Efficient Transfer Hydrodehalogenation of Halophenols Catalyzed by Pd Supported on Ceria

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ABSTRACT: The transfer hydrodehalogenation (THD) of halophenols is efficiently catalyzed by palladium supported on high surface ceria (Pd/CeO_2) under mild conditions (65 °C) using isopropanol (*i*PrOH) as hydrogen source. The reactivity of 4-halophenols (4-X-PhOH) varies in the order 4-F-PhOH > 4-Cl-PhOH > 4-Br-PhOH >> 4-I-PhOH and appears to be controlled by the desorption of halides from the catalyst surface. Kinetic analysis of the reactions and temperature programmed surface reaction (TPSR) experiments indicate that oxidative addition of C-X bonds and H-abstraction from isopropoxide compete for the same active sites on Pd. The catalyst was able to conduct the THD of various hazardous pollutants and emerging contaminants (DDT, pentachlorophenol, pentafluorophenol and triclosan).

KEYWORDS: transfer hydrodehalogenation, cerium oxide, Pd, haloaromatics, pesticides, emerging contaminants

1. Introduction

Halophenols are commonly used as pesticides, biocides and wood preservers. As such, they are often released to the environment where they can negatively impact several organisms, either through their immediate toxicity or by inducing long term reproductive effects and cancers.[1-5] Therefore, developing dehalogenation methods is critical from an environmental standpoint. A common approach for removing halogen atoms from organic compounds is catalytic hydrodehalogenation.[6-14] Because this process utilizes H_2 as a reagent, it requires pressurized equipment and involves hazards such as high flammability or explosion. In addition, H_2 is mostly generated via natural gas steam reforming that produces CO_2, and therefore has an important environmental footprint.[15-17]

A practical and greener alternative to accomplish this transformation is transfer hydrodehalogenation (THD).[18-21] In THD, partially oxidized molecules donate labile hydrogen to the target compounds in the form of hydrides. Replacing molecular hydrogen with donors has operational and safety benefits, since it eliminates the need of using complicated setups for handling flammable gases.[21] Many studies have used formic acid for the transfer hydrodechlorination of aqueous 4-chlorophenol (4-Cl-PhOH) over Pd-based catalysts.[22-26] However, during the process, formate is oxidized to CO_2. The production of CO_2 can be avoided by selecting a different type of reducing agent. For example, when isopropanol (*i*PrOH) is used as hydrogen donor it becomes acetone, which can then be recovered and reused. In addition, *i*PrOH can be used as the reaction solvent, it is inexpensive, and can be produced from renewable feedstocks.[27-29] For example, Ukisu *et al*. used *i*PrOH as both H-donor and solvent in transfer hydrodehalogenations of aryl halides over Pd, Pt and Rh based catalysts.[30-36] While these catalysts were capable of eliminating Cl and Br from the substrates, their activity towards F was generally low. This is not surprising given that C-F are among the strongest bonds that carbon can form.[37] This makes fluorinated compounds resistant to

biological degradation and enables their bioaccumulation, which ultimately has led to consider them as persistent organic pollutants.[38]

Previously, we reported that Pd supported on ceria (Pd/CeO_2) is highly active for the hydrodehalogenation (HDH) of halophenols -including fluorophenols- under mild reaction conditions (35 °C, 1 bar H_2).[9] The high HDH activity of this catalyst is attributed to the cooperativity between the redox active support and the catalytic metal. Specifically, dissociative adsorption of halophenols onto the redox active vacany sites of ceria results in electron-rich phenoxides which are much more reactive towards halide substitution by H. Importantly, the redox sites of CeO_2 have also been utilized for transfer hydrogenation processes. For instance, short chain alcohols can bind to these redox sites and dehydrogenate to produce reducing equivalents. For example, by using *i*PrOH as the hydrogen donor, Pd and Ni supported on CeO_2 were able to catalyze the transfer hydrogenation of phenol and ketones.[39-41]

In this work, we explored Pd/CeO_2 as catalyst for THD of halophenols using *i*PrOH as hydrogen donor. We observed that Pd is a much more active catalyst when supported on CeO_2 than on SiO_2 or carbon. The activity of Pd/CeO_2 catalyzed halophenol THD was the highest for 4-fluorophenol (4-F-PhOH) and decreased with increasing size of the halides. This tendency suggests that reactivity is ultimately determined by the strength of Pd/CeO_2-halogen interactions.

2. Results and discussion

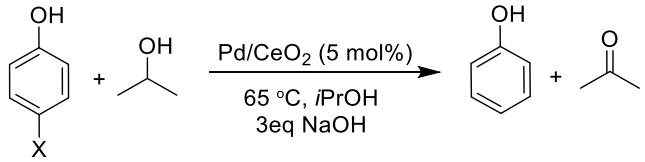
2.1 Catalyst characterization

The high surface ceria support (194 $m^2\ g^{-1}$) was prepared by evaporation-induced self-assembly as previously reported.[9, 40, 47] Impregnation of the support with $Pd(O_2CCH_3)_2$ via incipient wetness followed by calcination in air at 350 °C and reduction at the same

temperature under flowing H_2 provided the Pd/CeO_2 catalyst (0.88 wt % Pd by ICP-OES). The textural properties of the support and catalyst are summarized in Table S1. The XRD pattern (Fig. S5) of Pd/CeO_2 displayed only peaks corresponding to CeO_2 (JCPDS 34-0394) with no Pd diffractions suggesting a high metal dispersion due to its strong interaction between the catalyst and the support.[48-51] H_2 pulsed chemisorption confirmed the high Pd dispersion (61 %), HR-TEM micrographs revealed the support was mainly terminated on the thermodynamically stable (111) plane, and EDS mapping in STEM-HAADF showed a homogeneous distribution of the metal catalyst with particle size smaller than 2 nm (Fig. S6).

2.2 Transfer hydrodehalogenation (THD) activity of Pd/CeO_2

Scheme 1. Transfer hydrodehalogenation of 4-halophenols (4-X-PhOH)



We first benchmarked the catalytic activity of Pd/CeO_2 for the transfer hydrodehalogenation (THD) of 4-fluorophenol (4-F-PhOH) using *i*PrOH as hydrogen donor (Scheme 1) by comparing it to the activities of Pd/SiO_2 and Pd/C. The reactions were performed for 2 h at 65 °C under N_2 using 5 mol % of catalyst and 3 equivalents of NaOH with respect to the fluorine atom in the substrate. Pd was a significantly more active catalyst when immobilized on CeO_2 than on the other two supports giving up to 62 % phenol product under these mild conditions compared to 9.8 % on SiO_2 and no conversion on carbon (Fig. S7). This remarkable difference in activity reflects prior observations of enhanced hydrogenation activity of Pd when supported on CeO_2 as opposed to other traditional materials. The high activity of Pd on CeO_2 has been attributed to high dispersion due to strong metal-support interactions, and to activation of the hydroxyl moieties of substrates and hydrogen donors via dissociative adsorption onto oxygen vacancies of the support. [40, 47, 52, 53]

The spent Pd/CeO_2 catalyst had similar properties to those of the fresh material. Its XRD pattern showed no diffractions corresponding to Pd, suggesting that the metal did not undergo aggregation during the reaction (Fig. S8). The lack of Pd sintering was confirmed by EDS mapping in STEM, with the particles remaining below 2 nm in size (Fig. S9). Interestingly, the Pd 3d XP spectrum of the spent catalyst shows a higher fraction of Pd(0) than the fresh catalyst (84 % vs. 67 %, respectively, Fig. S10), indicating that the metallic sites are regenerated under the reaction conditions.

Variation of Pd/CeO_2 THD activity with halogen type. We then examined the reactivities of different 4-halophenols (4-X-PhOH) using Pd/CeO_2 catalyst under the same reaction conditions (10 mM 4-X-PhOH in *i*PrOH, 3 eq NaOH, 5 mol % Pd, 65 °C, N_2 purge). We observed that the substrate reactivities decreased with increasing size of the halogen: 4-F-PhOH > 4-Cl-PhOH > 4-Br-PhOH >> 4-I-PhOH (Fig. 1, Fig. S11). This behavior contrasts with many reports on hydrodehalogenation (HDH) and THD, especially because F removal has proven very difficult using other catalytic systems.[36, 54] A notable exception is the recent work by Sawama *et al.* in which Pt/C was able to catalyze THD of fluoroarenes using aqueous *i*-PrOH at 100 °C.[55]

The difficulty of removing F from organic compounds is attributed to the strength of the C-F bonds.[8, 56] However, C-F bond activation can be attained by oxidative addition into group 10 metals, which can efficiently donate electron density to the carbon atom.[57-60] In our catalytic system the reaction rate of 4-F-PhOH THD was significantly higher than those of the Cl- and Br- compounds (Turnover frequencies (TOF) of halophenol conversion: 4-F-PhOH $14.9 \pm 0.1\ h^{-1}$ vs. 4-Cl-PhOH $12.0 \pm 0.1\ h^{-1}$ vs. 4-Br-PhOH $4.12 \pm 0.03\ h^{-1}$, 10 mM 4-X-PhOH in *i*PrOH 65 °C, 5 mol % catalyst, 3 eq NaOH) and the full conversion of 4-F-PhOH was achieved within 4 h (Fig. S11).

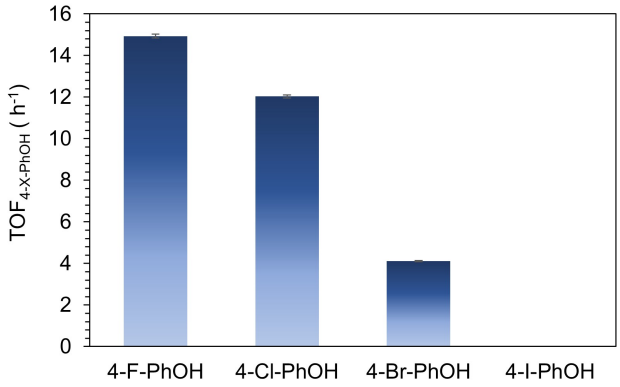


Figure 1. TOF of 4-halophenol (4-X-PhOH) transfer hydrodehalogenation (THD) catalyzed by Pd/CeO_2 in *i*PrOH. Conditions: 10 mM 4-X-PhOH in *i*PrOH, 3 eq NaOH, 5 mol % Pd, 65 °C, N_2 purge 5 min (20 mL min^{-1}).

In contrast to the high activity of the fluorinated compound, 4-I-PhOH was practically inert under our reaction conditions. Since C-F are the strongest and C-I the weakest C-X bonds (bond dissociation energies: 456 kJ mol^{-1} and 222 kJ mol^{-1}, respectively)[8] we infer that C-X bond cleavage is not the limiting factor in the Pd/CeO_2 catalyzed THD. In fact, we have previously observed that oxidative addition of C-X bonds to Pd/CeO_2 can proceed even at room temperature.[53] Therefore, the reductive elimination of Pd-chemisorbed intermediates should present much higher barriers and act as the limiting factor in this reaction. Since the strength of Pd-halogen interactions increases with halogen size (Pd-F < Pd-Cl < Pd-Br < Pd-I)[61, 62] it is reasonable to assume that the THD reaction involves facile oxidative addition of C-X bond to Pd and a much more difficult reductive elimination of the halide from a C-Pd-X intermediate.

These inferences are supported by energy analysis and molecular dynamics (MD) simulations of the 4-X-PhOH reactions over Pd clusters on CeO_2. The Pd/CeO_2 models were generated using a ML-derived potential based on DFT energetics.[63] [64] For details, see the Supporting Information (Section S1). Analysis of these MD simulations which statistically sample adsorption, desorption, and reaction processes over the supported Pd nanoclusters indicated that the dissociative adsorption of the substrates onto Pd is exergonic, confirming a facile first step of the reaction. These analyses also indicated that the desorption of NaX byproduct from the Pd surface is endergonic and becomes more difficult as the size of the

halogen increases (Table 1). Recent studies by the López, Pérez-Ramírez and Groß groups have also indicated that chemisorption of halides onto metals with large work functions such as Pd result in predominantly covalent interactions, whose strength increases with halogen polarizability, *i.e.* size.[65-67] Thus, the smallest halogen F presents the lowest degree of covalency, the weakest bonding to the metal surface and the highest disruption of the metal's work function. All these results support the idea that the differences in reactivity between the substrates is controlled by the removal of the halide from the Pd catalyst (Fig. S12).

Table 1. Calculated energies for the oxidative addition of halophenols, desorption of sodium halides from Pd nanocluster and isoporopxide oxidation from MD simulations (all values calculated in eV, for details see section S1)

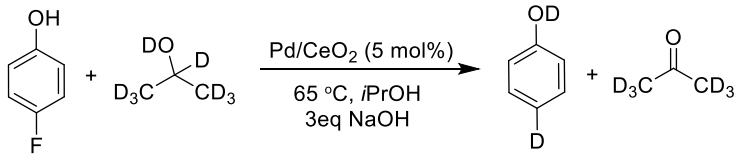
	F	Cl	Br	I
Oxidative addition of halophenol: $\Delta E_{4\text{-X-PhOH} + Pd \rightarrow X\text{-Pd-PhOH}}$	-0.50	-0.90	-1.80	-2.35
Halogen desorption: $\Delta E_{Na\text{-Pd-X} \rightarrow NaX + Pd}$	0.57	1.37	1.40	2.06
Isopropoxide oxidation: $\Delta E_{C3H7ONa + Pd \rightarrow (CH3)2C=O + Na^+ + H\text{-Pd}}$	-0.55			

Interestingly, our MD simulations also suggested that F atoms tend to migrate from the metal to the CeO_2 support while the other halogens remain on Pd. We confirmed experimentally that ca. 7 % of F^- is indeed adsorbed onto CeO_2 when the material is exposed to a 10 mM solution of NaF in water-isopropanol mixtures. In contrast, none of the other halides are taken up by the CeO_2 support when exposing the material to their sodium salts under the same conditions. Thus, it is likely that there is spillover of F^- onto the support, which may help freeing active sites on Pd and thereby contribute to the higher reactivity of 4-F-PhOH in our catalytic system. MD studies of F adsorption onto various porous and crystalline surfaces show that its binding energies decrease in the order $CeO_2 > SiO_2 > C$ (Table S2).

While reductive elimination can occur at room temperature in presence of H_2 (except for iodide), use of a weaker reducing agent such as *i*PrOH should imply a much higher reaction barrier. In fact, previous studies have shown that C-H bond dissociation in *i*PrOH is usually

rate limiting in transfer hydrogenation reactions and thus can impact the reductive elimination step (*i.e.*, coupling of the adsorbed -PhOH and -H).[35, 68-71] Indeed, comparison of the THD kinetics of 4-F-PhOH using regular and deuterium-labeled isopropyl alcohol (*i*PrOH-d_8, Scheme 2) monitored by solution NMR revealed a large primary kinetic isotope effect (k_H/k_D = 8), further suggesting that the cleavage of the C-H bond in the alcohol controls the rate of the reaction and in turn regulates the reductive elimination. (Fig. 2a). Moreover, replacement of F with D in the product when using *i*PrOH-d_8 (Figs. 2b, S13) confirmed that the alcohol is the reducing agent in the reaction.

Scheme 2. Transfer hydrodehalogenation of 4-fluorophenol using *i*PrOH-d_8



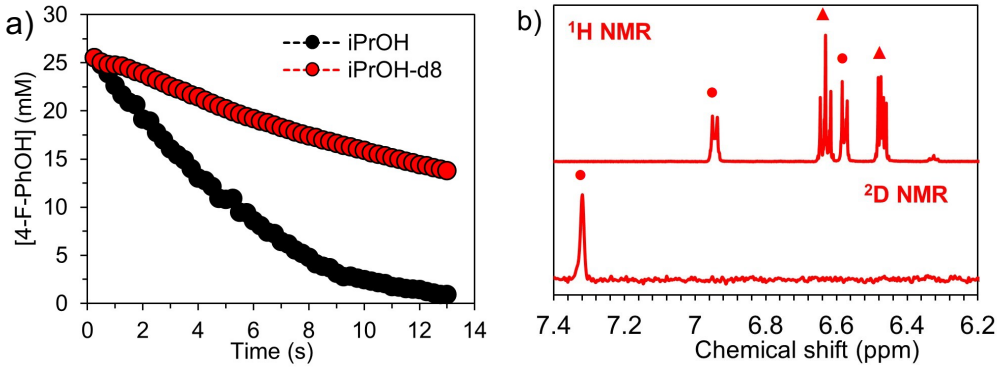


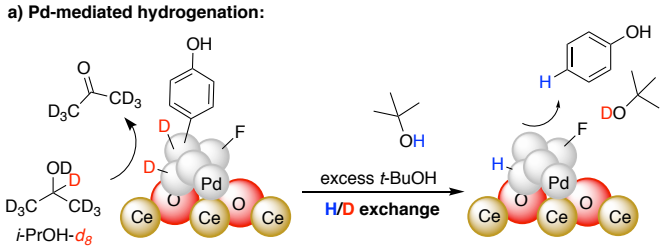
Figure 2. a) Kinetic plots of Pd/CeO_2 catalyzed THD of 4-F-PhOH obtained by solution NMR using *i*PrOH (●) and *i*PrOH-d_8 (●). Conditions: 25 mM 4-F-PhOH in 1 mL *i*PrOH or *i*PrOH-d_8, 3 eq NaOH, 5 mol % Pd, 65 °C, N_2 purge 2 min (60 mL min^{-1}). b) ^{1}H-NMR (top) and ^{2}D-NMR (bottom) spectra of the 4-F-PhOH THD reaction using *i*PrOH-d_8 collected at 13 h. The ^{1}H-NMR displays signals of unreacted 4-F-PhOH (▲) and protons in positions 2 and 3 of the PhOH product (●). The ^{2}D-NMR shows the signal corresponding to the D in position 4 of the product (●).

2.3 Pathways of hydride transfer from iPrOH to 4-X-PhOH

The transfer of hydride from *i*PrOH to the halophenols could take place either through initial formation of Pd-H or in a direct way, via a Meerwein-Ponndorf-Verley (MPV) type mechanism (Scheme 3).[21] Because in an MPV type mechanism the α-H of *i*PrOH does not

adsorb onto the metal, it should not be exchangable.[72, 73] Therefore, it is possible to distinguish between these two mechanisms by performing the reaction with deuterium-labeled *i*PrOH in a protic solvent: if D atoms from *i*PrOH-d_8 are transferred to the Pd (*i.e.* if the mechanism is metal-mediated) they could be exchanged with the H of the protic solvent. To the contrary, if the reaction proceeds via an MPV type mechanism, no H/D exchange should be possible. This implies that the reaction should yield phenol-H_6 if the mechanism involves transfer to Pd or phenol-d_1 if it proceeds via the MPV route (Scheme 3).[73] We performed the THD of 4-F-PhOH in a mixture of 20 % *i*PrOH-d_8 and 80 % *tert*-butyl alcohol (*t*BuOH), containing 3 eq of NaOH and 5 mol % Pd/CeO_2 at 65 °C. Importantly, because *t*BuOH lacks α-H it cannot act as hydride donor. The reaction was performed for 4 h, giving about 50 % conversion. GC-MS analysis of the reaction media revealed exclusive formation of phenol-H_6 (m/z = 94, Fig. S14) indicating that H, and not D was incorporated into the product. Furthermore, the ^{1}H-NMR of the product also showed proton signals for phenol, whereas no signals were obtained in the ^{2}D-NMR spectrum confirming that all the products were protonated rather than deuterated (Fig. 3). These findings indicate that THD over a Pd/CeO_2 catalyst involves initial transfer of the hydride from the alcohol to the metal, which is then relayed to the chemisorbed aromatic compound.

Scheme 3. Possible mechanisms of hydride transfer.



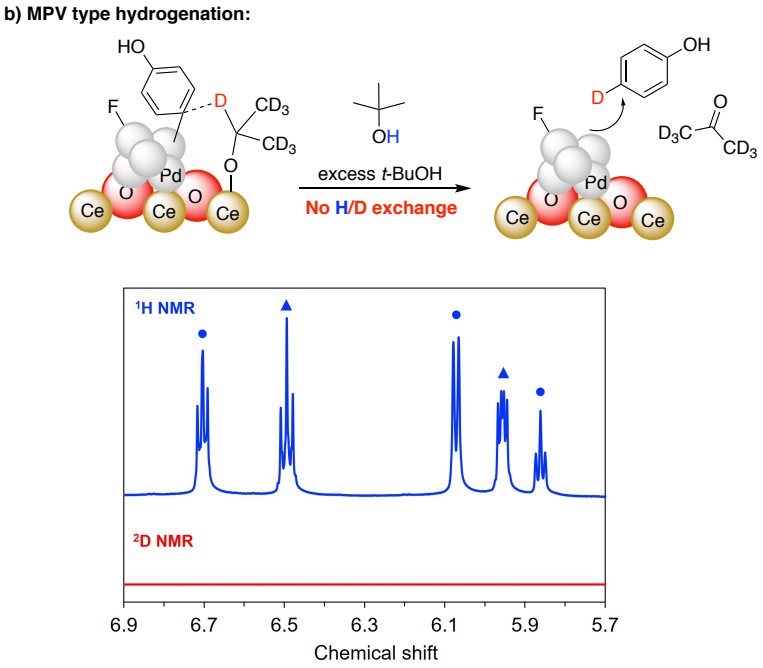


Figure 3. ^{1}H-NMR (blue trace) and ^{2}D-NMR (red trace) of 4-F-PhOH reaction in solution containing 20 % *i*PrOH-d_8 and 80% *t*-butyl alcohol. ● – Phenol ▲– 4-F-PhOH. Conditions: 25 mM 4 mL 4-F-PhOH, 3eq of NaOH, 5 mol % Pd (50 mg), 65 °C, N_2 purge 5 min (20 mL min^{-1}).

2.4 Substrate and reactant compete for active sites on Pd

We followed the kinetics of the rate limiting *i*PrOH oxidation step via ^{1}H NMR (Fig. 4, Fig. S15) and observed that the initial rate of acetone formation was ca. 50 % higher in absence than in presence of halophenols. The lower rates in presence of halophenols suggest that the substrate competes with *i*PrOH for active sites on the catalyst. Furthermore, the acetone formation rates decreased with increasing halogen size in the substrate (Fig. S10), which is consistent with the halophenol reactivity trends observed above. This trend in acetone formation rates suggests that the *i*PrOH-substrate competition is regulated by the strength of the halide-Pd interactions. As noted above, the strength of these halide-Pd interactions increases with halide size. [61, 62] Therefore, halide desorption likely controls reaction rates by restricting the number of accessible sites for *i*PrOH oxidation. The facile desorption of the lighter halides restores Pd surface sites to enable further *i*PrOH oxidation. This explains why acetone concentration keeps increasing in presence of F- and Cl-PhOH but

plateaus in absence of the halophenols. It is likely that the Pd surface becomes saturated with H- in absence of the acceptors (*i.e.* the halophenols). For example, acetone concentration is higher in presence of 4-F-PhOH and 4-Cl-PhOH than in the halophenol-free reaction after 12 h (Fig. 4). In contrast, the strong chemisorption of I- onto Pd completely hinders access of *i*PrOH to the metal surface for delivery of H and results in a small amount of acetone that barely increases over time (Fig. S15d). In addition to blocking active sites, Pablo-García *et al.* observed that chemisorbed halogens modify the work function of the metal, significantly affecting the adsorption energy of organic species,[59] which may also contribute to the decrease in isopropanol conversion in presence of halophenols.

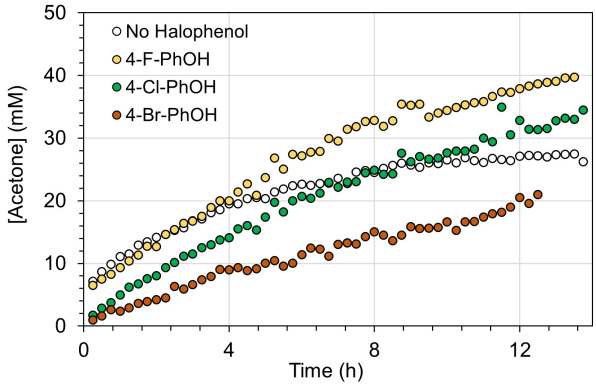


Figure 4. Kinetics of Pd/CeO_2 catalyzed acetone formation in presence and absence of halophenols monitored by ^1H NMR. The acetone levels in the 4-I-PhOH experiment were barely above noise. Conditions: 25 mM 4-X-PhOH, 1 mL *i*PrOH, 3eq NaOH, 5 mol % Pd (13mg), 65 °C, N_2 purge 2 min (60 mL min^{-1}).

The competition between halophenol and *i*PrOH for active sites on Pd is further evidenced by the variation of initial reaction rates as a function of substrate concentration. Increasing the concentration of 4-F-PhOH from 5 to 50 mM resulted in growing THD rates. However, higher concentrations of the substrate (75 mM) led to a drop in initial rates (Fig. 5). The resulting bell-shaped profile is characteristic of competitive binding to catalytic sites,[46, 74-76] *i.e.* higher 4-F-PhOH concentrations decrease the number of active sites available for *i*PrOH oxidation. This competitive kinetics including the down-turn in in THD rate for higher 4-F-PhOH concentrations was modeled using a steady-state analysis of rate equations which

describe dissociative adsorption of 4-F-PhOH and H-transfer to the Pd nanoclusters, as well as slower desorption of F from the metal (for model derivation see SI section S2).

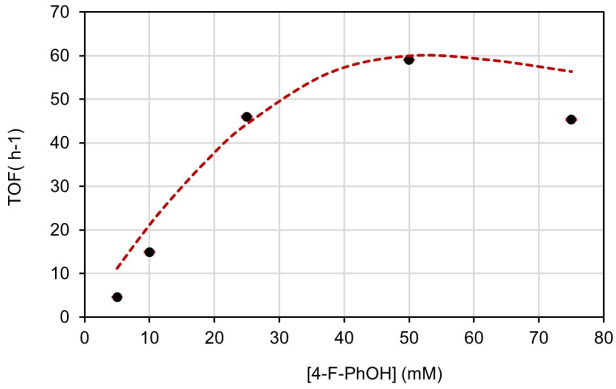


Figure 5. Variation of the initial rates of 4-F-PhOH THD in *i*PrOH obtained with substrate concentrations. The points are experimental data and the red trace corresponds to a kinetic model of competitive adsorption. Conditions: 10-75 mM 4-F-PhOH in *i*PrOH, 3 eq NaOH, 5 mol % Pd, 65 °C, N_2 purge 2 min (60 mL min^{-1}).

2.5 Additional factors controlling hydride abstraction

Temperature programmed surface reaction (TPSR) experiments provided additional details about the factors that control hydride abstraction from iPrOH. CeO_2 and Pd/ CeO_2 were soaked in iPrOH overnight followed by air drying. The materials were then gradually heated under Ar flow while the evolving acetone was monitored with an MS detector. The base peak of acetone (m/z = 43) was used to track its formation. First, we examined the iPrOH oxidation activity of the CeO_2 support. We observed acetone evolution at a temperature of maximum desorption (Tmax) of ca. 280 °C (Fig. 6). Tmax is proportional to the activation energy of acetone formation.[43, 44] Using the Redhead equation[43], we estimated the activation energy for the reaction on the CeO_2 support at 158 kJ mol-1 (Table S3). The oxidation of alcohols on CeO_2 has been explained through a mechanism that involves dissociative adsorption on the surface to give alkoxide and hydroxyl groups followed by direct dehydrogenation to yield acetone and molecular hydrogen (Scheme 4).[77-80] As expected, having the metal on the support (Pd/CeO_2) resulted in a significantly lower activation barrier for the reaction (115 kJ mol-1, Tmax = 130 °C, Fig. 6, Table S3). In this

case, hydride formation should involve 2 steps: 1) alcohol dissociation on the CeO_2 support to give hydroxyl and isopropoxide, and 2) hydride abstraction to give Pd-H and release acetone.[81-83]

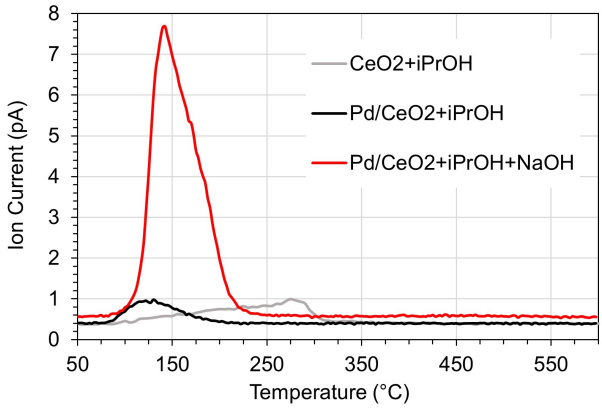
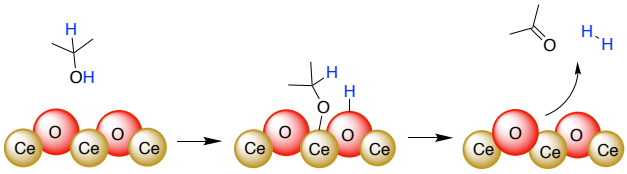
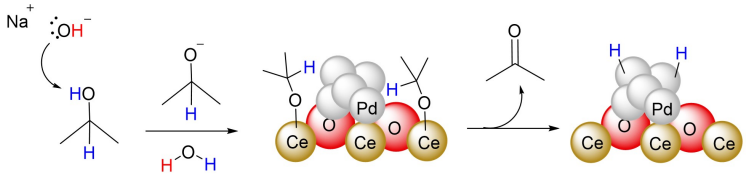


Figure 6. TPD-MS profile for TPSR of *i*PrOH solution with/without NaOH adsorbed on Pd/CeO_2 catalyst. The m/z = 43 signal corresponds to acetone. The table shows the mass normalized area of the TPD-MS profile for TPSR. – CeO_2 – Pd/CeO_2 – Pd/CeO_2 + NaOH

Scheme 4. Hydroxyl abstraction of *i*PrOH on CeO_2.[77, 79]



Scheme 5. H abstraction of *i*PrOH on Pd/CeO_2



Adding NaOH to the *i*PrOH-impregnated Pd/CeO_2 increases acetone production by almost one order of magnitude (Fig.6, Table S3). Basic compounds have been traditionally employed to activate the *i*PrOH donor for hydrogen release.[35, 40] Deprotonation effected by the strong base gives an electron rich isopropoxide that has a higher propensity for undergoing C-H bond cleavage[35, 68, 69] and hydride transfer (Scheme 5).[70, 81] Because of the mild acidity of *i*PrOH (pK_a = 17.1) the weakly basic sites on CeO_2 have a limited efficiency for proton abstraction.[39, 84] Consistently, no conversion is obtained when the THD is attempted in absence of base under our mild reaction conditions (10 mM 4-F-PhOH

in 4 mL *i*PrOH, 5 mol % Pd, N_2 purge 2 min at 60 mL min^{-1}, 65 °C 4 h). While the reaction using 3 eq of NaOH results in full conversion, the use of K_2CO_3 (3 eq) results in low conversion (10 %) over the same time and conditions likely due to its moderate basicity (pK_b 3.7). 4-F-PhOH THD rates increase sharply with NaOH addition up to 3 eq, but higher amounts of base do not provide significant additional improvement in reactivity (Fig. S16). While addition of NaOH to the *i*PrOH impregnated Pd/CeO_2 enhanced acetone production in the TPSR experiments, T_{max} was shifted to a somewhat higher value (142.5 °C) indicating a small increase in the activation barrier (118 kJ mol^{-1}), likely due to adsorption of excess OH^- onto Pd.

We then conducted the TPSR experiments using the catalyst impregnated with the actual reaction mixtures (10 mM halophenol and 3 eq NaOH in *i*PrOH) and continued to monitor the evolution of acetone (m/z = 43) under Ar stream. The presence of halophenol reduced the acetone formation by a factor of ~6 compared to the reaction in absence of halophenols (Fig. 7, Table S4). This result is consistent with the observation of a drop in the initial rate of acetone formation upon addition of halophenol in the NMR experiments (Fig. 4), and supports the idea that halophenol and *i*PrOH compete for the same active sites on Pd. As the halogen size increased, the TPSR profiles revealed a steady shift in T_{max}, with the resulting activation energy increasing in the order: 4-F-PhOH (125 kJ mol^{-1}) < 4-Cl-PhOH (126 kJ mol^{-1}) < 4-Br-PhOH (127 kJ mol^{-1}) << 4-I-PhOH (132 kJ mol^{-1}), which is again consistent with the trends of THD activity, acetone formation rates and our analysis based on ML-aided MD simulations. Furthermore, XPS analysis of the spent catalyst after THD of 4-I-PhOH revealed clear shoulders in the Pd region of the spectrum that were fitted to Pd(II) peaks at 337.1 eV for $3d_{5/2}$ and 342.5 eV for $3d_{3/2}$ (Fig. S17). The deconvoluted peaks corresponded to at least 33 % of the full Pd 3d signal, strongly suggesting Pd-I was present. The existence of Pd-I bonds was further confirmed by the XP spectrum of the I 3d region, which showed

peaks at 619.1 eV for the $3d_{5/2}$ and 630.2 for the $3d_{3/2}$ signals, characteristic of metal iodides (Fig. S18).[85-87]

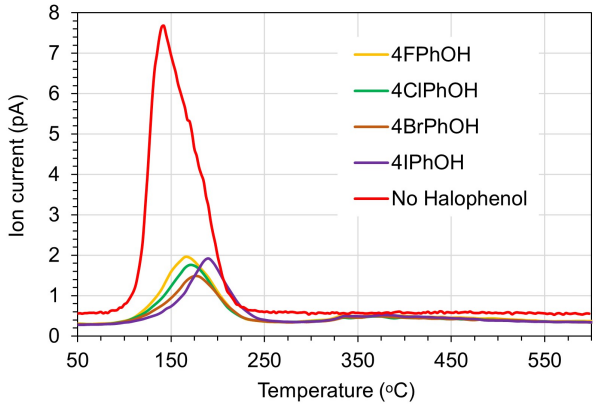


Figure 7. TPSR profiles of 10mM halophenol in *i*PrOH solutions preadsorbed on Pd/CeO_2 catalyst. The impregnated solutions also contained 3 eq NaOH. The profiles are derived from signals obtained with a MS detector at m/z = 43 assigned to acetone.

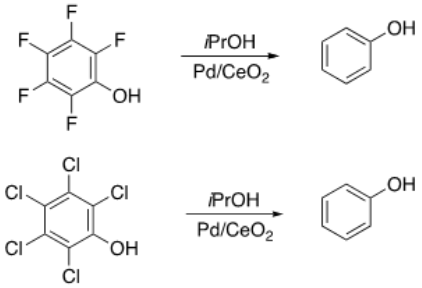
2.6 THD of polyhalogenated contaminants over Pd/CeO_2

We then evaluated Pd/CeO_2 as catalyst for the THD of polyhalogenated pollutants DDT, pentachlorophenol (PCP), pentafluorophenol (PFP), and Triclosan. While the widely used antiseptic Triclosan (personal care products, pharmaceuticals, textiles, etc.) is currently only considered an emergent contaminant despite its inherent toxicity,[88, 89] DDT and Pentachlorophenol (PCP) are listed among 12 persistent organic pollutants (POPs) by the Stockholm Convention due to their toxicity and recalcitrance.[90] Although DDT and PCP usage has decreased, they have not been fully eliminated. Dechlorination of these contaminants has been pursued through various methods, but only few investigations have demonstrated full halogen removal.[30, 91-96] Fluorinated organics have gotten less attention since they have been considered more physiologically inactive. However, recent reports demonstrated that they have significant biological effects,[97, 98] and that they tend to accumulate in the environment.[99-102] Importantly, their manufacturing and consumption has skyrocketed over the last couple of decades.[103, 104]

Because of their structural similarity, we first compared the THD of PCP and PFP over Pd/CeO_2 (5 mol% and 3 eq NaOH with respect to halides, 65 °C, Scheme 6). After 2 h of

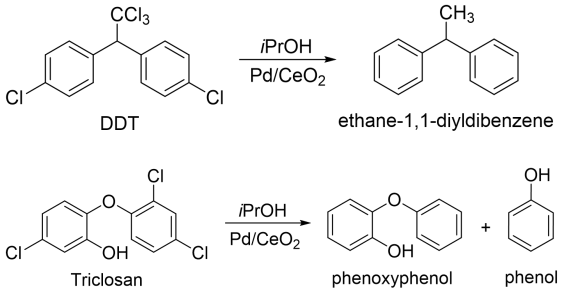
reaction both pentahalophenols gave complete conversion. However, while PFP underwent full defluorination to exclusively produce phenol, PCP yielded a mixture of mono-, di-, tri- and tetra-chlorophenols along with phenol (Figures S19, S20). This difference in phenol selectivity between PFP and PCP is consistent with the higher THD reactivity observed for 4-F-PhOH than 4-Cl-PhOH under our reaction conditions. Thus, PCP required a longer reaction time (4 h) for complete dechlorination to phenol.

Scheme 6. THD of pentafluoro- and pentachlorophenol.



We then performed the THD of DDT at 65 °C for 6 h using the same conditions as those employed with PCP and PFP. The reaction proceeded with complete conversion to the fully dechlorinated 1,1-diphenylethane product (scheme 7, Fig. S21). Finally, we also carried out the THD of Triclosan over Pd/CeO_2 (5 mol% and 3 eq NaOH with respect to halides, 65°C for 6h, scheme 7, Fig. S22). The reaction showed a complete dechlorination yielding phenoxyphenol as the major product (70% selectivity). Interestingly, we also observed a significant fraction of phenol (30 % selectivity) in the products, indicating that along with hydrodechlorination, the conditions led to transfer hydrogenolysis. Previous studies have shown that Pd can catalyze C-O bond cleavage under transfer hydrogenation conditions.[20, 105-108]

Scheme 7. THD reactions of DDT and Triclosan catalyzed by Pd/CeO_2 in *i*PrOH.



3. Conclusions

In sum, Pd/CeO_2 catalyzes the THD of halophenols using solutions of NaOH in *i*PrOH at 65°C. H/D exchange experiments confirmed that the alcohol is the reducing agent, and its large kinetic isotope effect indicates that hydride abstraction from *i*PrOH is the rate limiting step of the reaction. The addition of strong base to the reaction facilitates this conversion because it leads to the formation of electron rich isopropoxide species, with higher hydride donation capacity than neutral *i*PrOH. The catalytic cycle of halophenol THD on Pd/CeO_2 involves an oxidative addition of C-X into Pd, α-H abstraction from isopropoxide to form Pd-H, followed by reductive elimination of phenol. The reaction rates decrease with increasing halogen size, while fluorophenol gives fast conversions, iodophenol is almost inert under our reaction conditions. The low iodophenol reactivity is attributed to the strength of its interaction with Pd, which results in active site blocking. The persistence of the Pd-I bond is confirmed by XPS analysis of the Pd 3d and I 3d regions in the catalyst after the reaction. NMR and TPSR experiments showed that the Pd-halide interaction influences the rate of hydride generation from the *i*PrOH donor because it limits the availability of Pd sites. Because oxidative addition and α-H abstraction compete for the same sites in Pd, reactant concentrations need to be carefully tuned in order to maximize rates. Finally, Pd/CeO_2 proved to be a competent catalyst for the conversion of toxic polyhalogenated compounds into halogen free compounds via THD.

Credit authorship contribution statement

Pranjali J. Naik: Investigation, Methodology, Writing - original draft. **Pranaw Kunal**: Investigation, Validation. **Igor I. Slowing**: Conceptualization, Methodology, Supervision, Writing – reviewing and editing. **Da-Jiang Liu:** Investigation, Validation, Writing – reviewing and editing. **James Evans:** Investigation, Validation, Writing – reviewing and editing.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:

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