

# Non-Innocent Role of the Ceria Support in Pd-Catalyzed Halophenol Hydrodehalogenation

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**ABSTRACT:** The hydrodehalogenation (HDH) of halophenols is efficiently catalyzed by palladium supported on high-surface ceria (Pd/ CeO<sub>2</sub>) under mild conditions (35 °C, 1 atm H<sub>2</sub>). A combination of NMR, diffuse reflectance infrared Fourier transform spectroscopy, Raman spectroscopy, and XPS studies and HDH kinetics of substituted halobenzenes suggests that the reaction proceeds mainly *via* a sequence of dissociative adsorption of phenolic hydroxyl onto the support, oxidative addition of the C-halogen bond to Pd, and reductive elimination to give phenol and hydrogen halide. The dissociative adsorption of the -OH group onto oxygen vacancies of the ceria support results in an electron-rich intermediate that facilitates the turnover-limiting reductive elimination step. In contrast, the direct pathway catalyzed by Pd without dissociative adsorption of the reactants on the support takes place at a slower rate. The mechanistic



insights gained in this study were used to modify the reaction conditions for enabling HDH of recalcitrant halides such as fluorides and iodides.

**KEYWORDS:** hydrodehalogenation, dissociative adsorption, oxygen vacancies, cerium oxide, redox active support, palladium, carbon-halogen bond activation

### ■ INTRODUCTION

Recent studies have shown that the reducible CeO<sub>2</sub> support plays an active role in metal-catalyzed hydrogenation and hydrodeoxygenation of phenols and lignin model compounds.<sup>1-11</sup> Dissociative adsorption of the phenolic hydroxyl on the CeO<sub>2</sub> surface yields phenoxy groups activated at Lewis acidic cerium centers that provide high reactivity toward ring hydrogenation at ambient  $H_2$  pressure.<sup>12,13</sup> For ringsubstituted phenols, the reaction with H<sub>2</sub> may lead to other conversions in addition to ring hydrogenation. For example, methoxy groups in compounds such as guaiacol or eugenol may be cleaved from the ring via hydrodemethoxylation, a pathway that competes with the dearomatization reaction.<sup>8,14</sup> Interestingly, when using  $Pd/CeO_2$  as the catalyst, the hydrodemethoxylation selectivity of guaiacol increases with decreasing H<sub>2</sub> pressure.<sup>14</sup> This selectivity dependence on pressure is not observed with Pd supported on other materials, such as activated carbon, and is attributed to the interaction between the hydroxyl group of the phenolic substrates and the  $CeO_2$  support at the Pd-CeO<sub>2</sub> interface.

Substituted phenolics are a common motif in a variety of chemical commodities. For example, halophenols are widely used as synthetic building blocks, pesticides, fungicides, and wood preservers and are also common pollutants.<sup>15–17</sup>

Although Pd/CeO<sub>2</sub> catalyzes halogen removal from aromatics *via* hydrodehalogenation (HDH),<sup>18–24</sup> it is not clear how the presence of the hydroxyl group in halophenols affects this reactivity or if it can also induce an alternative dearomatization pathway as is the case with methoxyphenols.

In this work, we explored the effect of hydroxyl on the Pd/ $CeO_2$ -catalyzed HDH of halophenols. We established that analogous to the hydrogenation of phenol and alkoxyphenols, the –OH group enhances the rate of HDH compared to non-hydroxylated substrates by dissociatively adsorbing onto the support. The effect of this mode of binding on the reaction kinetics is explained in terms of the overall reaction mechanism.

# **EXPERIMENTAL SECTION**

**Reagents.** Cerium(III) nitrate hexahydrate  $(Ce(NO_3)_3 \cdot 6H_2O)$  and palladium(II) acetate  $(Pd(O_2CCH_3)_2)$  were

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purchased from Sigma-Aldrich. 4-Chlorophenol, 4-bromophenol, 4-iodophenol, 1-chloro-4-fluorobenzene, 4-chlorotoluene, 4-chloroanisole, 4-chloroaniline, hydriodic acid (57 wt %), and 1 wt % Pd on carbon were purchased from Aldrich. 4-Bromo-2-chlorophenol was purchased from Acros Organics. 4-Bromo-3-chlorophenol and 2-bromo-4-chlorophenol were purchased from Alfa Aesar. Hexane (HPLC grade), sodium iodide, sodium bromide, hydrochloric acid, and ethanol were purchased from Fisher. Benzene- $d_6$  was purchased from Cambridge Isotope Laboratories. Sodium hydroxide (NaOH) pellets and hydrobromic acid (48 wt %) were obtained from Fisher Scientific. Pluronic P104 was obtained from BASF. All chemicals were used as received without further purification.

**Synthesis of High-Surface-Area Ceria.** This material was prepared following our previously published method.<sup>11</sup> In a typical synthesis,  $Ce(NO_3)_3 \cdot 6H_2O$  (8.80 g, 20.3 mmol) and the nonionic block copolymer surfactant Pluronic P104 (10.1 g, 1.71 mmol) were dissolved in ethanol (200 mL) with vigorous stirring (800 rpm) for 3 h. The solution was cast into a large crystallization dish and placed into an oven preheated at 65 °C for evaporation. After 12 h, the gel was placed into a preheated (150 °C) oven for an additional 12 h. The yellow powder was calcined in air at 450 °C for 4 h with a ramp rate of 1 °C min<sup>-1</sup>.

**Synthesis of Ceria Nanorods.** This material was prepared following a previously published method.<sup>25</sup> An aqueous solution of  $Ce(NO_3)_3$ · $6H_2O$  (0.4 M, 6.96 g, 40 mL) and NaOH (10.3 M, 115.2 g, 280 mL) was mixed and kept under stirring (30 min) at r.t. The solution was transferred into a Teflon-lined stainless-steel autoclave for hydrothermal treatment in an oven (100 °C for 24 h). The precipitate was separated by centrifugation and washed several times with deionized (DI) water and ethanol. The obtained precipitate was dried under vacuum at r.t. and then calcined at 450 °C for 4 h with a ramp rate of 1 °C min<sup>-1</sup>.

**Synthesis of Silica.** This material was prepared following a previously published method.<sup>26</sup> Hexadecyltrimethylammonium bromide (5.0 g, 13.7 mmol) was dissolved in DI water (2.4 L) followed by addition of NaOH (2 M, 17.5 mL). The solution was stirred for 1 h at 80 °C. Tetraethyl orthosilicate (25.0 mL, 113 mmol) was then added dropwise to the solution over 10–12 min. Stirring was continued for 2 h at 80 °C. The solution was filtered, washed with abundant water and methanol, vacuum-dried overnight, and then calcined at 550 °C for 6 h with a ramp rate of 1 °C min<sup>-1</sup>.

**Synthesis of Pd/M<sub>x</sub>O<sub>2</sub>.** The supported Pd catalysts were prepared by incipient wetness impregnation with a 1 wt % Pd loading relative to the mass of the supports. In a typical synthesis,  $Pd(O_2CCH_3)_2$  (0.0419 g, 0.187 mmol) was dissolved in acetone (4.0 mL). The support (2.00 g) was placed in a mortar and impregnated with the Pd solution in 0.2 mL increments. After each impregnation step, the catalyst was mixed thoroughly with a pestle until seemingly dry. The material was calcined at 350 °C for 2 h with a 2.5 °C min<sup>-1</sup> ramp rate and then reduced under flowing hydrogen at 350 °C for 2 h with a 2.5 °C min<sup>-1</sup> ramp rate. The flow of hydrogen gas was set at 0.25 mL s<sup>-1</sup>.

Synthesis of Sodium 4-Chlorophenoxide. A NaOH solution (5.1 mmol in 20 mL methanol) was added dropwise to a 4-chlorophenol (4-Cl-PhOH) solution (5.0 mmol in 15 mL of methanol) under a  $N_2$  atmosphere while stirring at 550 rpm and at r.t. The solution was stirred for additional 30 min at r.t. followed by solvent evaporation under vacuum.

HDH Reactions. In a typical procedure, the catalyst (20 mg, 1.9  $\mu$ mol Pd) and 4-Cl-PhOH solution (4 mL, 10 mM, solvent) were added to a 10 mL glass tube. The tube was sealed with a septum and purged with  $H_2$  for 5 min at a rate of 20 mL min<sup>-1</sup>, and the pressure relief needle was removed. The reaction tube was then placed in an oil bath that was maintained at 35 °C under stirring (800 rpm). After the desired time, the reaction mixture (hexane) was centrifuged. For the reaction in water, the products were extracted with ethyl acetate (1 mL, 4 times). A 200  $\mu$ L aliquot of the solution was taken, mixed with 50  $\mu$ L of a 4-methylbenzylalcohol (25 mM) internal standard, diluted to 1.00 mL with ethanol, and analyzed using an Agilent GC-MS instrument (7890A, 5975C) with an HP-5MS column. The run started at 60 °C held for 2 min, and the temperature was then ramped to 150  $^\circ$ C at 10  $^\circ$ C min<sup>-1</sup>. Then, the temperature was ramped to 300 °C at 20 °C min<sup>-1</sup>, and then it was held at 300 °C for 1 min. Mass balances between 90 and 100% were obtained for all the catalytic conversions.

Apparent rate constants were calculated from the time versus  $\ln[\text{substrate}]$  plots and normalized to the amount of Pd catalyst employed in the reaction ( $M_{\text{Pd}}$ ). Full kinetic profiles were modeled as a sequence of 4-Cl-PhOH HDH and hydrogenation of the intermediate PhOH according to

 $[4ClPhOH] = [4ClPhOH]_0 e^{-k_1 t}$ 

 $[cyclohexanone] = [4ClPhOH]_0$ 

$$\left[1 - \frac{1}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\right]$$

$$[PhOH] = \frac{k_1 [4ClPhOH]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

where  $k_1$  is the pseudo-first order rate constant for the first step (obtained from the initial rate measurement) and  $k_2$  is the pseudo-first order rate constant for the second step.

Surface Area and Porosimetry. Textural properties of the supports and catalysts were measured by nitrogen sorption isotherms at -196 °C using a Micromeritics Tristar analyzer. The surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. Pretreatment of samples was done under flowing N<sub>2</sub> for 6 h at 100 °C.

Inductively Coupled Plasma-Optical Emission Spectroscopy. Pd loadings were analyzed using a PerkinElmer Optima 2100 DV inductively coupled plasma-optical emission spectroscope. Pd-containing samples (5 mg) were digested for 24 h in 2 mL of aqua regia. After digestion, the solution was diluted to 12 mL using DI water (17.6 M $\Omega$  cm). The solution was filtered, and the filtrate (12 mL) was used to analyze the amount of Pd in the samples.

**Powder X-ray Diffraction.** Diffraction patterns were collected on a Bruker Siemens D500 X-ray diffractometer equipped with Cu K $\alpha$  radiation (40 kV, 44 mA) over the range of 10–100° (2 $\theta$ ). PXRD samples were prepared by placing fine powders onto a background-less polycarbonate sample holder. Crystallite sizes were calculated using the Scherrer equation

$$D_{hkl} = \frac{K\lambda}{\beta\,\cos\theta}$$

**Pulse Chemisorption.**  $H_2$  chemisorption analysis was carried out by first pretreating the reduced samples at 250 °C under 10.0%  $H_2$  in Ar for 30 min to assure complete reduction of the Pd metal, followed by flowing Ar for 30 min at 250 °C to remove excess hydrogen from Pd crystallites. The sample was then cooled under Ar to -20 °C for pulse chemisorption measurements (10.0%  $H_2$  in Ar). The Pd dispersion of the catalysts was calculated on the basis of the equation

$$D \% = \frac{S_{\rm f} * M * V_{\rm ad}}{m^* W^* V_{\rm m}} * 100$$

where  $S_{\rm f}$  = stoichiometry factor (Pd/H<sub>2</sub> molar ratio) = 2, M = atomic mass of Pd (106.42 g mol<sup>-1</sup>),  $V_{\rm ad}$  = volume of chemisorbed H<sub>2</sub> (mL) under standard temperature and pressure (STP) conditions, m = mass of the sample (g), W = weight fraction of Pd in the sample as determined by ICP-OES (0.011 g of Pd/g of sample), and  $V_{\rm m}$  = molar volume of H<sub>2</sub> (22414 mL mol<sup>-1</sup>) under STP conditions.

The cubic crystallite size of palladium was calculated on the basis of the equation

Pd crystallite size (nm) = 
$$\frac{6AM_{Pd}}{m \times W_{Pd} \times d_{Pd} \times N_A \times SA_{Pd}}$$

where  $AM_{Pd}$  = atomic mass of Pd (106.42 g/mol), m = mass of the sample (g),  $W_{Pd}$  = weight fraction of Pd in the sample as determined by ICP-OES (0.0106 g of Pd per gram of the sample),  $d_{Pd}$  = density of palladium (1.202 × 10<sup>-20</sup> g nm<sup>-3</sup>),  $N_A$  = Avogadro's number (6.023 × 10<sup>23</sup> mol<sup>-1</sup>), SA<sub>Pd</sub> = palladium surface area from the equation above (nm<sup>2</sup> g<sup>-1</sup> of Pd). The number 6 is derived from assuming cubic geometry.

**Electron Microscopy.** Transmission electron microscopy (TEM) was conducted using an FEI Tecnai G2 F20 field emission microscope at 200 kV. High-angle annular dark-field imaging (HAADF) in scanning TEM (STEM) and elemental mapping were done on an FEI Titan Themis 300 Cubed aberration-corrected STEM microscope at 200 kV. Samples were prepared by placing 2–3 drops of dilute ethanol suspensions onto lacey-carbon-coated copper grids.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy. The analyses were conducted on a Bruker VERTEX 80 FT-IR spectrometer with OPUS software. Material preparation:100 mg of Pd/CeO<sub>2</sub> + 2 mL of 10 mM 4-Cl-PhOH in hexane were stirred overnight. The next day, the solution was separated from the catalyst. The catalyst was dried under vacuum at r.t. for 8 h and then loaded onto a DRP-SX3 (Praying Mantis accessory) micro sample cup. The measurements were carried out at r.t. using a DLaTGS detector with a KBr window (range 12,000–250 cm<sup>-1</sup>).

**Solution Calorimetry.** Heats of adsorption were determined using a 6755 Parr Solution calorimeter equipped with a rotating sample glass cell. 100 mL of aqueous acid solution (0.1 M) was freshly prepared and placed inside a Dewar. 0.3 g of Pd/CeO<sub>2</sub> was weighed directly on the detachable bottom holder of the rotating sample cell. The change in temperature was monitored over a period of 10 min after releasing the catalyst into the acid solution. The evolved energy (Q), enthalpy of adsorption ( $\Delta H_{\rm ads}$ ), and enthalpy of desorption ( $\Delta H_{\rm des}$ ) were calculated as follows

$$Q = (\Delta T)(e)$$
$$\Delta H_{ads} = \frac{-Q}{m}$$
$$\Delta H_{des} = -(\Delta H_{ads})$$

where  $\Delta T$  is the net corrected temperature change, *e* is energy equivalent determined by standardization, and *m* is the amount of catalyst in the experiment. All values were normalized to the moles of Pd in the catalyst. A blank experiment using only the Pd/CeO<sub>2</sub> catalyst and the solvent (no acid) was performed to account for the heat released during catalyst wetting/mixing.

For the enthalpy of adsorption of Cl-Ph, 500 mg of the catalyst was suspended in 81.5 g of hexadecane and set in the Dewar. The suspension was stirred until constant temperature (15–20 min). The Cl-Ph (250 mg) was then weighted directly on the detachable holder of the rotating sample cell. The change in temperature was monitored over 10 min after releasing the compound into the catalyst hexadecane suspension. The enthalpy of adsorption ( $\Delta H_{ads}$ ) was calculated as indicated above, but the term *e* included the heat capacity of hexadecane instead of water.

**X-ray Photoelectron Spectroscopy.** XPS analysis was done with a PHI 5500 multitechnique system using a standard Al X-ray source. 1 wt % Pd/CeO<sub>2</sub> catalyst was used in all cases except for halophenol adsorption studies, where a 5 wt % Pd/ CeO<sub>2</sub> was used to improve the signal to noise ratio. The Pd/ CeO<sub>2</sub> catalyst was prepared by deposition onto a double-sidedtape sample holder. Charge correction was accomplished by shifting the carbonaceous C 1s peak to 284.6 eV for all spectra. CasaXPS software was utilized to perform carbon-calibration, peak fitting, and deconvolution of the data. Pd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks were fitted using a spin—orbit splitting ratio of 3:2 into a doublet and a fixed doublet separation of 5.26 eV.<sup>27</sup>

**Raman Spectroscopy.** CeO<sub>2</sub> and 5 wt % Pd/CeO<sub>2</sub> samples were prepared by flushing with N<sub>2</sub> followed by H<sub>2</sub> at r.t. for 5 min and a rate of 20 mL min<sup>-1</sup>. Raman measurements were collected using an XploRA Plus Raman confocal upright microscope with a 532 nm excitation wavelength. The samples were exposed to 1.3 mW of laser power using a 10× objective. Raman spectra were obtained using a 1200 groves mm<sup>-1</sup> grating and three 60 s accumulations were averaged for each measured location; three different locations were measured on each sample.

UV–Visible Spectroscopy of Hydrodeiodination Reaction with Pyridine. UV–vis spectra were collected in an HP 8454 UV–visible spectroscopy system. For the hydrodeiodination (HDI) reaction, Pd/CeO<sub>2</sub> (20 mg, 1.9  $\mu$ mol Pd), 4-iodophenol (4-I-PhOH) solution (4 mL, 10 mM, hexane), and pyridine (2 equivs) were added to a 10 mL glass tube. The tube was purged with H<sub>2</sub> for 5 min at a rate of 20 mL min<sup>-1</sup> and then stirred for 1 h at 35 °C. The catalyst was removed by centrifugation, the hexane supernatant was evaporated under vacuum, and the residue was then diluted with 4 mL of ethyl acetate. The ethyl acetate solution was then analyzed by UV– visible spectroscopy. A control solution was prepared by dissolving sodium iodide (10 mM, 4 mL) and pyridine (2 equivs) in water. Pyridinium iodide was then extracted using ethyl acetate and analyzed by UV–visible spectroscopy.

**NMR Spectroscopy.** <sup>1</sup>H NMR spectra were collected on an AVANCE NEO 400 MHz system equipped with a narrowbore 9.4 T/400 MHz magnet. Pd/CeO<sub>2</sub> was degassed at 100 °C under vacuum for 24 h. The pre-dried catalyst was then introduced into NMR tubes containing 4-Cl-PhOH solution (1 mL, 100 mM, benzene- $d_6$ ) or only benzene- $d_6$  as a control.

 $^{13}$ C transverse relaxation rate ( $R_2$ ) measurements were acquired on gel-stabilized NMR samples<sup>27</sup> prepared by following previously described procedures.<sup>28</sup> Briefly, the appropriate amount of the nanoparticle and the 12hydroxyoctadecanamide gelator was weighed directly into an NMR tube followed by the addition of 10 mM substrate solution in cyclohexane- $d_{12}$  to produce a 0.5 wt % nanoparticle and a 0.5 wt % gelator sample. The capped NMR tube was placed into a sonic bath (Branson 1800) and heated to a temperature of  $\sim$ 70 °C. The sample was sonicated for 5–10 min on a 100% power sonic setting followed by a 100% power degas setting for 5-10 min until the nanoparticles were evenly dispersed and the gelator was dissolved. The NMR tube was immediately transferred into an ice bath for 5-10 s to facilitate rapid gelation. Reference samples in the absence of the nanoparticle were prepared following the same procedure described above. <sup>13</sup> $C R_2$  experiments were performed at 25 °C on a Bruker 800 MHz spectrometer equipped with a triple resonance z-gradient cryoprobe. <sup>13</sup>C  $R_2$  was measured using a double INEPT-based CPMG sequence with proton decoupling during the <sup>13</sup>C relaxation period.<sup>10</sup> The <sup>13</sup>C carrier frequency was set at the center of the aromatic region of each molecule. The CPMG field strength was set to 1 kHz. For each sample, spectra at 14 different relaxation delays were acquired in an interleaved manner to obtain the  ${}^{13}CR_2$  relaxation decay curve. The observed relaxation decays were fitted to a monoexponential decay function  $ae^{-R_2 t}$ , where *a* is a scaling factor,  $R_2$  is the transverse relaxation rate, and t is the variable relaxation delay. Experiments were acquired with 32 dummy scans and 128 scans with a recycle delay of 4 s between each scan. <sup>13</sup>C  $\Delta R_2$  values were calculated as the  $R_2$  rate measured in the presence of the nanoparticle minus the  $R_2$  rate measured on a reference sample in the absence of the nanoparticle.

# RESULTS AND DISCUSSION

Catalyst Characterization. The high-surface ceria support  $(201 \text{ m}^2 \text{ g}^{-1})$  was synthesized via evaporation-induced selfassembly as previously reported<sup>12</sup> and impregnated with  $Pd(O_2CCH_3)_2$  via incipient wetness. The material was then calcined in air at 350 °C and reduced under flowing H<sub>2</sub> at the same temperature to give the Pd/CeO<sub>2</sub> catalyst. The physical properties of the support and catalyst (Pd/CeO<sub>2</sub>, 1 wt % Pd) are summarized in Table S1. The XRD pattern (Figure S1a) of Pd/CeO<sub>2</sub> revealed only peaks attributed to CeO<sub>2</sub> (JCPDS 34-0394) with no observable Pd diffractions, suggesting high metal dispersion due to its strong affinity for the support.<sup>29</sup> The high Pd dispersion (61%, crystallite size 1.3 nm) was confirmed by sub-ambient H<sub>2</sub>-pulsed chemisorption and EDS mapping in STEM-HAADF (Figure 1). The facile cycling between the Pd(+2) and Pd(0) states of the catalyst under mild conditions was evidenced by XPS analysis of the material. Exposing the freshly reduced catalyst to air at room temperature gave approximately equivalent amounts of +2 and 0 oxidation states of the metal. Treating this partially oxidized catalyst with a stream of H<sub>2</sub> at room temperature led to a dramatic enhancement of the Pd(0) peak (335.15 eV) at the expense of the Pd(+2) signal (336.85 eV) (Figure S2).

Hydroxy–Support Interactions Favor the HDH Activity of Pd/CeO<sub>2</sub>. We tested the HDH activity of Pd/CeO<sub>2</sub> by flowing H<sub>2</sub> (5 min, 20 mL min<sup>-1</sup>) into the headspace



**Figure 1.** (a) TEM, (b) HR-TEM, (c) STEM-HAADF micrographs of Pd/CeO<sub>2</sub> and (d) EDS map of Pd corresponding to the image in (c).

of a 4-Cl-PhOH solution (10 mM in hexane, 5 mol % Pd, 35 °C, Scheme 1). The complete conversion took place within 15

#### Scheme 1. Catalytic Hydrogenation of 4-Cl-PhOH





**Figure 2.** a) Kinetics of Pd/CeO<sub>2</sub>-catalyzed 4-Cl-PhOH HDH in hexane. Discontinuous lines represent fitting to a model of two consecutive pseudo-first-order reactions (see the Experimental Section). [Blue ( $\bullet$ )] 4-Cl-PhOH, O PhOH, and  $\Box$  cyclohexanone. (b) Apparent HDH rate constants of different substrates; the three bars to the left correspond to reactions in hexane and the bar to the right correspond to reactions in water. Conditions: 10 mM 4-Cl-PhOH, 5 mol % Pd, 35 °C, H<sub>2</sub> purge 5 min (20 mL min<sup>-1</sup>).



**Figure 3.** a) Proposed dissociative adsorption of 4-Cl-PhOH onto  $v_0$  sites in Pd/CeO<sub>2</sub> leading to water production. (b) NMR spectra of 4-Cl-PhOH before (black trace, middle) and after (red trace, top) addition of Pd/CeO<sub>2</sub> shows water evolution upon substrate adsorption. The spectrum of Pd/CeO<sub>2</sub> is shown as a control (green trace, bottom) and displays only a trace water signal. (c) DRIFT spectra of 4-Cl-PhOH adsorbed onto Pd/CeO<sub>2</sub> (red trace, top) compared to pure 4-Cl-PhOH (black trace, bottom) shows a blue shift in vC-O, indicative of phenoxide formation upon dissociative adsorption on  $v_0$ . (d) O 1s XP spectrum of freshly reduced catalyst before (black fitting, bottom) and after adsorbing 4-Cl-PhOH (red fitting, top). The decrease in O<sub>β</sub> signal upon substrate addition indicates  $v_0$  occupancy. (e) TEM image of the Pd/CeO<sub>2(nanored)</sub> catalyst. (f) Raman spectra of CeO<sub>2</sub> (black trace) and CeO<sub>2(nanored)</sub> (red trace) normalized to the F<sub>2g</sub> band (458 cm<sup>-1</sup>); the inset shows nanorods having a higher D-band intensity than the original CeO<sub>2</sub>, indicating a larger number of  $v_0$ . (g) Kinetics of Pd/CeO<sub>2(nanored)</sub>-catalyzed 4-Cl-PhOH HDH reaction in hexane under the same conditions as in Figure 2. [Blue ( $\bullet$ )] 4-Cl-PhOH,  $\bigcirc$  PhOH,  $\square$  cyclohexanone.

min (Figure 2a), giving only PhOH. Longer reaction times resulted in PhOH hydrogenation to cyclohexanone. The delay in PhOH hydrogenation reflects the large difference between the two reaction rates: the apparent rate constant of 4-Cl-PhOH HDH is 1 order of magnitude larger than that of pure PhOH hydrogenation under the same conditions ( $k_{4-\text{Cl-PhOH}}$  $8.1 \pm 0.7 \text{ s}^{-1} \text{ M}_{\text{Pd}}^{-1}$  vs  $k_{\text{PhOH}}$   $0.8 \pm 0.1 \text{ s}^{-1} \text{ M}_{\text{Pd}}^{-1}$ , respectively, Figure S3). No Cl-substituted cyclohexanone/cyclohexanol products were detected, suggesting direct ring hydrogenation of 4-Cl-PhOH is disfavored under these conditions. This result contrasts with a prior observation of Pd/CeO<sub>2</sub> guaiacol (2-MeO-PhOH) hydrogenation in which rates of hydrodemethoxylation and ring hydrogenation were comparable and gave mixtures of cyclohexanol and 2-MeO-cyclohexanol.<sup>14</sup>

A comparison between the HDH rates of 4-Cl-PhOH and chlorobenzene (Cl-Ph) under the same conditions (Figure 2b) provides evidence that the phenolic –OH moiety is beneficial for Pd/CeO<sub>2</sub> activity ( $k_{\rm Cl-Ph}$  3.4 ± 0.3 s<sup>-1</sup> M<sub>Pd</sub><sup>-1</sup>, Figure S4). The effect of the –OH functional group on reactivity likely involves binding to the surface of the support, which may include dissociative adsorption onto oxygen vacancies ( $v_o$ ) and hydrogen bond donation.<sup>12</sup> Replacing hexane with water as a solvent results in a *ca.* 10-fold drop of the HDH activity ( $k_{4-\rm Cl-PhOH}$  1.0 ± 0.1 s<sup>-1</sup> M<sub>Pd</sub><sup>-1</sup>, Figure S5), suggesting that this solvent competes with the phenolic –OH for binding sites on CeO<sub>2</sub>.<sup>33–35</sup> Replacing –OH with –OMe gives a HDH rate

 $(k_{4-\text{Cl-PhOMe}} 5.0 \pm 0.3 \text{ s}^{-1} \text{ M}_{\text{Pd}}^{-1}$  in hexane, Figure S6) closer to that of Cl-Ph, further suggesting that the specific interactions of -OH with CeO<sub>2</sub> are relevant for catalysis.

Using Pd/SiO<sub>2</sub> (Figure S7 and Table S2) as a catalyst results in a 4-Cl-PhOH HDH rate 7 times lower than Pd/CeO<sub>2</sub>  $(k_{4-Cl-PhOH} (Pd/SiO_2) 1.1 \pm 0.1 \text{ s}^{-1} \text{ M}_{Pd}^{-1}$ , Figure S8). Because SiO<sub>2</sub> is capable of H-bonding with the phenolic –OH, this type of interaction cannot be the reason of the high Pd/CeO<sub>2</sub> activity. However, since the reaction using Pd/C as a catalyst gives even lower activity ( $k_{4-Cl-PhOH} (Pd/C) 0.3 \pm 0.02 \text{ s}^{-1} \text{ M}_{Pd}^{-1}$ , Figure S9), H-bonding interactions still have a positive effect on Pd/SiO<sub>2</sub> activity.

Substrate–Catalyst Interaction Involves O–H and C– Cl Bond Cleavage. We first investigated the interactions between the 4-Cl-PhOH substrate and the Pd/CeO<sub>2</sub> catalyst using solution NMR. To this end, we determined how the <sup>13</sup>C transverse relaxation rates ( $\Delta R_2$ ) of the substrate signals change when the catalyst is added to the solution. The value of  $\Delta R_2$  is proportional to the fraction of molecules that bind the catalyst surface and lose magnetization because of the slower molecular tumbling of adsorbed species.<sup>9,10,28</sup> Although we observed a large increase in transverse relaxation rate (average  $\Delta R_2$  7.0 ± 0.3 s<sup>-1</sup>) when setting 4-Cl-PhOH in the presence of the catalyst, no significant changes ( $\Delta R_2 \sim 0 \text{ s}^{-1}$ ) were observed when the catalyst was added to solutions of Cl-Ph or 4-Cl-PhOMe (Figure S10). These results indicate that while 4-



**Figure 4.** a) Cl 2p XP spectrum of 4-Cl-PhOH adsorbed onto the catalyst. The peak is deconvoluted into Cl  $2p_{3/2}$  and Cl  $2p_{1/2}$  signals assigned to metal-bound Cl (yellow traces) and a peak at 201 eV characteristic of organic-bound Cl (gray trace). (b) Pd 3d XP spectra of the freshly reduced catalyst before (black fitting, bottom) and after adsorbing 4-Cl-PhOH (red fitting, top). The positive shift and increase in the Pd(II) signal upon substrate addition indicate oxidative Pd–Cl bond formation. (c) <sup>13</sup>C-RD profiles for the meta-C of 4-Cl-PhOH (red) and PhOH (blue) in the absence (unfilled) and presence (filled) of Pd/CeO<sub>2</sub>.  $R_2$  extracted from fitting exponents ( $I = a e^{-R_2 t}$ ); the corresponding  $\Delta R_2$  indicate moderate and strong substrate–catalyst binding for PhOH and 4-Cl-PhOH, respectively.

Cl-PhOH interacts strongly with the catalyst, the nonhydroxylated haloaromatics have a weaker affinity for Pd/ CeO<sub>2</sub>. It is well known, though, that aromatic species have strong interactions with Pd(111). Therefore, rather than implying the absence of interaction, the  $\Delta R_2 \sim 0$  observed for Cl-Ph indicates that its magnitude is not detectable by this method. We measured the interaction of Cl-Ph with the catalyst *via* calorimetry. Our measurement indicated a  $\Delta H_{ads}$  of 67 kJ mol<sup>-1</sup>, which is in agreement with DFT calculations of adsorption energies of aryl molecules with Pd(111).<sup>36</sup>

Interestingly, PhOH gave a smaller  $\Delta R_2$  (4.3 ± 0.4 s<sup>-1</sup>) than 4-Cl-PhOH when set in contact with the catalyst (Figure 4c). This result suggests that while the primary interaction between 4-Cl-PhOH and Pd/CeO<sub>2</sub> involves the –OH group, the Cl may also contribute to adsorption, likely establishing a secondary interaction with the catalyst.

A series of additional spectroscopy experiments suggest that the interaction between the hydroxyl group of 4-Cl-PhOH with Pd/CeO<sub>2</sub> involves dissociative adsorption of -OH onto the  $v_0$  sites of the support. First, addition of a pre-dried catalyst (150 °C under vacuum overnight) to a dry benzene- $d_6$  solution of 4-Cl-PhOH results in a decrease in the intensity of 4-Cl-PhOH signals and the emergence of a water peak in the <sup>1</sup>H NMR spectrum (Figure 3b). Water formation likely involves two steps: first, 4-Cl-PhOH adsorbs dissociatively onto the binding site  $(v_0)$ , relaying its proton to a surface O, and the resulting surface OH is then further protonated and displaced by an additional 4-Cl-PhOH molecule (Figure 3a). Thus, the lower activity in water can be explained by the solvent shifting the binding equilibrium of dissociative adsorption to the left and competing to fill  $v_0$  sites. No water is formed when Pd/ CeO<sub>2</sub> is added to benzene-d<sub>6</sub> solutions of Cl-Ph or 4-Cl-PhOMe, further confirming that the O-H bond in the substrate is required for this type of adsorption. Second, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis of 4-Cl-PhOH adsorbed from hexane solution onto Pd/CeO<sub>2</sub> reveals a shift in the C-O stretching band. This band appears at 1273 cm<sup>-1</sup> in the adsorbed 4-Cl-PhOH compared to 1254  $\text{cm}^{-1}$  in the pure compound (Figure 3c). The shifted band matches the vibrational frequency of the C-O bond in sodium 4-chlorophenoxide (4-Cl-PhONa, Figure S11), strongly suggesting the formation of a phenoxy-cerium ionic interaction. Third, impregnation of the freshly reduced catalyst with 4-Cl-PhOH results in a decrease in the contributions of  $O_{\beta}$  and  $Ce^{3+}$  signals to the O1s (Figure 3d)

and Ce3d (Figure S12) XP spectra from 55 to 34% and 51 to 38%, respectively (Tables S3 and S4). The fraction of Ce<sup>3+</sup> and  $O_{\beta}$  of the signals is proportional to the number of  $v_{oi}^{37}$  therefore, adsorption of the reactant decreases the concentration of  $v_0$ . Finally, the Raman spectra of the catalyst indicate a small drop in the intensity of the D-band upon impregnation with 4-Cl-PhOH. This band is associated with vacancy sites in the support;  $^{6,13,37-39}$  therefore, its decrease is also consistent with  $v_0$  site occupation *via* dissociative adsorption of 4-Cl-PhOH (Figure S13).

Because CeO<sub>2</sub> nanorods have a larger number of  $\nu_{o}$  sites than the (111) terminated high-surface CeO<sub>2</sub>,<sup>37</sup> we also prepared a Pd/CeO<sub>2(nanorod)</sub> catalyst (Table S5, Figure 3e) to examine the effect of increasing the number of vacancies on catalysis. Raman spectroscopy analysis confirmed an *ca.* 1.3 times higher number of vacancies in the nanorods ( $I_{\rm D}/I_{\rm F_{2g}}$ 0.020) than in the original high-surface CeO<sub>2</sub> ( $I_{\rm D}/I_{\rm F_{2g}}$  0.015, Figure 3f).<sup>6,13,37–39</sup> Consistent with our hypothesis, the 4-Cl-PhOH HDH rate using Pd/CeO<sub>2(nanorod)</sub> ( $k_{4-\rm Cl-PhOH}$  11.7 ± 0.4 s<sup>-1</sup> M<sub>Pd</sub><sup>-1</sup>) was 1.4 times higher than that of the original Pd/ CeO<sub>2</sub> (Figure 3g), strongly suggesting that substrate binding to  $\nu_{o}$  sites is beneficial to catalyst performance.

In addition to -OH binding to  $v_0$  sites of the support, other spectroscopic data suggest that the C-Cl bond of the substrate is cleaved upon adsorption to produce Pd-Cl bonds. First, DRIFTS analysis of 4-Cl-PhOH adsorbed onto the catalyst shows a sharp peak at 354 cm<sup>-1</sup> and only a weak signal at 541 cm<sup>-1</sup> attributed to the C<sub>Ar</sub>–Cl stretch (Figure S14).<sup>40,41</sup> The 354 cm<sup>-1</sup> signal is absent in the pure compound and can be assigned to the stretching mode of a Pd-Cl bond.<sup>42-</sup> Second, XPS analysis of the catalyst impregnated with 4-Cl-PhOH indicates binding energies for the Cl  $2p_{3/2}$  and Cl  $2p_{1/2}$ (198.6 and 200.3 eV, respectively, 67%) that match those of Pd-bound Cl, along with a peak centered at 201 eV (33%) assigned to carbon-bound Cl (Figure 4a).<sup>47,48</sup> In addition, the Pd 3d region of the impregnated catalyst indicates emergence of  $3d_{5/2}$  and  $3d_{3/2}$  peaks at 337.9 and 343.5 eV, respectively. These signals have higher binding energies than those of PdO (336.9 and 342.2 eV, respectively) and can be assigned to Pd(II) in Pd-Cl bonds (Figure 4b).<sup>49</sup> The XP spectra also indicate that the fraction of Pd(II) in the catalyst increased from 20 to 27% upon addition of 4-Cl-PhOH, further confirming that the process involves oxidation of the metal. Finally, the interaction of the C-Cl bond with Pd is consistent with the observation that 4-Cl-PhOH binds more strongly than PhOH to the catalyst ( $\Delta R_2$  7.0 ± 0.3 vs 4.3 ± 0.4 s<sup>-1</sup>, respectively) as the former binds via the C–Cl and –OH portions of the molecule while the latter can only bind via the –OH component (Figure 4c). Thus, the combination of NMR, DRIFTS, Raman, and XPS analyses suggests that the reactant is likely bound to both the Pd catalyst and the CeO<sub>2</sub> support.

**Possible Mechanistic Steps of Pd/CeO<sub>2</sub>-Catalyzed 4-Cl-PhOH HDH.** The observation of Pd–Cl and Pd–C bonds in the reactant-exposed material suggests the reaction involves facile oxidative addition of the  $C_{Ar}$ –Cl bond to the metal, as proposed by Ding *et al.*<sup>50</sup> The absence of Ullman coupling products (biphenols) when attempting the reaction under H<sub>2</sub>free conditions even after 24 h rules out a radical pathway for the metal insertion into the  $C_{Ar}$ –Cl bond.<sup>51,52</sup> Instead, the oxidative addition could proceed *via* a three-centered adduct.<sup>53</sup> To generate the final products, the chemisorbed species must react with H adatoms on the Pd surface and undergo a reductive elimination.

The higher HDH rate observed for 4-Cl-PhOMe than Cl-Ph (Figure 2b) indicates that the electronic effects of groups in the ring are also relevant for catalysis. Indeed, the correlation of the reaction rates for a series of substituted Cl-Ph to the corresponding Hammett parameters indicates that the reaction is favored by electron-donating groups (Figures 5, S15-S20). In



**Figure 5.** Hammett plot for HDH reactions over  $Pd/CeO_2$  in hexane. Reaction conditions: 10 mM substrate in hexane, 5 mol % Pd, 35 °C, and 5 min H<sub>2</sub> purge (20 mL min<sup>-1</sup>).

homogeneous Pd-catalyzed couplings, the rates of reductive elimination are usually enhanced by increasing the electrondonating capacity of the reactants.<sup>54</sup> This is consistent with the negative slope of the Hammett plot, which indicates that donating groups compensate for the loss in electron density at the reaction center as the  $C_{Ar}$ -Pd bond is replaced by  $C_{Ar}$ -H. These results suggest that reductive elimination is the turnover limiting step of the reaction. The same trend has been observed before by Ding *et al.*<sup>50</sup> Notably, while the 3-OH groups are well outside the correlation, replacing their  $\sigma$  value (+0.12) with that of 3-O<sup>-</sup> anions  $(-0.47)^{55}$  results in a good alignment with the trend defined by the other substituents. This observation suggests that in addition to enhancing substrate binding, dissociative adsorption of phenols onto the support is beneficial for catalysis because it increases the electron-donating effect of -OH groups by forming  $-O^-$ , which lowers the barrier of the reductive elimination step. Thus, the combined results suggest a mechanism that involves an initial activation of 4-Cl-PhOH via dissociative adsorption likely at the metal-support interface, followed by oxidative

addition to Pd(0) and turnover-limiting reductive elimination to complete the catalytic cycle (Scheme 2). We note that the proposed mechanism does not rule out the direct reaction of halophenol with Pd, that is, oxidative addition without involving an interaction with the support. While this direct pathway must also be taking place, its rate is likely lower than the reaction mediated by dissociative adsorption on the support, given the higher rate of the strongly adsorbing 4-Cl-PhOH ( $k_{4-\text{Cl-PhOH}}$  8.1 s<sup>-1</sup> M<sub>Pd</sub><sup>-1</sup>,  $\Delta R_2$  <sup>13</sup>C NMR 6 s<sup>-1</sup>) than that of the more weakly interacting Cl-Ph ( $k_{\text{Cl-Ph}}$  3.4 s<sup>-1</sup> M<sub>Pd</sub><sup>-1</sup>,  $\Delta R_2 \sim 0$  s<sup>-1</sup>).

Effect of Halogen on Catalytic Turnover. The reductive elimination step of 4-Cl-PhOH HDH involves desorption of phenol and hydrogen chloride from the catalyst. To assess the impact of halogen on the reaction kinetics, we compared the Pd/CeO<sub>2</sub> HDH activities of all 4-halophenols. The reactivity under our reaction conditions followed the order 4-Cl-PhOH ~ 4-Br-PhOH  $\gg$  4-F-PhOH  $\gg$  4-I-PhOH (Figures S21-\$23). Arranging the apparent rate constants as a function of halogen size suggests a volcano plot, with the smallest (F) and largest (I) halides showing much lower activities than the intermediate ones (Figure 6a). While fluorine is usually difficult to remove from organic compounds because of the strength of the C–F bonds [bond dissociation energy (BDE) 456 kJ mol<sup>-1</sup>]<sup>56–61</sup> and its reaction rate  $(k_{4-F-PhOH} 0.35 \pm 0.04)$  $s^{-1}\;M_{Pd}^{~-1})$  is one order of magnitude lower than those of the Cl- and Br-compounds, full conversion can still be achieved within 4 h under the mild conditions employed in this work (35 °C, 1 bar H<sub>2</sub>, 5 mol % catalyst, Figure S21). In contrast, despite C-I being the weakest of all the C-X bonds (BDE 222 kJ mol<sup>-1</sup>), the conversion of 4-I-PhOH is by far the slowest of all the substrates tested ( $k_{4-I-PhOH}$  0.044  $\pm$  0.009 s<sup>-1</sup>  $M_{Pd}^{-1}$ ). The reason for this low reactivity may be that iodine binds strongly to Pd,<sup>62</sup> which should result in active site blocking that prevents catalytic turnover. The strong binding of I to Pd is evidenced by comparing the XP spectra of the spent catalysts after reaction with 4-Cl-PhOH and 4-I-PhOH (Figure S24). While the fraction of Pd(II) in the spent catalyst after reaction with 4-Cl-PhOH is comparable to that in the freshly reduced catalyst (18 vs 20%, respectively), the amount of Pd(II) in the spent catalyst after reaction with 4-I-PhOH is much larger (45%). This result along with the I  $3d_{5/2}$  XPS peak at 619.8 eV (Figure S25), characteristic of metal iodides,  $^{63-65}$ suggests that iodine remains adsorbed to the surface of Pd and blocks it from further reaction. Therefore, we speculate that the observed reactivity pattern results from a balance between the relative barriers of cleaving the carbon-halogen (C-X)bonds during oxidative addition versus desorbing halogen halides (HX) from the catalyst after the reductive elimination step.

Because the BDE of halogen–carbon bonds decreases in the order C–F > C–Cl > C–Br > C–I,<sup>60,66</sup> the rates of oxidative addition of the 4-halophenols should increase with the halogen size (Figure 6b, red markers and line). To estimate the barrier of HX elimination, we measured the heats of adsorption of HX from the solution onto the catalyst (Table S6). Taking the heats of desorption as the negative of these data results in the trend HCl < HBr < HI (Figure 6b, green markers and line; we note that due to its reaction with glass, it was not possible to collect the value for HF). If HF follows this trend, then the reductive elimination rates should decrease with the atomic mass of halogen, that is, a tendency contrary to that of oxidative addition. We notice that this order of desorption

# Scheme 2. Plausible Mechanism for HDH of 4-Cl-PhOH Catalyzed by Pd/CeO<sub>2</sub> in Hexane<sup>a</sup>



<sup>*a*</sup>(i) Dissociative adsorption of the substrate at interfacial O vacancies ( $v_o$ ) giving 4-Cl-PhO<sup>-</sup> species, followed by (ii) oxidative addition of the C-Cl bond to Pd(0) that finally undergoes (iii) reductive elimination with chemisorbed H adatoms to give the end products. A slower direct pathway indicating oxidative addition of the substrate on Pd is indicated with the red curved arrow.



**Figure 6.** (a) Comparison of HDH apparent rate constants of 4-halophenols over  $Pd/CeO_2$  in hexane. (b) C–X BDE (red markers and line) and H–X heats of desorption from the catalyst (green markers and line) as indicators of energy barriers for the oxidative addition and reductive elimination steps of 4-X-PhOH HDH reactions. X corresponds to halogens, dark circles F, light circles Cl, light squares Br, and white squares I. Reaction conditions: 10 mM substrate in hexane, 5 mol % Pd, 35 °C, and 5 min H<sub>2</sub> purge (20 mL min<sup>-1</sup>).

energies is consistent with the trends in the strength of halogen–Pd interactions reported in the literature.<sup>67</sup> Taking then the highest energy values (either BDE or HX desorption) for each halogen in Figure 6b gives an inverse-volcano plot of barriers (highlighted lines), which explains the observed volcano plot of 4-X-PhOH reactivities: the lowest activities of 4-F-PhOH and 4-I-PhOH result from the highest BDE (C–F) and desorption energy (H–I), respectively.

If larger halides give faster oxidative addition rates and more stable Pd-X intermediates than smaller halides, one can expect that the HDH selectivity of halophenol mixtures should favor the conversion of the larger halides. Indeed, the HDH of a mixture of 4-Cl-PhOH and 4-Br-PhOH (10 mM each, 5 mol % catalyst) results in full 4-Br-PhOH conversion but only 39% conversion of 4-Cl-PhOH even after 1 h of reaction. This result contrasts with the slightly higher  $k_{\rm HDH}$  for 4-Cl-PhOH than 4-Br-PhOH in single halophenol HDH experiments (8.1 vs 7.4 s<sup>-1</sup>  $M_{Pd}^{-1}$ , respectively). The preference for hydrodebromination (HDB) over hydrodechlorination (HDC) in mixed systems is consistent with the high selectivity in the HDH of bromo-chlorophenols: the reactions of 4-Br-2-Cl-PhOH, 4-Br-3-Cl-PhOH, and 2-Br-4-Cl-PhOH yield exclusively the chlorinated products after 10 min under our standard conditions (Scheme 3).

These results suggest that the fast formation of the more stable Pd–Br intermediate during HDB inhibits the rate of HDC. Even stronger HDC inhibition is observed for equimolar 4-I-PhOH and 4-Cl-PhOH mixtures (10 mM each, 5 mol % Pd relative to total halophenols) where 16% 4-I-PhOH but no 4-Cl-PhOH conversion is observed after 1 h of treatment.

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# Scheme 3. HDH Reactions of Bromo-Chlorophenols Catalyzed by $Pd/CeO_2$ in Hexane



Consistently, 4-I-PhOH has also an inhibitory effect on HDB of 4-Br-PhOH (12% *vs* no conversion, respectively, under the same reaction conditions). Finally, a mixture of 4-F-PhOH and 4-Cl-PhOH gives quantitative HDC but barely any hydrodefluorination (2%) (Figure 7). Ultimately, the HDH



Figure 7. Pd/CeO<sub>2</sub>-catalyzed HDH reactions on 4-halophenol mixtures. In every mixture, selectivity favors elimination of the largest halogen. Conditions: 1 h reaction, 10 mM of each substrate in hexane, 5 mol % Pd relative to total halophenols, 35 °C, and 5 min H<sub>2</sub> purge (20 mL min<sup>-1</sup>).

reactivity for halophenol mixtures increases with decreasing C–X BDE. One must notice that for every pair of halophenols, the conversion of the most active species gives the same value as that observed in the individual reactions. For example, HDI 1 h conversions range from 10 to 16% in their mixtures and is 10% in the reaction of 4-I-PhOH alone. HDB 1 h conversion is 100% when 4-Br-PhOH is reacted alone or mixed with 4-Cl-PhOH but 0% when mixed with 4-I-PhOH. HDC 1 h conversion is 100% when reacted alone or mixed with 4-F-PhOH but is only 39% when mixed with 4-Br-PhOH or 0% when mixed with 4-I-PhOH. These results suggest that the faster formation of the Pd–X intermediate with the larger halide and its slow elimination as H–X blocks the access of the smaller halides to active sites and thereby decreases their HDH rates.

The low or even lack of HDH reactivity in iodoarenes with Pd catalysts has been widely documented<sup>68–71</sup> and therefore represents a significant challenge. Because our results suggest that the low activity is due to strong adsorption of the

reductive elimination byproduct onto Pd, we decided to use pyridine as HI scavenger with the aim of favoring turnover. Indeed, addition of pyridine to the 4-I-PhOH reaction mixture resulted in a dramatic enhancement in reactivity. The rate of HDI was proportional to the pyridine concentration (Figure S26). Analysis of the UV–vis spectrum of the supernatant indicated that the reductive elimination product (HI) was likely desorbed in the form of pyridinium iodide (Figure S27).

#### CONCLUSIONS

In summary, the catalytic activity of Pd/CeO<sub>2</sub> for the HDH of halophenols benefits from the interaction of hydroxyl groups in the substrate with the support. The Hammett plot of the reaction shows that increasing the electron density on haloaromatic substrates enhances the rates of HDH. Therefore, the high halophenol HDH activity of the catalyst can be attributed to electron-rich phenoxide species generated upon dissociative adsorption of the substrate onto the support. Formation of these phenoxide species is evidenced by NMR, DRIFT, XP, and Raman spectroscopies. Overall, the catalytic cycle of halophenol HDH on Pd/CeO<sub>2</sub> seems to follow a sequence of dissociative adsorption, oxidative addition, and reductive elimination, with the last step being turnover-limiting. The direct pathway that does not involve adsorption to the support also takes place albeit at a slower rate. The catalytic activity depends strongly on the nature of the halogen. Arranging the rates of Pd/CeO<sub>2</sub>-catalyzed HDH as a function of halogen size gives a volcano-type plot. Specifically, the HDH rates for individual halophenols decrease in the order 4-Cl-PhOH  $\sim$  4-Br-PhOH  $\gg$  4-F-PhOH  $\gg$  4-I-PhOH. This reactivity order is likely due to a balance between the relative barriers for C-X bond cleavage and H-X desorption during the oxidative addition and reductive elimination steps of the reaction, respectively. The HDH reactivity order, however, favors conversion of larger halides when the reaction is performed on mixed substrates (i.e., halophenols containing different halogens or mixtures of different halophenols). The likely reason for this difference is that larger halides have lower BDE and therefore undergo oxidative addition faster than the smaller halides. However, once the larger halide is chemisorbed on the catalyst, it blocks active sites for reaction with the smaller halides. The strong adsorption of iodine on Pd results in poor HDH activity. However, addition of pyridine to the reaction mixture facilitates reductive elimination in the form of pyridinium iodide, which ultimately restores catalyst turnover..

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c02716.

Physical properties of the CeO<sub>2</sub> support and Pd/CeO<sub>2</sub> catalysts; wide-angle XRD patterns; Pd 3d XPS spectra of the freshly reduced catalyst; kinetics of Pd/CeO<sub>2</sub>-catalyzed PhOH hydrogenation in hexane and Cl-Ph HDH reaction in hexane, 4-Cl-Ph HDH reaction in water, and 4-Cl-PhOMe HDH reaction in hexane; TEM images; kinetics of Pd/SiO<sub>2</sub>- and Pd/C-catalyzed 4-Cl-PhOH HDH reaction in hexane; <sup>13</sup>C  $\Delta R_2$  of PhOH, 4-Cl-PhOH, 4-Cl-PhOMe, and Cl-Ph; DRIFT spectrum of sodium 4-Cl-PhONa; Ce 3d XP spectra of the freshly reduced catalyst under H<sub>2</sub> flow at room temperature; Ce 3d XPS peak assignment and relative area of peaks;

Raman spectra of Pd/CeO<sub>2</sub> and 4-Cl-PhOH adsorbed onto Pd/CeO<sub>2</sub>; DRIFT spectra of 4-Cl-PhOH adsorbed onto Pd/CeO<sub>2</sub> compared to that of pure 4-Cl-PhOH; kinetics of Pd/CeO<sub>2</sub>-catalyzed 4-PhNH<sub>2</sub>, 3-Cl-PhOH, 4-Cl-PhCH<sub>3</sub>, 1-Cl-4-F-Ph, 1,3-diCl-Ph, 1,4-diCl-Ph, 4-F-PhOH, 4-Br-PhOH, and 4-I-PhOH; Pd 3d XPS spectra of the fresh catalyst after 4-Cl-PhOH and 4-I-PhOH HDH reactions in hexane; I 3d XP spectrum of spent catalyst after 4-I-PhOH reaction in hexane; calorimetry data of acid adsorption on to the Pd/CeO<sub>2</sub> catalyst; and UV-visible spectra of the supernatants of the ceriacatalyzed 4-I-PhO hydrodeiodination reaction performed in the presence of pyridine (PDF)

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#### Notes

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