_2 on an oxygen vacancy (O_{vac}) of CeO_2 nanorods
416 was 2.37 eV . This indicated that the CB would preferentially adsorb on an O_{vac} in the
417 presence of O_2 , which then dissociate to leave Cl, inhibiting further activation of O_2
418 and leading to catalyst deactivation. After acid modification and in the presence of H_2O ,
419 CB was found to preferentially co-adsorb with H_2O on the phosphate groups with a
420 calculated co-adsorption energy of 2.77 eV . This was even larger than the sum of the
421 individual adsorption energies of CB (0.5 eV) and H_2O (0.63 eV) and suggested that
422 on the HP- CeO_2 catalyst with H_2O present, CB adsorption mainly occurs on the
423 phosphate group rather than on the O_{vac} . Such a co-adsorption was shown to induce a
424 hydrolysis reaction and converted the CB into phenol (band at 1585 cm^{-1} in **Figure 6(b)**)
425 and HCl (**Figure 5(b)**), leading to excellent stability in the hydrolytic destruction of
426 CB.

427 **3.5 By-products analyses**

428 Any residual compounds on the catalyst were extracted using dichloromethane,
429 and then injected into GC/MS system for analyses. As shown in **Figure 7(a)**, after the
430 $250\text{ }^\circ\text{C}$ with H_2O , HP- CeO_2 did not retain chlorinated organics on the surface. Only
431 trace amounts of alcohols and phenol species were detected, further suggesting the
432 occurrence of hydrolysis reaction on the catalyst. As for the CeO_2 , distinct
433 dichlorobenzene was detected, which could be converted into chlorophenol and
434 subsequently condense to form the PCDD/Fs⁵¹.



435

436 **Figure 7.** (a) Coke accumulation on the catalyst surface and (b) gaseous compounds in the effluent
 437 in the catalytic oxidation of CB over HP-CeO₂ and CeO₂ in the presence of H₂O stream (Note: other
 438 tiny peaks unlabeled present for Si-O analogous came from the chromatographic column or long-
 439 chain organics).

440 The organic by-products in the off-gas were quantitatively identified. This was
 441 conducted through capturing the off-gas in an airbag, and analyzed using a calibrated
 442 GC/MS system. As shown in **Figure 7(b)**, approximately 19 types of organic products
 443 were detected in the off-gas. The HP-CeO₂ at 250 °C test with H₂O exhibited fewer
 444 chlorinated organics (less than 8 µg/m³) in comparison with the CeO₂ (about 30 µg/m³).
 445 In particular, this catalyst did not generate dichlorobenzene in the off-gas where the
 446 CeO₂ produced 4.11 µg/m³ *p*-dichlorobenzene, which would be transferred to
 447 chlorophenols, leading to the condensation reaction forming dioxins. Indeed, after
 448 being subjected to 17 toxic dioxins measurement (see **Table S3**), the CeO₂ generated
 449 about 12 kinds of dioxin species in the off-gas (note: the surficial accumulation of
 450 dioxin was negligible), but none of the dioxins were detected in the HP-CeO₂.
 451

452 **ASSOCIATED CONTENT**

453 **Supporting Information**

454 TEM images, catalysis physical properties, stability test, additional FTIR analyses,
455 DFT calculations and dioxin measurements are in the supplemental section. This
456 material is available free of charge via the Internet at <http://pubs.acs.org>.

457 **ACKNOWLEDGEMENT**

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