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Role of base addition in the liquid-phase hydrodechlorination of 2,4-dichlorophenol over Pd/Al_2O_3 and Pd/C

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Abstract

The aqueous-phase batch hydrodechlorination (HDC) of 2,4-dichlorophenol (2,4-DCP), over 1 wt/wt% Pd/Al_2O_3 and Pd/C has been investigated with/without the addition of NaOH, NH_4OH, LiOH, KOH, RbOH, and CsOH; bulk solution pH spanned the range 1.5–13. The reaction was operated in the kinetic-controlled regime with 2-chlorophenol (2-CP) as the only intermediate partially dechlorinated product which reacts further to yield phenol; cyclohexanone was formed over Pd/Al_2O_3, but not Pd/C, prior to the completion of dechlorination. An increase in fractional dechlorination with the addition of base was observed and can be attributed to a suppression of HDC inhibition due to the HCl that is generated. The initial HDC activity and selectivity delivered by both catalysts were pH dependent and differences in response to bulk solution pH variations are discussed in terms of the nature of the reactive species in solution and the amphoteric behavior of the Pd supports. The Pd/Al_2O_3 catalyst is characterized by a high surface charge density while Pd/C bore a low basic functionality density on a high surface area carrier. A maximum initial HDC rate over Pd/Al_2O_3 was attained at pH 7–9 while a higher pH ($\geqslant 9$) results in more effective HDC for Pd/C, effects that are linked to chloroarene dissociation and surface charge effects. In the case of Pd/C, the initial HDC rate with the addition of alkali metal hydroxide ($0.074\ \mathrm{mol\,dm^{-3}}$) increased in the order $Li^+ \approx Na^+ < K^+ \approx Rb^+ < Cs^+$, a sequence that matches the adsorption affinity on a negatively charged carbon surface; HDC over Pd/Al_2O_3 was insensitive to the nature of the alkali metal cation. The action of NH_4OH, as a weak base, is also considered.

Keywords: Liquid-phase hydrodechlorination; Pd/C; Pd/Al_2O_3; 2,4-Dichlorophenol; 2-Chlorophenol; Base addition

1. Introduction

Contamination of water and soil by chlorophenolic compounds now represents a significant environmental burden due their widespread industrial use and inherent toxicity and persistence in the environment [1]. 2,4-Dichlorophenol (2,4-DCP), the focus of this study, is a high-volume feedstock chemical used in the synthesis of pharmaceuticals and the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) of which 26,300 tons were produced in the US in 1995 [2]. The large-scale production and usage of 2,4-DCP has led to growing concern regarding operation safety [3] and the treatment of related effluent and polluted ground/surface water [4,5]. With increasingly more restrictive landfill legislation and the possibility of hazardous by-product release during incineration [6], catalytic processing represents a far more progressive alternative. Catalytic hydrodechlorination (HDC) as a reductive approach is now viewed as a promising emerging technology [7] that, when compared with traditional oxidation methods, presents the following advantages [8–10]:

(i) low-temperature nondestructive transformation with no directly associated NO_x/SO_x emissions;
(ii) no associated dioxin and dibenzofuran formation; and
(iii) selective Cl removal to generate recyclable products.

HCl is generated during HDC and can act to poison the catalytically active metal [11,12]. In the liquid-phase operation the presence of an inorganic base serves as a proton scavenger, maintaining the catalytic metal in a reduced state and limiting Cl interaction(s) [9,13]. In the aqueous-phase HDC of 4-chlorophenol (4-CP) over Ru/C, the addition of NaOH was also found to “activate” the reactant and neu-

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tralize acidic sites on the carbon support [14]. In the HDC of chlorobenzene in methanol over Pd/$AlPO_4$–SiO_2, it was found that the beneficial effects of NaOH depended on Pd dispersion and support composition [15]. It is fair to state that the consequences of base addition on liquid-phase HDC activity/selectivity are still not well established and the role of metal support is unclear. We have undertaken a fundamental study of base (NaOH, LiOH, KOH, RbOH, CsOH, and NH_4OH) addition in governing 2,4-DCP HDC, focusing on the impact of pH on reactant/catalyst interactions at the solid/liquid/gas interface. The effect of the support (activated carbon vs alumina) in modifying the intrinsic Pd activity is also assessed.

2. Experimental

2.1. Materials

2,4-DCP, 2-CP, LiOH, NaOH, KOH, RbOH, and CsOH (all 99+%) were purchased from Aldrich Chemical Co. and NH_4OH (36.5–38%, AR) was supplied by Mallinckrodt Baker, Inc.; all the chemicals were used as received. Catalysts with the nominal loadings 1% wt/wt Pd/C and 1% wt/wt Pd/Al_2O_3 (supplied by Aldrich) were sieved (ATM fine test sieves) into batches of particle diameter < 325 mesh (45 µm). Stock 2,4-DCP and 2-CP solutions were prepared with deionized water (electronic resistance $\geqslant 15$ MΩ). The concentration of the aqueous base solutions was determined by standard acid titration.

2.2. Catalytic procedure

All the liquid-phase HDC reactions were carried out in a modified commercial stirred-glass reactor (Ken Kimble Reactors Ltd.) equipped with a H_2 supply at a constant (Brooks mass-flow controller) volumetric flow rate (250 $cm^3\,min^{-1}$). There was no measurable conversion in the absence of the H_2 supply; it has been shown previously [16] that hydrolysis of CPs in NaOH only occurs to a significant degree at elevated temperatures and $[NaOH]/[CP] = 6$. Liquid coolant (ca. 278 K) was used to condense all volatiles: loss of the reactor liquid contents in the H_2 flow was negligible ($< 0.5\%$ v/v). A glass impeller provided effective agitation at a stirring speed of 1100 rpm. This choice of stirring speed and H_2 flow rate served to minimize transport limitations as described elsewhere [17] along with a full description of the catalytic reactor. A recirculator (Julabo) was used to stabilize the reaction temperature at 303 ± 0.5 K. At the beginning of each experiment, the 2,4-DCP or 2-CP aqueous solution was charged and agitated in a He flow (50 $cm^3\,min^{-1}$). A known amount of (aqueous) base solution was added to bring the total liquid volume to 0.1 dm^3 and the temperature was allowed to stabilize. The Pd/C catalyst was charged without precontact with H_2. In the case of Pd/Al_2O_3, a ca. 2 cm^3 catalyst slurry in deionized water was preactivated with a separate H_2 flow for at least 10 min and the “preactivated” catalyst was then introduced into the reactor (time $t = 0$ for reaction), where the “preactivation” served to circumvent the occurrence of an extended induction period (4–10 min) that was observed for reaction with Pd/Al_2O_3 in the absence of a H_2 precontact. The pH of the reaction mixture was monitored continuously using a Dow-Corning pencil electrode coupled to a data logging and collection system (Pico Technology Ltd.). The initial 2-CP and 2,4-DCP concentrations were 0.0570 and 0.0285 $mol\,dm^{-3}$, respectively, with a catalyst concentration $(C_{cat}) = 0.3\ g_{cat}\,dm^{-3}$. The Cl/Pd ratio was kept at ca. 1000 (mol/mol) throughout this study and the initial [base]/[organic-Cl] was in the range 0–1.7 for NaOH, 0.2–1.3 for LiOH, KOH, RbOH, and CsOH and 0–5.2 for NH_4OH. A noninvasive liquid sampling system via in-line filters allowed a controlled syringe removal of aliquots (0.5 cm^3) of reactant/product(s). Prior to analysis, the basic solution samples were neutralized with dilute CH_3COOH (ca. 0.2 $mol\,dm^{-3}$).

2.3. Product analysis and activity/selectivity evaluation

The composition of the reaction/product mixture was analyzed by gas chromatography (Perkin-Elmer Auto System XL), employing an FID and a DB-1 J&W Scientific capillary column (i.d. = 0.2 mm, length = 50 m, film thickness = 0.33 µm). The relative peak area percentage was converted to mol% using regression equations based on detailed calibration and the detection limit corresponded to a feedstock conversion < 0.4 mol%: overall analytical reproducibility was better than ±5%. The concentration of organic species (2,4-DCP, 2-CP, and phenol) in the bulk liquid phase was determined from the total mass balance in the reaction mixture where the organic species were taken to be nonvolatile and the effect of uptake on the supports was negligible [17–19]. The HCl produced/H_2 consumption ($mol\,dm^{-3}$) during reaction were calculated from the molar balance based on GC analysis. The conversion of 2,4-DCP ($X_{2,4\text{-DCP}}$) is defined by

$$X_{2,4\text{-DCP}} = \frac{([2,4\text{-DCP}]_0 - [2,4\text{-DCP}])}{[2,4\text{-DCP}]_0}, \tag{1}$$

where the HDC selectivity (as a percentage) with respect to 2-CP ($S_{2\text{-CP}}$) is given as the mol% 2-CP in terms of the total moles of product(s) formed, i.e.,

$$S_{2\text{-CP}}\% = \frac{[2\text{-CP}]}{[2,4\text{-DCP}]_0 - [2,4\text{-DCP}]} \times 100. \tag{2}$$

The initial 2,4-DCP consumption rate ($(R_{2,4\text{-DCP}})_0$) was determined using a pseudo-first-order linear regression from temporal concentration profiles.

2.4. Catalyst characterization

The Pd content was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Vista-PRO, Varian Inc.) from the diluted extract of aqua regia.

The BET surface area was measured using the commercial CHEM-BET 3000 (Quantachrome Instrument). After outgas at 523 K for 30 min, at least 2 cycles of nitrogen adsorption–desorption in the flow mode were employed to determine total surface area using the standard single-point BET method; the calculated BET surface area is quoted as the average. The Pd particle size distributions of the fresh and used catalysts were determined by transmission electron microscopy (TEM, JEOL 2000). At least 700 individual Pd particles were counted for each catalyst and the mean Pd particle sizes are quoted as the surface-area-weighted average particle size ($\bar{d}_{\mathrm{Pd}}$) according to $\bar{d}_{\mathrm{Pd}} = \sum_i n_i d_i^3 / \sum_i n_i d_i^2$ [20], where n_i is the number of particles of diameter d_i and $\sum_i n_i > 700$. The pH associated with the point of zero charge ($\mathrm{pH_{pzc}}$) for both catalysts was determined using the potentiometric mass titration technique (PMT) [21]. Three different catalyst masses were immersed in 50 $\mathrm{cm^3}$ 0.1 $\mathrm{mol\,dm^{-3}}$ NaCl to which a known amount of 0.1 $\mathrm{mol\,dm^{-3}}$ NaOH was added to adjust the initial solution pH to ca. 11. A 0.1 $\mathrm{mol\,dm^{-3}}$ HCl solution was used as titrant, added to the slurry which was sealed in PET vials for 24 h with continuous agitation in a He atmosphere. The acidity of the aqueous catalyst slurries at equilibrium was measured with a pH meter (Corning, Model 440) equipped with a polymer-body, liquid-filled combination electrode. Calibration before each pH measurement employed standard buffer solutions (pH 4.0 and 10.0).

3. Results

3.1. Catalyst characteristics

The Pd content, BET, and specific Pd surface areas are given in Table 1. The Pd phase on the lower surface area Al_2O_3 support is in the form of smaller metal particles (predominantly 0–6 nm), i.e., higher specific Pd surface area. The latter can be attributed to stronger Pd/support interaction(s) due to electron transfer from the Al_2O_3 support [22–24]. In the case of Pd/C, the supported Pd particles exhibit a broad size range (<2 to >20 nm) with a spherical morphology that is indicative of weak Pd/support interaction [22]. Hydrogen chemisorption measurements, reported elsewhere [18], also revealed a higher metal dispersion associated with Pd/Al_2O_3. In an earlier study [17], we presented HDC activity/selectivity responses that are suggestive of differences in the intrinsic HDC behavior of supported Pd catalysts with different Pd content/dispersion. An explicit consideration of Pd particle size effects is beyond the scope of this paper which is focused on the impact of solution pH in determining HDC performance of Pd (at a comparable loading) on two supports. To this end, $\mathrm{pH_{pzc}}$ is a critical catalyst property, defined as the pH value at which the accessible surface of the wetted catalyst particle possesses neither a net positive nor a negative charge [25]. At a $\mathrm{pH} < \mathrm{pH_{pzc}}$ the catalyst surface will bear a positive charge which favors interaction with anionic species. Conversely, where $\mathrm{pH} > \mathrm{pH_{pzc}}$ the surface will exhibit a higher affinity for cationic species in solution. The experimentally determined $\mathrm{pH_{pzc}}$ suggests a weak basicity for both catalysts, diagnostic of the amphoteric nature of the supports. The basicity of Pd/Al_2O_3 can be attributed to the Al–OH group and is well established in the aqueous chemistry of inorganic oxides [26]. In the case of Pd/C, the presence of different (O or N containing) functional groups allied to π-electron density at the carbon basal planes may contribute to the overall weakly basic surface [25,27]. The precise source and nature of these contributions is outside the remit of this paper, where the emphasis is placed firmly on the role of surface charge and bulk solution pH in determining HDC by supported Pd. Although an identification of the surface functionalities may help in understanding the surface/solute interaction(s), it has been demonstrated [28,29] that a knowledge of surface charge variation with solution pH is sufficient in elucidating the role of surface chemistry in the adsorption of substituted phenols on carbon [28] and oxides [29] in aqueous media.

Table 1
Characterization data for the unused catalysts

	Pd/C	Pd/Al_2O_3
BET surface area ($\mathrm{m^2\,g_{cat}^{-1}}$)	1037	160
Pd content (% wt/wt)	1.01	1.17
Surface-area-weighted average Pd particle size ($\bar{d}_{\mathrm{Pd}}$, nm)	14.5	2.2
Specific Pd surface area (S_{Pd}, $\mathrm{m^2\,g_{Pd}^{-1}}$)[a]	34.4	227
pH at the point of zero charge ($\mathrm{pH_{pzc}}$)	8.5	7.8

[a] $S_{\mathrm{Pd}} = 6/(\rho \bar{d}_{\mathrm{Pd}})$, $\rho = 12.02\ \mathrm{g\,cm^{-3}}$.

3.2. Effects of base addition on the HDC performance of Pd/Al_2O_3

3.2.1. NaOH addition: HDC of 2,4-DCP and 2-CP

In order to investigate the role of NaOH addition, 2,4-DCP HDC was conducted where the initial NaOH concentration ($[\mathrm{NaOH}]_0$) spanned the range 0.012–0.09 $\mathrm{mol\,dm^{-3}}$ ($[\mathrm{NaOH}]_0/[\mathrm{organic\text{-}Cl}]_0 = 0.2$–$1.6$); the resultant catalytic results are summarized in Table 2. Typical temporal liquid-phase compositions and pH profiles associated with reaction at the two $[\mathrm{NaOH}]_0$ extremes are shown in Fig. 1. It can be seen (Fig. 1a) that 2,4-DCP HDC proceeded in a stepwise fashion with 2-CP as the sole partially dechlorinated product. Cyclohexanone (resulting from phenol hydrogenation) appeared as product before dechlorination had reached completion but with low selectivity ($\leqslant 5\%$). The absence of 4-CP as product may be explained on the basis of steric hindrance where the *ortho*-Cl is more resistant to H_2 cleavage [17,18,30]. The initial HDC rate ($(R_{\mathrm{HDC}})_0$) was raised in the presence of base but declined with increasing $[\mathrm{NaOH}]_0$ while the fractional dechlorination (X_{Cl} after 120 min) was significantly higher with an increase in $[\mathrm{NaOH}]_0$. The X_{Cl} parameter is a useful indicator of HDC "stability" where the lower X_{Cl} associated with reaction in the absence of

Table 2
Effects of NaOH addition on 2,4-DCP HDC over Pd/Al_2O_3

$[NaOH]_0$ ($mol\,dm^{-3}$)	$[NaOH]_0/[organic\text{-}Cl]_0$	$(R_{HDC})_0$ ($mmol_{Cl}\,min^{-1}\,g_{cat}^{-1}$)	$(R_{2,4\text{-}DCP})_0$[a]$/(R_{HDC})_0$[b]	X_{Cl}[c]	$Y_{C=O}\%$[d]	pH (0–120 min)
0	0	2.9	0.88	0.68	4.1	4.8–1.5
0.012	0.23	6.0	0.79	0.75	4.6	7.9–1.7
0.025	0.44	5.9	0.74	0.85	5.2	8.7–1.8
0.037	0.65	4.9	0.73	0.95	4.5	12.1–2.0
0.049	0.85	3.3	0.87	0.98	4.0	12.5–2.4
0.058	1.02	3.5	0.90	0.96	3.6	12.6–9.1
0.074	1.30	3.4	0.88	0.92	3.4	12.9–11.1
0.090	1.58	3.8	0.87	0.89	3.9	12.9–12.4

[a] Initial rate of consumption of 2,4-DCP, calculated from zero-order linear regression of the temporal [2,4-DCP] profiles.
[b] Initial HDC rate, defined as the initial rate of Cl removal and calculated from zero-order linear regression of the temporal HCl product concentration profiles.
[c] Fractional dechlorination after 120 min.
[d] Percentage yield of cyclohexanone after 120 min.

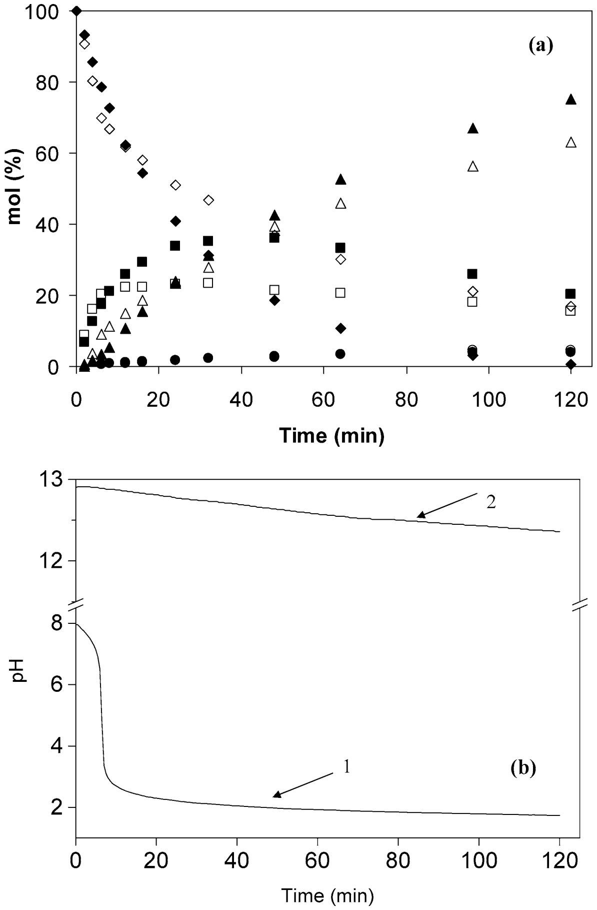

Fig. 1. HDC of 2,4-DCP over Pd/Al_2O_3: (a) liquid-phase composition in terms of mol% 2,4-DCP (◆,◇), 2-CP (■,□), phenol (▲,△), and cyclohexanone (●,○) as a function of time; (b) pH of the bulk solution as a function of time; (1) $[NaOH]_0 = 0.012\ mol\,dm^{-3}$ (open symbols); (2) $[NaOH]_0 = 0.09\ mol\,dm^{-3}$ (solid symbols).

base or dilute base addition ($[NaOH]_0 < 0.037\ mol\,dm^{-3}$) is indicative of catalyst deactivation due to HCl inhibition, as demonstrated elsewhere for the liquid-phase HDC of chlorobenzene [15]. The solution pH associated with the dilute [NaOH] system decreased from ca. 8 to 2 with the release of HCl during HDC (Fig. 1b); the drop of pH from 7 to 4 at ca. 6 min can be linked to the complete consumption of NaOH. A consequent HCl inhibition of the HDC of both 2,4-DCP and 2-CP can be observed after ca. 6 min (Fig. 1a). The pH associated with the higher $[NaOH]_0$ exhibited a slight decrease from 12.9 to 12.4, a response linked to excess NaOH addition. The pH variations during HDC (from low to high $[NaOH]_0$) span the broad range 12.9–1.7. As the pK_a values of 2,4-DCP, 2-CP and phenol are, respectively, 7.89, 8.56, and 10.0 [31], the nature of the reactants/products in bulk solution switches from chloropenolate/phenolate anions to the chlorophenolic/phenolic form as the pH is lowered from 12 to 5. Moreover, the surface charge of Pd/Al_2O_3, with an associated $pH_{pzc} = 7.8$, is also pH dependent. It is to be expected that the chloroarene/catalyst interactions and HDC rates are pH sensitive and affected by the addition of NaOH. In the absence of NaOH, the initial pH is 4.8 and drops to 1.5 after 120 min 2,4-DCP HDC (Table 1). Where $pH \leqslant 5$, the chlorophenolic species dominates (> 99.9 mol/mol%) and interaction with a positively charged alumina surface is unfavorable. Consequently, $(R_{HDC})_0$ rate was lower than that obtained in the presence of NaOH. Over the $[NaOH]_0$ range 0.012–0.025 $mol\,dm^{-3}$ the initial pH (8–9) is such that the reactant in solution is a combined chlorophenolate/chlorophenolic species (11–93 mol/mol% 2,4-DCP dissociation) and the Pd/Al_2O_3 surface is weakly charged, accessible to both species. The corresponding $(R_{HDC})_0$ exhibited a significant increase to attain a maximum (Table 1). The lower ratio of initial 2,4-DCP consumption to HDC rate ($(R_{2,4\text{-}DCP})_0/(R_{HDC})_0$) over $[NaOH]_0 = 0.012$–$0.037\ mol\,dm^{-3}$, i.e., enhanced complete dechlorination, suggests that the retention of 2-CP on the weakly charged surface favors full HDC to phenol. Over the higher $[NaOH]_0$ range (0.037–0.090 $mol\,dm^{-3}$), where the corresponding initial $pH > 12$, the catalyst bears a negative charge and presents an unfavorable surface to chlorophenolate/phenolate anions. The higher $[OH^-]$ inhibits HDC with a resultant drop in $(R_{HDC})_0$ and X_{Cl} but HDC efficiency is still greater than that achieved in the absence of

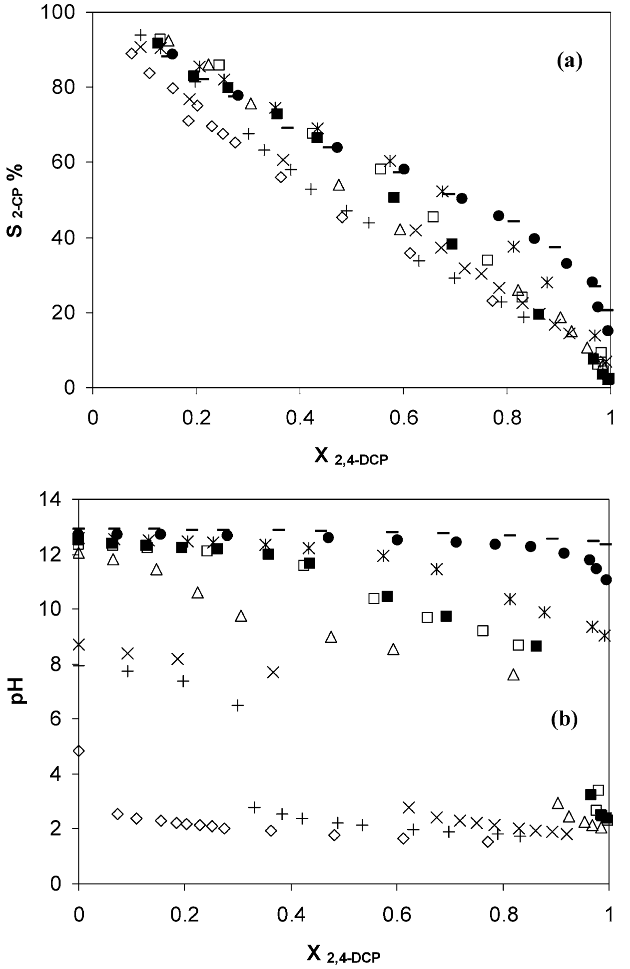

Fig. 2. HDC of 2,4-DCP over Pd/Al_2O_3: (a) selectivity with respect to 2-CP ($S_{2\text{-CP}}$) as a function of fractional 2,4-DCP conversion ($X_{2,4\text{-DCP}}$) and (b) pH of the bulk solution as a function of $X_{2,4\text{-DCP}}$; $[NaOH]_0 = 0.000$ (◇), 0.012 (+), 0.025 (×), 0.037 (△), 0.049 (■,□), 0.058 (∗), 0.074 (●), 0.090 (—) $mol\,dm^{-3}$; $[2,4\text{-DCP}]_0 = 0.0285\ mol\,dm^{-3}$; solid and open symbols represent repeated runs.

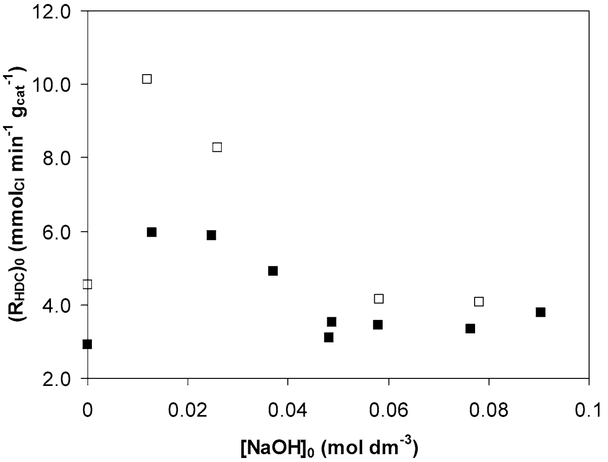

Fig. 3. Initial HDC rate ($(R_{HDC})_0$) as a function of $[NaOH]_0$ in the HDC of 2,4-DCP (■) and 2-CP (□) over Pd/Al_2O_3: $[2,4\text{-DCP}]_0 = 0.0285\ mol\,dm^{-3}$; $[2\text{-CP}]_0 = 0.0570\ mol\,dm^{-3}$.

base. The latter is diagnostic of an overall greater reactivity of chlorophenolate species for C–Cl H_2 scission, as noted elsewhere [14]. The return to higher $(R_{2,4\text{-DCP}})_0/(R_{HDC})_0$ values at $[NaOH]_0 > 0.049\ mol\,dm^{-3}$ suggests that the electrostatic repulsion exhibited by the negatively charged catalyst surface with respect to the chlorophenolate anions limits the extent of complete dechlorination to phenol. The yield of cyclohexanone ($Y_{C=O}$%) after 120 min HDC exhibited little variation with NaOH addition; i.e., the subsequent hydrogenation step is insensitive to solution pH.

The addition of NaOH also impacted on HDC selectivity as illustrated in Fig. 2, where the results of repeated runs are included to demonstrate experimental reproducibility. The lowest 2-CP selectivity ($S_{2\text{-CP}}$) values were recorded in the absence of base while NaOH addition where $[NaOH]_0 = 0.0–0.025\ mol\,dm^{-3}$ (initial pH < 9) had no significant effect on the selectivity/conversion trends. With an increase in $[NaOH]_0$ ($0.025–0.049\ mol\,dm^{-3}$), $S_{2\text{-CP}}$ values were higher at lower $X_{2,4\text{-DCP}}$ but declined to coincide on a common selectivity/conversion trend line at higher $X_{2,4\text{-DCP}}$ (Fig. 2a). The latter can be linked to a common drop of pH below 10 with increasing conversions (Fig. 2b). In the case where the pH (after 120 min) > 11 ($[NaOH]_0 = 0.074–0.09\ mol\,dm^{-3}$), the selectivity trends overlapped with a higher $S_{2\text{-CP}}$ maintained at greater $X_{2,4\text{-DCP}}$. The increase in $S_{2\text{-CP}}$ at higher pH suggests that the secondary conversion of 2-CP to phenol was inhibited to a greater degree at higher $[OH^-]$ when compared with the 2,4-DCP to 2-CP step. In order to probe differences in 2,4-DCP and 2-CP HDC behavior with NaOH addition, $(R_{HDC})_0$ for 2,4-DCP and 2-CP at different $[NaOH]_0$ are compared in Fig. 3. It can be seen that the overall HDC response for 2-CP conversion is similar to 2,4-DCP, i.e., increase in $(R_{HDC})_0$ to a maximum with the addition of NaOH and a subsequent decline at higher $[NaOH]_0$. Both $(R_{HDC})_0$ maxima can be linked to a more effective interaction between the chlorophenolate anions and the weakly charged catalyst surface where the initial solution pH is 7–9. The consistently higher HDC rates for 2-CP, particularly evident where $[NaOH]_0 = 0–0.025\ mol\,dm^{-3}$, suggests that (at a common starting Cl/Pd ratio) the additional Cl substituent has a deactivating effect as noted elsewhere [9,30]. The drop in $(R_{HDC})_0$ at higher $[NaOH]_0$ ($\geqslant 0.057\ mol\,dm^{-3}$) in both cases can be attributed to electrostatic repulsion between the negatively charged surface and the chlorophenolate anions at higher pH (> 11). Comparing 2,4-DCP with 2-CP, the presence of the second electron-withdrawing Cl substituent serves to more effectively accommodate the negative charge of the 2,4-dichlorophenolate anion through delocalization over the aromatic ring with a resultant weaker electrostatic repulsion between the anions and the negative charged catalyst surface than is the case for 2-CP. This may contribute to a lesser 2,4-DCP HDC inhibition at higher pH, a response that is supported by the greater relative drop in 2-CP $(R_{HDC})_0$, where $[NaOH]_0 \geqslant 0.057\ mol\,dm^{-3}$ (Fig. 3) and is consistent with

Table 3
Effects of NH_4OH addition on 2,4-DCP HDC over Pd/Al_2O_3: nomenclature as in Table 2

$[NH_4OH]_0$ ($mol\,dm^{-3}$)	$[NH_4OH]_0/[organic\text{-}Cl]_0$	$(R_{HDC})_0$ ($mmol_{Cl}\,min^{-1}\,g_{cat}^{-1}$)	$(R_{2,4\text{-}DCP})_0/(R_{HDC})_0$	X_{Cl}	$Y_{C=O}\%$	pH (0–120 min)
0	0	2.9	0.88	0.68	4.1	4.8–1.5
0.013	0.23	5.9	0.78	0.72	5.1	7.7–1.5
0.058	1.02	3.9	0.79	1.0	6.9	9.7–7.7
0.074	1.30	4.1	0.80	1.0	6.9	9.9–8.8

a higher $S_{2\text{-}CP}$ for 2,4-DCP HDC at higher $[NaOH]_0$ (see Fig. 2a).

3.2.2. NH_4OH addition: HDC of 2,4-DCP

It has been reported [13,32] that NaOH, as a strong base, can leach supported Pd into solution and damage the pore structure of the support when used in liquid-phase chlorobenzene HDC at high concentration ($> 0.5\,mol\,dm^{-3}$). We did not detect, in our studies, any significant loss of Pd or alteration to the BET surface area over the 120 min 2,4-DCP HDC in the presence of [NaOH]. The utilization of weak bases such as NH_4OH, CH_3COONa or organic amines in liquid-phase reactions can, nonetheless, serve as viable alternatives [9]. The use of CH_3COONa and organic amines has decided economic and environmental remediation drawbacks while the application of NH_4OH has been found to be superior to NaOH in the liquid HDC of CPs over Pd/C, leading to significantly higher HDC activity [9]. The results of NH_4OH addition on 2,4-DCP HDC over Pd/Al_2O_3 are included in Table 3. As in the case of NaOH, HDC activity was highest at lower $[NH_4OH]_0$ ($0.013\,mol\,dm^{-3}$) and the reaction was inhibited at higher $[NH_4OH]_0$ (0.058–$0.074\,mol\,dm^{-3}$). The $(R_{HDC})_0$ values at higher $[NH_4OH]_0$ are slightly greater than those associated with NaOH at the same concentration (Table 2). This suggests a lesser inhibition associated with lower $[OH^-]$, where the pK_b of $NH_4OH = 4.75$ and only ca. 1.6 mol% of NH_4OH dissociates in water at $[NH_4OH] = 0.074\,mol\,dm^{-3}$ compared with a total dissociation of NaOH. At higher $[NH_4OH]_0$, complete dechlorination ($X_{Cl} = 1$) was achieved, which represents greater efficiency than that associated with NaOH (Table 2). The selectivity trends at every $[NH_4OH]_0$ overlapped with that recorded in the absence of base. Such an insensitivity to NH_4OH addition (where $pH < 10$) suggests that the 2-chlorophenolate anion may experience a lesser electrostatic repulsion with the weakly negatively charged catalyst surface: lower $[OH^-]$ does not limit the 2-CP to phenol step to the same extent. The utilization of excess NH_4OH ($0.074\,mol\,dm^{-3}$) was accompanied by a narrow pH span (9.9–8.8) (Table 3) and ultimately led to complete dechlorination. A slightly higher $Y_{C=O}$ and lower $(R_{2,4\text{-}DCP})_0/(R_{HDC})_0$ was obtained at higher $[NH_4OH]_0$ ($> 0.058\,mol\,dm^{-3}$) when compared with the NaOH system (see Tables 2 and 3) and follows from enhanced HDC as a result of weaker repulsion between chlorophenolate/phenolate anion(s) and the catalyst surface.

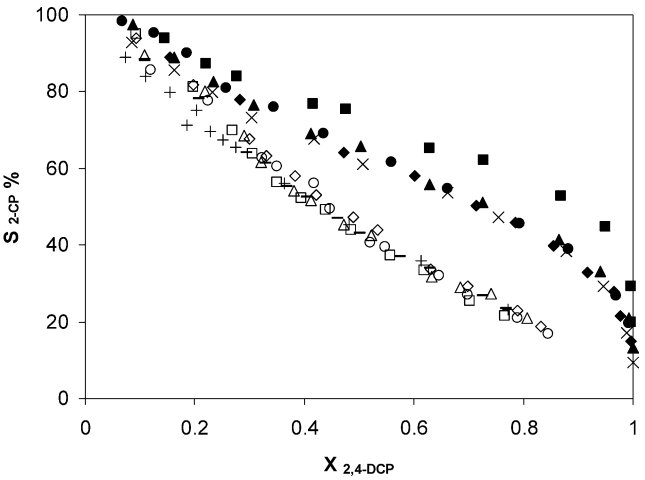

Fig. 4. Effect of concentration and nature of the alkali metal hydroxide on the selectivity with respect to 2-CP ($S_{2\text{-}CP}\%$) as a function of the fractional 2,4-DCP conversion ($X_{2,4\text{-}DCP}$) in the HDC of 2.4-DCP over Pd/Al_2O_3: $[AMOH]_0 = 0.000\,mol\,dm^{-3}$ (+), $0.013\,mol\,dm^{-3}$ (LiOH (○), NaOH (◇), KOH (△), RbOH (—), and CsOH (□)) and $0.074\,mol\,dm^{-3}$ (LiOH (●), NaOH (◆), KOH (▲), RbOH (×), and CsOH (■)); $[2,4\text{-}DCP]_0 = 0.0285\,mol\,dm^{-3}$.

3.2.3. LiOH, KOH, RbOH, and CsOH addition: HDC of 2,4-DCP

We have demonstrated that the liquid-phase HDC activity associated with Pd/Al_2O_3 is dependent on bulk solution pH with rate inhibition under strongly basic conditions. While NH_4OH has proved to be a more effective additive, the possible role of the countercation was probed by examining the action of the four alkali metal (AM) hydroxides (i.e., LiOH, KOH, RbOH, and CsOH), taking two extreme initial concentrations ($[AMOH]_0 = 0.013$ and $0.074\,mol\,dm^{-3}$); the results are given in Table 4. At a given $[AMOH]_0$ each reaction proceeded over a similar pH range with no significant difference in $Y_{C=O}$, $(R_{2,4\text{-}DCP})_0/(R_{HDC})_0$ ratio or X_{Cl}. However, the $S_{2\text{-}CP}$ associated with the higher $[CsOH]_0$ is notably greater (at $X_{2,4\text{-}DCP} > 0.4$) when compared with the other AMOH bases (Fig. 4), indicative of a more severe inhibition of the 2-CP to phenol step. At the higher $[AMOH]_0$, the catalyst bore a negative charge with a consequent preference for interaction with external cationic species. The adsorption enthalpies and affinity sequences for AM^+ on a negatively charged Al_2O_3 surface are known [33] to decrease in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$; i.e., the least favorable surface interaction under basic conditions is with external Cs^+. However, in aqueous solution Cs^+, with the

Table 4
Effects of varying the nature and concentration of the alkali metal hydroxide addition on 2,4-DCP HDC over Pd/Al_2O_3: nomenclature as in Table 2

$[AMOH]_0$ ($mol\,dm^{-3}$)	AMOH	$(R_{HDC})_0$ ($mmol_{Cl}\,min^{-1}\,g_{cat}^{-1}$)	$(R_{2,4\text{-}DCP})_0/(R_{HDC})_0$	X_{Cl}	$Y_{C=O}\%$	pH (0–120 min)
0		2.9	0.88	0.68	4.1	4.8–1.5
0.013	LiOH	6.8	0.76	0.77	5.2	8.0–1.8
	NaOH	6.0	0.79	0.75	4.6	7.9–1.7
	KOH	6.0	0.79	0.72	5.4	7.9–1.7
	RbOH	6.2	0.77	0.68	5.5	7.6–1.9
	CsOH	5.5	0.80	0.68	5.1	7.9–1.7
0.074	LiOH	3.4	0.88	0.89	6.1	12.9–11.3
	NaOH	3.4	0.88	0.92	3.4	12.9–11.1
	KOH	4.3	0.84	0.93	5.0	12.9–10.6
	RbOH	3.9	0.87	0.90	4.3	13.0–10.7
	CsOH	3.8	0.88	0.90	3.5	13.0–10.8

smallest hydrated ionic radius and greatest chemical polarizability (softness) [33,34] of the AM cations, can exhibit a stronger interaction with chlorophenolate anions at higher $[AMOH]_0$. This may result in the formation of an ion pair between chlorophenolate anions and Cs^+ cation at the interface that serves to inhibit further hydrogen scission of the *ortho*-substituted Cl resulting in the higher observed $S_{2\text{-CP}}$ values.

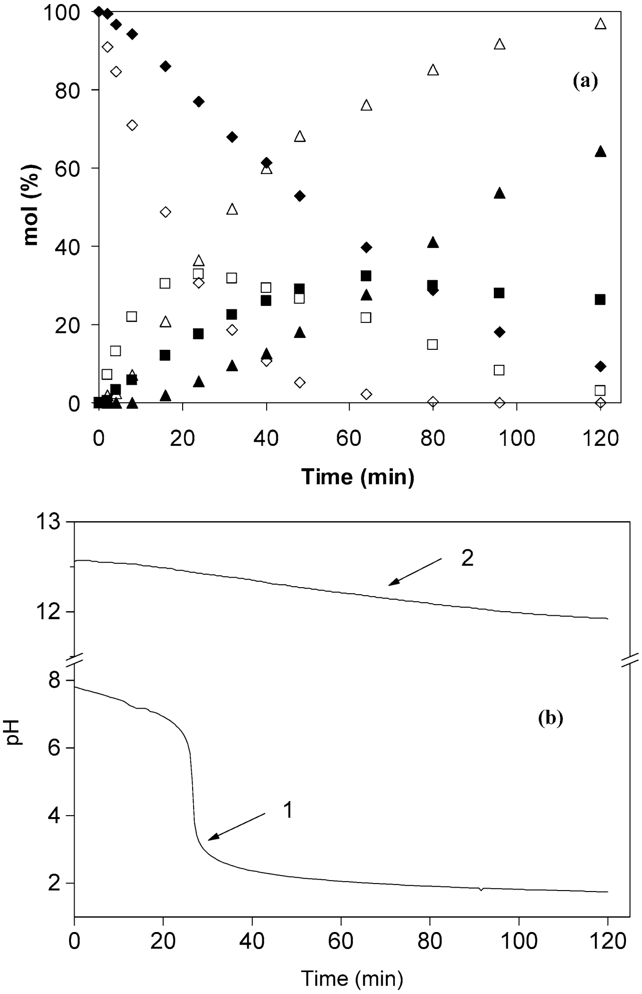

Fig. 5. HDC of 2,4-DCP over Pd/C: (a) liquid-phase composition in terms of mol% 2,4-DCP (◆,◇), 2-CP (■,□), and phenol (▲,△) as a function of time; (b) pH of the bulk solution as a function of time; (1) $[NaOH]_0 = 0.012\ mol\,dm^{-3}$ (solid symbols); (2) $[NaOH]_0 = 0.095\ mol\,dm^{-3}$ (open symbols).

3.3. *Effects of base addition on the HDC performance of Pd/C*

3.3.1. *NaOH addition: HDC of 2,4-DCP and 2-CP*

In liquid-phase chloroarene HDC, it has been demonstrated that Pd/C exhibits higher specific HDC activity than Pd supported on oxide supports, an effect that has been attributed to the greater adsorption capability of carbon [35] while the involvement of H_2 spillover may also be a contributing factor [18,19]. A commercial Pd/C catalyst of comparable Pd loading (see Table 1) to the Pd/Al_2O_3 catalyst was chosen to investigate the possible role of the support in modifying base addition effects on HDC. Over the $[NaOH]_0$ range 0.012–0.095 $mol\,dm^{-3}$ ($[NaOH]_0/[organic\text{-}Cl]_0 = 0.2\text{–}1.7$), Pd/C HDC performance is summarized in Table 5. The temporal liquid-phase compositions and pH profiles associated with the two $[NaOH]_0$ extremes are shown in Fig. 5. It can be seen (Fig. 5a) that the HDC of 2,4-DCP over Pd/C also proceeds sequentially with 2-CP as the sole partially dechlorinated product. In contrast to Pd/Al_2O_3, there was no evidence of any cyclohexanone formation over Pd/C during the course of HDC. The addition of NaOH significantly elevated both $(R_{HDC})_0$ and X_{Cl} (Table 5) but, unlike Pd/Al_2O_3 (see Table 2), both these parameters attained the highest values at the higher $[NaOH]_0$. In common with Pd/Al_2O_3, the solution pH associated with the lower $[NaOH]_0$ dropped from ca. 8 to 2 with, in this instance, an abrupt change at ca. 28 min (Fig. 5b). The pH associated with the higher $[NaOH]_0$ exhibited a lesser decrease from 12.6 to 11.9. It can be seen from the entries in Table 5 that $(R_{HDC})_0$ was largely unaffected by addition of dilute $[NaOH]_0$ ($\leqslant 0.012\ mol\,dm^{-3}$), exhibiting a significant increase when $[NaOH]_0$ was raised to 0.062 $mol\,dm^{-3}$ but was essentially invariant at higher concentrations, a re-

Table 5
Effects of NaOH addition on 2,4-DCP HDC over Pd/C: nomenclature as in Table 2

$[NaOH]_0$ ($mol\,dm^{-3}$)	$[NaOH]_0/[organic\text{-}Cl]_0$	$(R_{HDC})_0$ ($mmol_{Cl}\,min^{-1}\,g_{cat}^{-1}$)	$(R_{2,4\text{-}DCP})_0/(R_{HDC})_0$	X_{Cl}	pH (0–120 min)
0	0	0.9	0.94	0.64	5.0–1.5
0.012	0.23	1.0	0.87	0.65	7.8–1.8
0.025	0.44	1.7	0.73	0.67	9.0–2.0
0.037	0.65	2.6	0.80	0.82	12.0–2.3
0.049	0.86	3.3	0.83	0.95	12.3–2.5
0.062	1.08	3.9	0.88	0.95	12.4–7.5
0.074	1.30	3.9	0.90	0.94	12.5–10.3
0.095	1.67	4.2	0.89	0.97	12.6–11.9

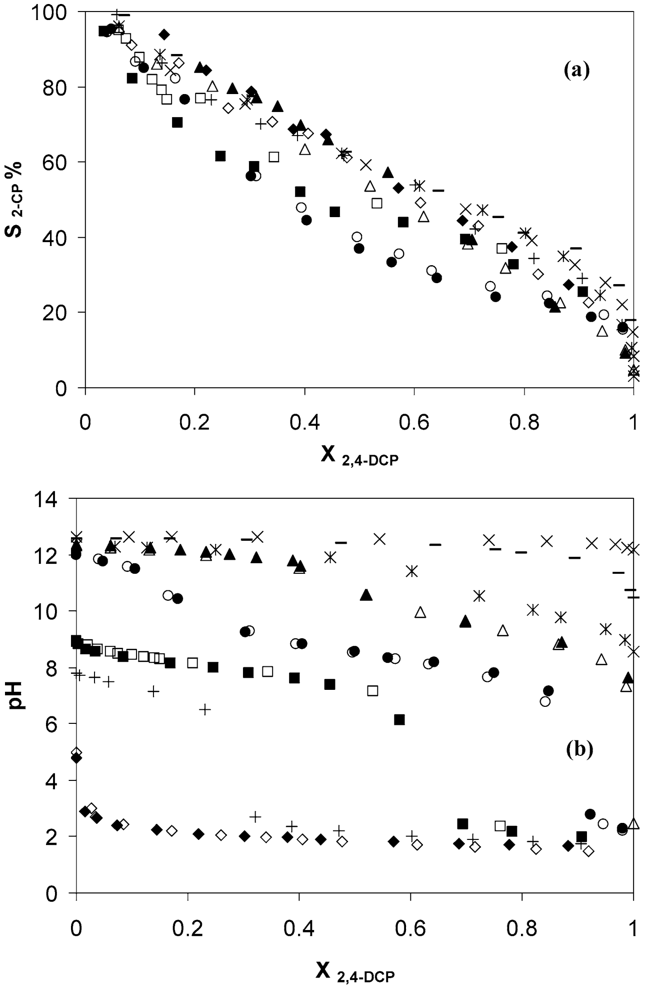

Fig. 6. HDC of 2,4-DCP over Pd/C: (a) selectivity with respect to 2-CP ($S_{2\text{-CP}}$) as a function of fractional 2,4-DCP conversion ($X_{2,4\text{-DCP}}$) and (b) pH of the aqueous solution as a function of $X_{2,4\text{-DCP}}$; $[NaOH]_0 = 0.000$ (◆,◇), 0.012 (+), 0.025 (■,□), 0.037 (●,○), 0.049 (▲,△), 0.062 (∗), 0.074 (—), and 0.095 (×) $mol\,dm^{-3}$; $[2,4\text{-DCP}]_0 = 0.0285\ mol\,dm^{-3}$; solid and open symbols represent repeated runs.

sponse that was matched by X_{Cl}. The lower value for the ratio $(R_{2,4\text{-DCP}})_0/(R_{HDC})_0$ at $[NaOH]_0 = 0.025\ mol\,dm^{-3}$ is significant, as also observed in the case of Pd/Al_2O_3 (Table 2), and suggests that the reaction pathway is sensitive to a change in the fraction of (chloro-)phenolate and (chloro-)phenolic species (initial pH ca. 9).

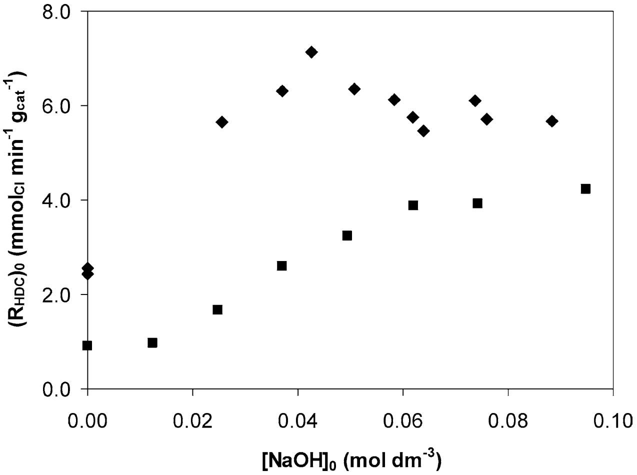

Fig. 7. Initial 2,4-DCP (■) and 2-CP (▲) HDC rates ($(R_{HDC})_0$) over Pd/C as a function of $[NaOH]_0$; $[2,4\text{-DCP}]_0 = 0.0285\ mol\,dm^{-3}$; $[2\text{-CP}]_0 = 0.057\ mol\,dm^{-3}$.

As observed with Pd/Al_2O_3, $S_{2\text{-CP}}$ was sensitive to $[NaOH]_0$, as shown in Fig. 6a, where the repeated runs were again highly reproducible. However, the selectivity pattern deviates significantly from that recorded for Pd/Al_2O_3 (see Fig. 2a). Where $[NaOH]_0 = 0.000$–$0.012\ mol\,dm^{-3}$, pH during the reaction < 8 (Fig. 6b) and the $S_{2\text{-CP}}$ vs $X_{2,4\text{-DCP}}$ profiles coincide but are significantly higher than those associated with Pd/Al_2O_3 at the same $[NaOH]_0$. With an increase in $[NaOH]_0$ (0.025–0.037 $mol\,dm^{-3}$) HDC over Pd/C delivered lower $S_{2\text{-CP}}$ values when the (temporal) reaction pH falls within 8–10, which are even lower than those associated with Pd/Al_2O_3. A further increase in $[NaOH]_0$ (0.049–0.062 $mol\,dm^{-3}$) with an associated pH mainly > 10 served to raise $S_{2\text{-CP}}$ to a level similar to that where $[NaOH]_0 \leqslant 0.012\ mol\,dm^{-3}$, approaching the selectivity associated with Pd/Al_2O_3 at the same $[NaOH]_0$ (see Fig. 2a). At higher $[NaOH]_0$, the distinctly higher values of $S_{2\text{-CP}}$ ($X_{2,4\text{-DCP}} > 0.6$) suggest an inhibition of the 2-CP to phenol step, a response similar to that observed for Pd/Al_2O_3 and which may be linked to the stronger electrostatic repulsion between 2-chlorophenolate anions and the negatively charged surface. Comparing the direct 2-CP and 2,4-DCP HDC over Pd/C as a function of $[NaOH]_0$ (Fig. 7), the 2-CP $(R_{HDC})_0$ exhibited a more significant increase

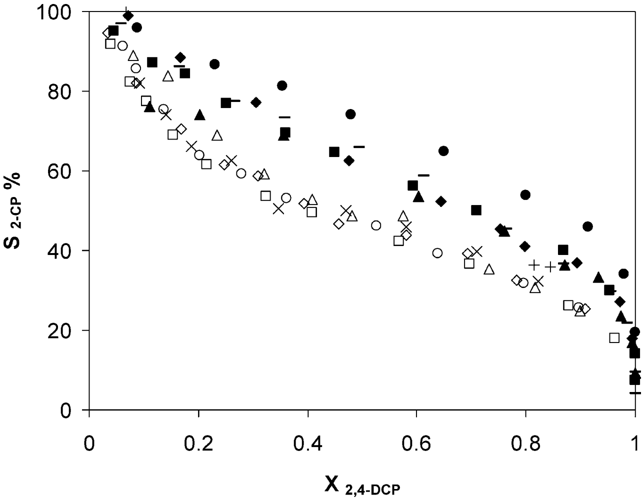

Fig. 8. Selectivity with respect to 2-CP ($S_{2\text{-CP}}$) as a function of fractional 2,4-DCP conversion ($X_{2,4\text{-DCP}}$) in the HDC of 2.4-DCP over Pd/C; $[\mathrm{AMOH}]_0 = 0.000\ \mathrm{mol\,dm^{-3}}$ (+), $0.025\ \mathrm{mol\,dm^{-3}}$ (LiOH (□), NaOH (◇), KOH (△), RbOH (×), and CsOH (○)) and $0.074\ \mathrm{mol\,dm^{-3}}$ ((LiOH (■), NaOH (◆), KOH (▲), RbOH (—), and CsOH (●)); $[2,4\text{-DCP}]_0 = 0.0285\ \mathrm{mol\,dm^{-3}}$.

where $[\mathrm{NaOH}]_0 \leqslant 0.049\ \mathrm{mol\,dm^{-3}}$ that may contribute to the lower $S_{2\text{-CP}}$ values at lower $[\mathrm{NaOH}]_0$ shown in Fig. 6a. The lower 2-CP HDC rates at $[\mathrm{NaOH}]_0 > 0.057\ \mathrm{mol\,dm^{-3}}$ can be linked to the higher $S_{2\text{-CP}}$ values where pH $\geqslant 10$, as is the case with $\mathrm{Pd/Al_2O_3}$.

3.3.2. NH_4OH addition: HDC of 2,4-DCP

Unlike the HDC response observed for $\mathrm{Pd/Al_2O_3}$ (Table 3), the addition of $\mathrm{NH_4OH}$ proved to be less effective (Table 6) in terms of $(R_{\mathrm{HDC}})_0$ and X_{Cl} over Pd/C. The highest $(R_{\mathrm{HDC}})_0$ was attained at $[\mathrm{NH_4OH}]_0 = 0.2$–$0.3\ \mathrm{mol\,dm^{-3}}$ (initial pH ca. 10), while the addition of dilute $\mathrm{NH_4OH}$ (ca. $0.01\ \mathrm{mol\,dm^{-3}}$) resulted in a significant increase (by a factor of 2) in the HDC activity of $\mathrm{Pd/Al_2O_3}$. This difference in response is again suggestive of a distinct pH dependence of the $(R_{\mathrm{HDC}})_0$ delivered by both catalysts. In every HDC operation where pH < 10.5, the selectivity with respect to 2-CP associated with $\mathrm{NH_4OH}$ addition was less than that achieved without base, reaching a minimum at $[\mathrm{NH_4OH}]_0 = 0.05\ \mathrm{mol\,dm^{-3}}$.

3.3.3. LiOH, KOH, RbOH, and CsOH addition: HDC of 2,4-DCP

Taking $[\mathrm{OH^-}]_0 = 0.025$ and $0.074\ \mathrm{mol\,dm^{-3}}$ as two extreme cases, 2,4-DCP HDC over Pd/C was conducted with the addition of LiOH, KOH, RbOH, and CsOH and the results are compared with those generated for NaOH addition in Table 7. At the lower $[\mathrm{AMOH}]_0$, the Pd/C HDC behavior exhibited no significant dependence on the nature of the AM hydroxide, as observed in the case of $\mathrm{Pd/Al_2O_3}$ (Table 4). At the higher $[\mathrm{AMOH}]_0$, the initial HDC rates exhibited a decided dependence and the following sequence of increasing $(R_{\mathrm{HDC}})_0$ emerges: LiOH $\approx$ NaOH $<$ KOH $\approx$ RbOH $<$ CsOH. This sequence coincides with the adsorption affinity sequence of alkali metal cations ($\mathrm{Li^+} < \mathrm{Na^+} < \mathrm{K^+} < \mathrm{Rb^+} < \mathrm{Cs^+}$) for a negatively charged carbon surface [33,34], suggesting a HDC pH dependence for Pd/C that is the result of alkali metal interactions at the interface and which is not evident for reactions involving $\mathrm{Pd/Al_2O_3}$; i.e., the alkali metal cations have a distinct cocatalytic role during HDC over Pd/C. Regardless, in common with $\mathrm{Pd/Al_2O_3}$, the selectivity trends observed for Pd/C are largely insensitive to the nature of the AM hydroxides at a given $[\mathrm{AMOH}]_0$ (Fig. 8). Moreover, as in the case of $\mathrm{Pd/Al_2O_3}$ (Fig. 4), reaction in the presence of the higher $[\mathrm{CsOH}]_0$ delivered consistently greater $S_{2\text{-CP}}$ at each $X_{2,4\text{-DCP}}$, an effect that we again ascribe to $\mathrm{Cs^+}$ interaction with chlorophenolate anions that hinders the 2-CP to phenol HDC step.

4. Discussion

4.1. Mass-transport considerations

The relative importance of physical/chemical control in the overall HDC of 2,4-DCP and 2-CP (with NaOH addition) over supported Pd has been the subject of previous reports [17,18,30]. Aqueous HDC of chlorophenols, as a three-phase system, was identified as a fast reaction over Pd/C and $\mathrm{Pd/Al_2O_3}$ where any transport constraints at gas/liquid and/or liquid/solid interfaces and/or the solid phase (intraparticle) can limit the true HDC rate [17]. Hydrogen transport at the external/internal liquid/solid interface was found to be the predominant physical constraint. It was confirmed that the reaction operated under kinetic control with stirring speeds > 1000 rpm, $\mathrm{H_2}$ flow rate $> 150\ \mathrm{cm^3\,min^{-1}}$, $[2,4\text{-DCP}]_0 = 0.0475\ \mathrm{mol\,dm^{-3}}$, $[2\text{-CP}]_0 = 0.095\ \mathrm{mol\,dm^{-3}}$, $[\mathrm{NaOH}]_0/[\text{organic-Cl}]_0 =$ ca. 1 mol/mol, $C_{\mathrm{cat}} \leqslant 0.5\ \mathrm{g\,dm^{-3}}$, and catalyst particle size $< 45\ \mu\mathrm{m}$. Under these conditions, the initial HDC rates ($T = 303$ K) were 3.6 and 5.6 $\mathrm{mmol\,g_{cat}^{-1}\,min^{-1}}$ for 2,4-DCP and 2-CP conversion, respectively, over Pd/C [18,30]. In the present study, where lower $[2,4\text{-DCP}]_0$ and $[2\text{-CP}]_0$ (0.0285 and $0.057\ \mathrm{mol\,dm^{-3}}$) and constant $[\text{organic-Cl}]_0/C_{\mathrm{cat}}$ ($C_{\mathrm{cat}} = 0.3\ \mathrm{g\,dm^{-3}}$) were employed, the $(R_{\mathrm{HDC}})_0$ values recorded for Pd/C were in the range 0.9–6.8 and 2.4–7.1 $\mathrm{mol\,g_{cat}^{-1}\,min^{-1}}$ for 2,4-DCP and 2-CP HDC, respectively; i.e., the same order of magnitude as the previous results and mass-transfer contributions can be taken to be negligible. In the case of $\mathrm{Pd/Al_2O_3}$, the highest HDC initial rate recorded ($T = 303$ K) under an established kinetic regime ($[\mathrm{NaOH}]_0/[\text{organic-Cl}]_0 = 1$), $[2,4\text{-DCP}]_0 = 0.0475\ \mathrm{mol\,dm^{-3}}$, and $C_{\mathrm{cat}} = 0.5\ \mathrm{g\,dm^{-3}}$) was 4.1 $\mathrm{mmol\,g_{cat}^{-1}\,min^{-1}}$ [30]. The $(R_{\mathrm{HDC}})_0$ values recorded in this study fall within 2.9–6.0 $\mathrm{mmol\,g_{cat}^{-1}\,min^{-1}}$ and can again be taken to be free from physical transport constraints. The observed responses to base addition reported in this study can then be attributed to chemical/catalytic phenomena.

Table 6
Effects of NH_4OH addition on 2,4-DCP HDC over Pd/C: nomenclature as in Table 2

$[NH_4OH]_0$ ($mol\,dm^{-3}$)	$[NH_4OH]_0/[organic\text{-}Cl]_0$	$(R_{HDC})_0$ ($mmol_{Cl}\,min^{-1}\,g_{cat}^{-1}$)	$(R_{2,4\text{-}DCP})_0/(R_{HDC})_0$	X_{Cl}	pH (0–120 min)
0	0	0.9	0.94	0.64	5.0–1.5
0.013	0.23	1.0	0.87	0.76	7.7–1.7
0.025	0.44	1.1	0.73	0.80	8.7–1.9
0.050	0.88	1.7	0.77	0.87	9.3–7.4
0.100	1.75	2.1	0.81	0.88	9.8–9.0
0.125	2.19	2.3	0.80	0.92	10.0–9.1
0.175	3.07	2.5	0.79	0.94	10.2–9.5
0.200	3.51	2.7	0.79	0.94	10.3–9.6
0.224	3.93	3.1	0.78	0.96	10.4–9.7
0.298	5.23	2.7	0.79	0.94	10.5–9.9

Table 7
Effects of varying the nature and concentration of the alkali metal hydroxide addition on 2,4-DCP HDC over Pd/C: nomenclature as in Table 2

$[AMOH]_0$ ($mol\,dm^{-3}$)	AMOH	$(R_{HDC})_0$ ($mmol_{Cl}\,min^{-1}\,g_{cat}^{-1}$)	$(R_{2,4\text{-}DCP})_0/(R_{HDC})_0$	X_{Cl}	pH (0–120 min)
0		0.9	0.94	0.64	5.0–1.5
0.025	LiOH	1.5	0.82	0.79	9.2–1.9
	NaOH	1.7	0.73	0.67	9.0–2.0
	KOH	1.0	0.86	0.68	8.6–1.9
	RbOH	1.3	0.85	0.68	8.5–2.1
	CsOH	1.2	0.89	0.67	9.1–2.1
0.074	LiOH	3.7	0.82	0.93	12.6–10.4
	NaOH	3.9	0.90	0.94	12.5–10.3
	KOH	5.5	0.76	0.98	12.5–10.0
	RbOH	5.3	0.82	0.96	12.5–10.0
	CsOH	6.8	0.84	1.0	12.7–10.1

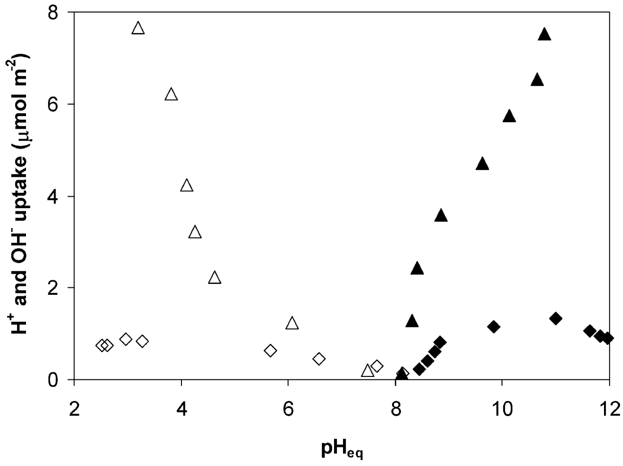

Fig. 9. H^+ (open symbols) and OH^- (solid symbols) uptake on Pd/Al_2O_3 (▲,△) and Pd/C (◆,◇) as a function of the equilibrium solution pH; $C_{cat} = 6\,g\,dm^{-3}$; $0.1\,mol\,dm^{-3}$ aqueous NaCl served as blank.

4.2. Effects of base addition: Pd/Al_2O_3 vs Pd/C

In this study, 2,4-DCP and 2-CP HDC was conducted over a broad pH range (1.5–13.0) with the addition of various bases. An understanding of the amphoteric nature of the catalyst surface is essential to explain the differences in HDC behavior exhibited by Pd/C and Pd/Al_2O_3 in response to changes in bulk solution pH. While the pH_{pzc} of Pd/Al_2O_3 (7.8) and Pd/C (8.5) are close, conversion of the PMT titration data (used to determine pH_{pzc}) into H^+ and OH^- uptake as a function of equilibrium solution pH is revealing, as can be judged from the entries in Fig. 9. The difference in H^+ and OH^- uptake (on a surface area basis) is such that a clear distinction in the behavior of Pd/Al_2O_3 and Pd/C emerges. This is manifest in the higher surface charge density (corresponding to the higher H^+ or OH^- uptake) of Pd/Al_2O_3 at the extreme pH values (< 6 or > 10). This should result in either a stronger electrostatic attraction ($pH < 6$) or repulsion ($pH > 10$) with respect to chlorophenolate anions in solution. Values for the pH_{pzc} and density of active surface hydroxyl groups (AlOH) for γ-Al_2O_3 have been reported [26,29,36,37] in the range 6.9–9.5 and 1.7–14 $\mu mol\,m^{-2}$, respectively, which are consistent with our results for Pd/Al_2O_3. As hydrated Al_2O_3 exhibits a weak chemical affinity for hydrocarbons [33,34], electrostatic rather than dispersion effects should dominate the interaction between chlorophenol(s)/phenol and Al_2O_3, as has been demonstrated in an FTIR analysis of phenolic uptake (and pH dependence) on Al_2O_3 [29,38]. The surface charge density is lower for Pd/C which possesses a high surface area (Table 1) with an uptake capacity that necessitates pH extremes (< 4 or > 10, see Fig. 9) to achieve surface saturation. The reported pH_{pzc} for activated carbon falls within the rather broad range 3–10, the actual value depending on the carbon source and nature of the pretreatment/activation [25,28,39,40]. To illustrate the heterogeneity of activated carbon surfaces, the HCl adsorption capacities of two commercially available carbon samples have been reported to span the range 0.016–1.73 $\mu mol\, m^{-2}$ [25]. Our PMT titration/BET data for Pd/C are consistent with a low density of basic functional groups on a high surface area carrier. Consequently, the possible interaction(s) between the carbon surface and the chlorophenols/phenol is (are) [28,41–43]:

(i) electrostatic attraction/repulsion associated with participating charged species;
(ii) nonelectrostatic attractions, i.e., dispersion (π–π electrons) effects between the aromatic ring (reactant in solution) and carbon surface, hydrogen bonding, and hydrophobic interaction.

The greater chemical affinity exhibited by carbon, when compared with Al_2O_3 for interaction with hydrocarbons allied to the lower surface charge density must translate into a greater importance of nonelectrostatic contributions. This is supported by the literature [14,28,39,41–44] dealing with the pH dependence of chlorophenol(s)/phenol adsorption on activated carbon. It is accepted [28,41,42] that uptake is favored under acidic conditions ($pH < 3$) where the interaction between the positively charged surface and the chlorophenolic/phenolic species is facilitated via the dispersion effect. The adsorption capacity declines at pH close to the pK_a of chlorophenol/phenol to drop (at $pH > 12$) to 22–80% of the uptake in acid media [14,39,41–44], an effect that is taken to result from electrostatic repulsion between the negatively charged carbon surface and the (chloro-)phenolate anions [28,41,42].

Features common to HDC over both Pd/C and Pd/Al_2O_3 are the increase in X_{Cl} with the addition of base (Tables 2–7), higher $S_{2\text{-CP}}$ at higher $[NaOH]_0$ (Figs. 2a and 8a), and the significant elevation of $S_{2\text{-CP}}$ with the addition of more concentrated CsOH (Figs. 4 and 8). The first effect can be attributed to a suppression of HCl poisoning, and the second a result of the more severe inhibition of the 2-CP to phenol step due to stronger electrostatic repulsion between the 2-chlorophenolate anions and the negatively charge surface at higher pH. The third response can be explained on the basis of a Cs^+/chlorophenolate ion pair formation that limits the degree of dechlorination of the sterically hindered *ortho*-Cl substituent. Taking 2,4-DCP HDC over Pd/Al_2O_3, a maximum $(R_{HDC})_0$ was attained at pH 7–9 with NaOH addition (Table 2). At $pH < 5$ the depletion of chlorophenolate anions in solution limits HDC while at $pH > 10$ the development of a negative charge on the support hinders reactant/catalyst interaction(s) leading to C–Cl scission. Bulk solution pH close to the chloroarene pK_a and Al_2O_3 pH_{pzc} is optimum, suggesting that chlorophenolate anions are more reactive than chlorophenolic species, as was proposed by Felis et al. [15]. In the case of Pd/C, a higher pH ($\geqslant 9$) results in more effective HDC (Table 5), indicative of the beneficial effects of chloroarene dissociation leading to higher $(R_{HDC})_0$. In contrast to Pd/Al_2O_3, the $(R_{HDC})_0$ delivered by Pd/C increased with increasing $[NaOH]_0$ ($> 0.037\ mol\, dm^{-3}$), a direct result of the difference in the chemical nature of Al_2O_3 and carbon surfaces. The latter bears a lower charge density (less electrostatic repulsion) and a stronger nonelectrostatic attraction with chlorophenolate anions in solution.

The difference in the selectivity response with respect to the partially dechlorinated 2-CP is evident where $pH < 10$. In the absence of base, a lower $S_{2\text{-CP}}$ was delivered by Pd/Al_2O_3 at a given $X_{2,4\text{-DCP}}$; compare the entries in Figs. 2a and 6a. This can be linked to the stronger electrostatic attraction between the 2-chlorophenolate anions and the positively charged Al_2O_3 ($pH < 5$, see Fig. 2b), where the delocalization of the negative charge on the 2-chlorophenolate anion is less effective than the disubstituted arene due to presence of the second electron-withdrawing *para*-Cl. Comparing the 2-CP HDC performance over Pd/Al_2O_3 with 2,4-DCP (Fig. 3), it is evident that the decline of $(R_{HDC})_0$ for 2-CP is more sensitive to the addition of NaOH (with a consequent reduction in positive surface charge density). By comparison, Pd/C exhibits a greater preference for interaction with chlorophenolic species at low pH. In terms of adsorption affinity, the uptake capacity of activated carbon for 2,4-DCP has been found to be ca. 1.5–6 times of that for 2-CP [45,46]. This can be linked to the greater solubility of 2-CP (28.5 compared with 4.5 $g\, dm^{-3}$ for 2,4-DCP) but is also the result of a weaker dispersion force between the 2-CP and the carbon surface. Under near neutral conditions (pH 8–10), the decrease in $S_{2\text{-CP}}$ (see Figs. 2a and 6a) suggests improved 2-CP conversion due to a more effective contribution of electrostatic forces; 2-CP dissociation at pH 8–10 is ca. 22–96 mol/mol%. A comparison of 2-CP HDC performance over Pd/C with 2,4-DCP (Fig. 7) reveals a more significant increase of 2-CP HDC rates at $[NaOH]_0 \leqslant 0.037\ mol\, dm^{-3}$ with a subsequent decline at $[NaOH]_0 > 0.057\ mol\, dm^{-3}$, demonstrating the role of electrostatic forces in determining 2-CP reactivity on Pd/C.

The response to NH_4OH addition over both catalysts follows the same trends established for NaOH. The higher $[NH_4OH]_0$ required to influence HDC performance can be attributed to the weaker basicity of NH_4OH which demonstrates further that HDC performance is governed by solution pH. An increase in HDC activity at higher $[AMOH]_0$ in the order of $CsOH > RbOH \approx KOH > NaOH \approx LiOH$ was only apparent for reactions over Pd/C, where the AMOH can be considered to behave as a cocatalyst. The activity sequence matches that of increasing AM^+ affinity for the negatively charged carbon surface where AM^+ interactions at the interface enhance $(R_{HDC})_0$. Such an effect is not without precedent in that it has been established [47,48] that the presence of charge-transfer cations influences the hydroprocessing activity of supported Pd through a modification of the supported metal site electron density. In the case of Pd/Al_2O_3, any beneficial effects due to increasing polarizability of the AM in solution is counterbalanced by the reverse sequence of the chemical affinity with the alumina surface and the resultant $(R_{HDC})_0$ is largely insensitive to the nature of the AM cation.

5. Conclusions

In the aqueous-phase batch HDC of 2,4-DCP over 1 wt/wt% Pd/Al_2O_3 and Pd/C in the absence and presence of base, the results of this study support the following conclusions:

(1) HDC over Pd/Al_2O_3 delivers a maximum $(R_{HDC})_0$ at pH 7–9 (NaOH addition), suggesting that both a depletion of chlorophenolate anions in solution ($pH < 5$) and the development of a negative charge on the support ($pH > 10$) hinders catalyst/reactant interaction(s) that facilitate C–Cl scission. In the case of Pd/C, a higher pH ($\geqslant 9$) results in more effective HDC due to the stronger dispersion forces between the aromatic ring of the chlorophenolate anions and the carbon surface.

(2) An increase in the ultimate fractional dechlorination with the addition of base is observed for both catalysts and can be attributed to a lessening of any inhibition due to the HCl product. Appreciably more concentrated NH_4OH, as a weak base, is required to significantly elevate HDC but a complete dechlorination of 2,4-DCP is possible.

(3) A higher $S_{2\text{-CP}}$ at higher $[NaOH]_0$ ($pH > 10$) is observed for both catalysts and can be linked to a suppression of the 2-CP to phenol HDC step as a result of the stronger electrostatic repulsion between the 2-chlorophenolate anion and the negatively charge surface. $S_{2\text{-CP}}$ differs for reaction over Pd/Al_2O_3 and Pd/C at $pH < 10$ where, in the absence of base, a higher $S_{2\text{-CP}}$ is delivered by Pd/C due to the weaker dispersion attraction between the 2-CP and the carbon surface while at pH 8–10 the lower $S_{2\text{-CP}}$ associated with Pd/C is the result of a more effective electrostatic interaction with the 2-chorophenolate anion.

(4) In the case of Pd/C, $(R_{HDC})_0$ at higher $[AMOH]_0$ ($0.074\ mol\,dm^{-3}$) increases in the order of $Li^+ \approx Na^+ < K^+ \approx Rb^+ > Cs^+$ which coincides with the adsorption affinity sequence on a negatively charged carbon surface where interaction with Pd/C through charge transfer must serve to raise the HDC activity of the Pd sites; the Pd/Al_2O_3 HDC rate is insensitive to the nature of the AM cation.

(5) A significantly higher $S_{2\text{-CP}}$ at higher $[CsOH]_0$ is observed for both catalysts and can be attributed to chlorophenolate anion/Cs^+ ion pair formation that hinders *ortho*-Cl dechlorination.

Notation

$[AMOH]_0$	Initial concentration of alkali metal hydroxide ($mol\,dm^{-3}$);
$[Base]$	Concentration of base ($mol\,dm^{-3}$);
C_{cat}	Concentration of catalyst ($g_{cat}\,dm^{-3}$);
$[2\text{-CP}]_0$	Initial concentration of 2-chlorophenol ($mol\,dm^{-3}$);
$\bar{d}_{Pd}$	Surface-area-weighted average Pd particle diameter (nm);
$[2,4\text{-DCP}]_0$	Initial concentration of 2,4-dichlorophenol ($mol\,dm^{-3}$);
$[NaOH]_0$	Initial concentration of NaOH ($mol\,dm^{-3}$);
$[Organic\text{-}Cl]_0$	Initial concentration of Cl associated with the aromatic feed ($mol\,dm^{-3}$);
pH_{pzc}	pH associated with the point of zero charge for the catalyst;
$(R_{2,4\text{-DCP}})_0$	Initial rate of consumption of 2,4-dichlorophenol ($mmol\,g_{cat}^{-1}\,min^{-1}$);
$(R_{HDC})_0$	Initial hydrodchlorination rate ($mmol_{Cl}\,g_{cat}^{-1}\,min^{-1}$);
$S_{2\text{-CP}}$	Hydrodechlorination selectivity with respect to 2-chlorophenol, defined by Eq. (2) (dimensionless);
X_{Cl}	Fractional dechlorination after 120 min reaction (dimensionless);
$X_{2,4\text{-DCP}}$	Fractional conversion of 2,4-dichlorophenol, defined by Eq. (1) (dimensionless);
$Y_{C=O}$	Yield of cyclohexanone after 120 min reaction (dimensionless).

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