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Catalyst deactivation during the liquid phase hydrodechlorination of 2,4-dichlorophenol over supported Pd: influence of the support

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Abstract

In the liquid phase hydrodechlorination (HDC) of 2,4-dichlorophenol (DCP) over 1% (w/w) Pd/C and 1% (w/w) Pd/Al_2O_3, operated in the kinetic controlled regime, 2-chlorophenol is the only intermediate partially dechlorinated product which reacts further to yield phenol; cyclohexanone is formed over Pd/Al_2O_3 prior to the completion of dechlorination. Reuse of the catalysts revealed an appreciable deactivation of Pd/C and a limited loss of activity in the case of Pd/Al_2O_3. The Pd content, BET surface area, temperature programmed reduction (TPR) and hydrogen chemisorption/temperature programmed desorption (TPD) characteristics of the fresh and used catalyst samples have been recorded. The results indicate that the Pd/C catalyst lost ca. 50% of the total surface area during HDC operation due to occluded organic species but this was readily recovered by TPR. Measurement of the Pd content in the catalysts pre-/post-reaction and in the reaction liquid has demonstrated that Pd leaching is not significant during reaction. The nature of the surface active hydrogen is probed, hydrogen desorption characteristics are discussed and the possible sources of activity loss are considered.

Keywords: Hydrodechlorination; 2,4-Dichlorophenol; Pd/C; Pd/Al_2O_3; Hydrogen chemisorption/desorption

1. Introduction

Contamination of water and soil by chlorophenolic compounds (CPs) now represents a significant environmental burden due to widespread industrial use of CPs and their inherent toxicity and persistence in the environment [1]. Chlorophenols have been employed as wood preservatives, pesticides/herbicide precursors and can be found in effluent streams associated with the pulp and paper industries [2]. 2,4-Dichlorophenol (DCP), the focus of this study, is a high volume feedstock chemical used in the synthesis of pharmaceuticals and the herbicide 2,4-dichlorophenoxyacetic (2,4-D) acid of which 26,300 t were produced in the US in 1995 [3]. The large scale production and usage of 2,4-DCP has led to growing concern regarding operation safety [4] and the necessary treatment of the related effluent and polluted ground/surface water [5,6]. It has been reported that the low 2,4-DCP biodegradation rate ($<15\,mg\,g^{-1}\,h^{-1}$) results in an unabated transport through waste water treatment stations [7]. Adsorption on activated carbon can serve to both separate CPs from diluted waste water and to compliment bioremediation [8,9]. However, while separation methodologies offer a means of concentration, recovery/reuse of the CPs is problematic, as is the treatment of the spent carbon adsorbent. With increasingly more restrictive landfill legislation and the possibility of hazardous by-product release during incineration [10], a catalytic based processing represents a far more progressive alternative. Most of the catalytic strategies adopted, to date, for CP detoxification

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are oxidative in nature (e.g. wet oxidation [11], photocatalytic degradation [12]). Catalytic hydrodechlorination (HDC) as a reductive approach is now viewed as a promising emerging technology [13]. The advantages of catalytic HDC compared with traditional oxidation methods (and even biological treatment) include [14–16]: low temperature non-destructive transformation with no directly associated NO_x/SO_x emissions; no associated dibenzo-*p*-dioxin and dibenzofuran formation; selective Cl removal to generate recyclable products.

The available literature supports the application of liquid phase catalytic HDC as a feasible CP waste detoxification methodology [16–19]. Phenol as the ultimate dechlorination product can be further converted over Pd/C (under ambient conditions) to less toxic cyclohexanone and cyclohexanol [15,20,21]. In our previous research, we demonstrated the viability of 2,4-DCP HDC by commercially available Pd/C and Pd/Al_2O_3 catalysts over the temperature interval 273–303 K and discussed the relative importance of the associated physical (transport)/chemical (kinetic) processes [22,23]. One critical issue associated with HDC is the appreciable catalyst deactivation [24]. In gas phase operation, catalyst deactivation has been linked to a HCl/Cl poisoning [25], carbon deposition [26] and metal sintering [27]. In liquid phase HDC, loss of catalyst activity has been attributed to a poisoning by the HCl product and a leaching of the metal component [15]. Due to the weak acidity of CPs, the addition of base can serve to both increase solubility as well as limiting HCl poisoning [28]. It should, however, be noted that a constant HDC of 4-CP in water was recorded over Pd supported on carbon cloth for up to 3 h without the addition of any base [20]. In order to facilitate the design of an optimal catalytic process, the intrinsic dechlorination behavior must be linked to catalyst structural characteristics. A full characterization of the catalyst pre- and post-HDC is therefore necessary which, when coupled with activity/selectivity data, can inform catalyst development. There is, however, limited literature available on catalyst characterization applied to liquid phase HDC [25,29–32]. In this study, the deactivation of 1% (w/w) Pd/C and 1% (w/w) Pd/Al_2O_3 catalysts during the liquid phase HDC of 2,4-DCP has been examined. The fresh and used catalysts have been analyzed in terms of Pd content, BET surface area, temperature programmed reduction (TPR), hydrogen chemisorption and subsequent temperature programmed desorption (TPD) in order to probe the structural changes that accompany deactivation.

2. Experimental

2.1. Materials

2,4-DCP (>99%) and NaOH (>99%) were purchased from Aldrich Chemical Co. and used as received. Catalysts with the nominal loadings 1% (w/w) Pd/C and a 1% (w/w) Pd/Al_2O_3 were also supplied by Aldrich. All the catalysts were sieved (ATM fine test sieves) into batches of varying particle diameter range: 200–325 mesh (75–45 μm), 325–400 mesh (45–37 μm) and <400 mesh (37 μm). The mean particle diameters in the batches as supplied were 89 μm (1% (w/w) Pd/C) and 69 μm (1% (w/w) Pd/Al_2O_3); these were determined on the basis of a distribution of particle sizes by weight. Stock 2,4-DCP solutions were prepared with deionized water (electronic resistance $\geq$15 MΩ).

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 ($250\,cm^3\,min^{-1}$); loss of reactor contents (organic reactant + product) was minimal. A glass impeller provided effective agitation at a stirring speed of 1100 rpm. This choice of stirring speed and hydrogen flow rate served to minimize transport limitations as described elsewhere [22] along with a full description of the catalytic reactor. A coolant circulating jacket connected to a cooling recirculator (Julabo) was used to stabilize the temperature to within ± 0.5 K. At the beginning of each experiment, $100\,cm^3$ of stock CP aqueous solution containing NaOH ([OH]/[Cl] slightly above $1\,mol\,mol^{-1}$) was charged with catalyst. The initial concentration of the 2,4-DCP used in this study was $0.0475\,mol\,dm^{-3}$ with a catalyst concentration of $0.5\,g_{cat}\,dm^{-3}$. The suspension was agitated in a He flow ($50\,cm^3\,min^{-1}$) and the temperature allowed to stabilize (273–303 K); hydrogen was then introduced (time $t = 0$ for reaction). A non-invasive liquid sampling system via in-line filters allowed a controlled syringe removal of aliquots ($0.5\,\mathrm{cm}^3$) of reactant/product(s). Prior to gas chromatographic analysis, the basic solution samples were neutralized with dilute acetic acid (ca. 0.2 M). Before reuse, the catalyst was washed at least three times with $50\,\mathrm{cm}^3$ deionized water and the final wash water sample was tested by GC to ensure that there was no significant organic component ($<0.2\,\mathrm{mmol\,dm}^{-3}$).

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 % was converted to mol% using regression equations based on detailed calibration and the detection limit typically corresponded to a feedstock conversion <0.4 mol%: overall analytic 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 non-volatile and the effect of uptake on the supports was negligible [20]. The HCl produced and hydrogen consumption during reaction ($\mathrm{mol\,dm}^{-3}$) have been calculated from the molar balance based on the GC analysis of organic content. The selectivity (as a percentage) with respect to 2-CP ($S_{2\text{-CP}}$) in the HDC of 2,4-DCP is defined as the mol% 2-CP in terms of the total moles of product(s) formed, i.e.

$$S_{2\text{-CP}}\,(\%) = \frac{[\text{2-CP}]}{[2,4\text{-DCP}]_0 - [2,4\text{-DCP}]} \times 100 \qquad (1)$$

where $[2,4\text{-DCP}]_0$ is the initial concentration of 2,4-DCP used in the reaction. The initial 2,4-DCP consumption rate was determined using a pseudo-first order linear regression from temporal concentration profiles. In every instance, HDC was accompanied by an induction period associated with catalyst activation and hydrogen transport. A time lag was employed to adjust the reaction time scale and the data within this time delay were neglected.

2.4. Catalysts characterization

Samples of 1% (w/w) Pd/C and 1% (w/w) Pd/Al_2O_3 catalysts before and after (120 min 2,4-DCP HDC at 303 K) use were characterized. The Pd contents of the catalyst samples were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Vista-PRO, Varian Inc.) from the diluted extract of aqua regia. The BET surface area, temperature programmed reduction, hydrogen chemisorption and temperature programmed desorption were determined using the commercial CHEM-BET 3000 (Quantachrome Instrument). After outgas at 523 K for 30 min, at least two 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. TPR of the sample followed the BET test in flowing ($20\,\mathrm{cm}^3\,\mathrm{min}^{-1}$) 5% (v/v) hydrogen in nitrogen, heating from room temperature at $10\,\mathrm{K\,min}^{-1}$ to 573 K; the TPR profile returned to baseline. The sample was maintained at 573 K for 8 h and then flushed in a pure dry nitrogen gas flow ($19\,\mathrm{cm}^3\,\mathrm{min}^{-1}$) for 30 min, cooled to room temperature and subjected to hydrogen chemisorption using a pulse titration (pulse volume = $0.1\,\mathrm{cm}^3$) procedure; hydrogen uptake is quoted as μmol H_2 at STP per g of catalyst. TPD followed the chemisorption in a pure dry N_2 flow ($19\,\mathrm{cm}^3\,\mathrm{min}^{-1}$) at $10\,\mathrm{K\,min}^{-1}$ to 573 or 723 K. The sample was maintained in the nitrogen flow at the final temperature for 30 min, cooled to room temperature and a second chemisorption–TPD cycle was conducted, followed (in the case of 1% (w/w) Pd/C) by a further TPR. Hydrogen uptake over both cycles was within ±5%; hydrogen uptakes quoted herein are the average values.

3. Results and discussion

3.1. Reaction studies

3.1.1. Effect of the Pd support

The HDC of 2,4-DCP can proceed in a stepwise and/or concerted fashion with 2- and 4-CP as partially dechlorinated products (see Fig. 1). We have shown previously [23] that the Cl component in 2,4-DCP is less susceptive to dechlorination than 2-CP or 4-CP

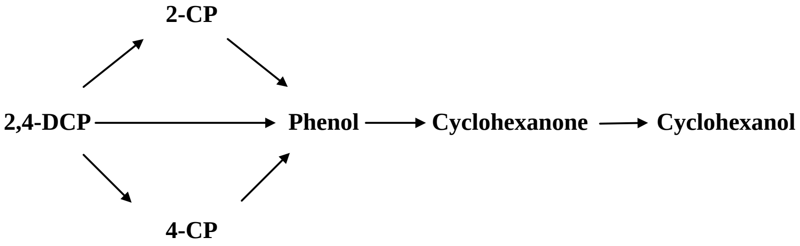

Fig. 1. Schematic of the HDC pathway for 2,4-DCP.

and invoked electronic and geometric effects to account for our observations. A typical product composition as a function of time for the HDC of 2,4-DCP over 1% (w/w) Pd/C and 1% (w/w) Pd/Al_2O_3, under identical reaction conditions, is shown in Fig. 2. It can be seen that the HDC pathway is very similar for the two catalysts. 2-CP was the only reactive intermediate product observed in terms of dechlorination and the absence of 4-CP may be explained on the basis of steric hindrance where the *ortho*-substituted Cl experiences a more restricted HDC [23]. The only deviation in catalytic behavior is the appearance of cyclohexanone (selectivity <5%) in the product associated with Pd/Al_2O_3 before dechlorination had reached completion. The relative importance of physical/chemical control in the overall HDC was considered at 273 and 303 K and the results are provided in Table 1. The initial HDC rate is defined as the initial rate of Cl removal and is calculated from pseudo-first order linear regression of the temporal HCl product concentration profiles. The initial 2,4-DCP consumption/HDC rates for both Pd/C and Pd/Al_2O_3 were independent of particle size for particles less than 45 μm, a response that is diagnostic of a catalytic system operating under kinetic control [22,23]. The initial rates with respect to catalyst mass were essentially the same for both catalysts over the temperature range, demonstrating that the nature of the support may not influence the 2,4-DCP HDC activation energy; $\Delta Ea = 55.8 \pm 1.1\,kJ\,mol^{-1}$ for 1% (w/w) Pd/C

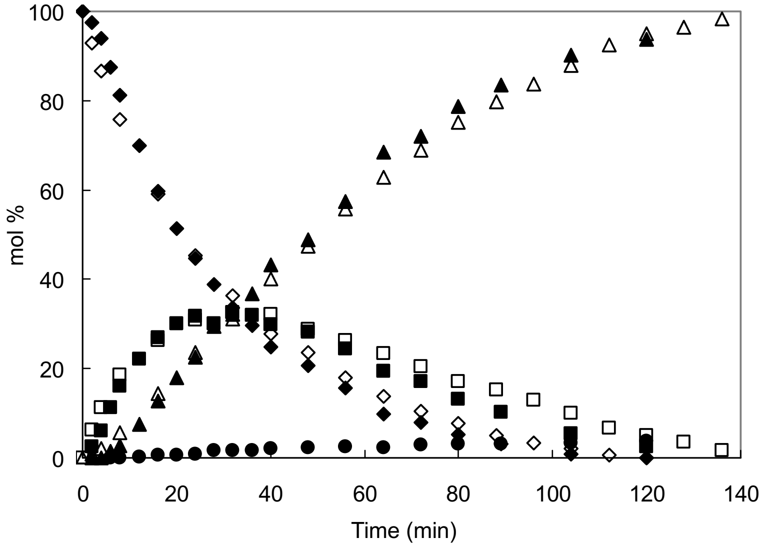

Fig. 2. HDC of 2,4-DCP over 1% (w/w) Pd/C and 1% (w/w) Pd/Al_2O_3 at 303 K: liquid phase composition (mol%) as a function of time (min) in terms of mol% 2,4-DCP (◆: Pd/Al_2O_3; ◇: Pd/C), 2-CP (■: Pd/Al_2O_3; □: Pd/C), phenol (▲: Pd/Al_2O_3; △: Pd/C) and cyclohexanone (●: Pd/Al_2O_3 only); catalyst particle size <37 μm.

Table 1
Effect of temperature and catalyst particle size on the HDC of 2,4-DCP over 1% (w/w) Pd/C and 1% (w/w) Pd/Al_2O_3

Catalyst	Temperature (K)	Catalyst particle size (μm)	Initial 2,4-DCP consumption rate ($mmol\,g_{cat}^{-1}\,min^{-1}$)	Initial HDC rate ($mmol\,g_{cat}^{-1}\,min^{-1}$)
1% (w/w) Pd/C	273	<37	0.33	0.37
	273	37–45	0.35	0.40
	303	<37	3.2	3.4
	303	37–45	3.4	3.6
1% (w/w) Pd/Al_2O_3	273	<37	0.36	0.41
	273	37–45	0.32	0.38
	303	<37	3.2	3.5
	303	37–45	2.9	3.2

[23]. The equivalency of the initial 2,4-DCP consumption and HDC rates also indicates that the direct dechlorination of 2,4-DCP to phenol is not significant and the reaction proceeds predominantly in a stepwise fashion over both catalysts.

3.1.2. *Catalyst reuse*

The possibility and extent of catalyst deactivation was probed by employing the same catalyst sample in a number of reaction cycles (of varying reaction/contact time); the initial reaction rates with reuse are given in Table 2, where the Cl/Pd ratios that are listed represent the molar ratio of HCl produced during reaction relative to the starting Pd. Both catalysts exhibited a decline in activity with reuse. While a possible loss of some catalysts particles from the reaction mixture cannot be completely discounted, it is clear that the Pd/C catalyst exhibited significant deactivation with a Cl/Pd ratio from 700 to 2000. The extent of HDC loss is clearly less severe in the case of Pd/Al_2O_3. The selectivity trends with respect to 2-CP production (see Fig. 3) for all recycled catalysts showed no significant difference from that generated for the corresponding fresh catalysts, albeit there is a discernible decrease in $S_{2\text{-CP}}$ over the recycled Pd/C. The deactivation lowered the overall 2,4-DCP consumption with no apparent specific impact on stepwise rather than complete dechlorination. Initially (at low $X_{2,4\text{-DCP}}$), the

Table 2
Initial 2,4-DCP consumption and HDC rates recorded for the fresh and reused 1% (w/w) Pd/C and 1% (w/w) Pd/Al_2O_3 at 303 K: catalyst particle size <45 μm

Catalyst	Reaction time (min)	Run	HCl produced before recycling (mmol)	Cl/Pd ratio ($mol\,mol^{-1}$)	Initial 2,4-DCP consumption rate ($mmol\,g_{cat}^{-1}\,min^{-1}$)	Initial HDC rate ($mmol\,g_{cat}^{-1}\,min^{-1}$)
1% (w/w) Pd/C	15	Fresh	3.5	745	3.1	3.8
		Reuse			1.2	1.3
	30	Fresh	4.9	1043	3.2	4.0
		Reuse			1.6	1.8
	60	Fresh	6.9	1469	3.7	4.5
		Reuse			1.8	1.9
	120	Fresh	9.4	2001	3.2	3.4
		Reuse			0.52	0.58
1% (w/w) Pd/Al_2O_3	60	Fresh	6.5	1383	2.9	3.3
		Reuse			2.6	3.1
	120	Fresh	9.4	2001	3.2	3.5
		Reuse			2.3	2.4

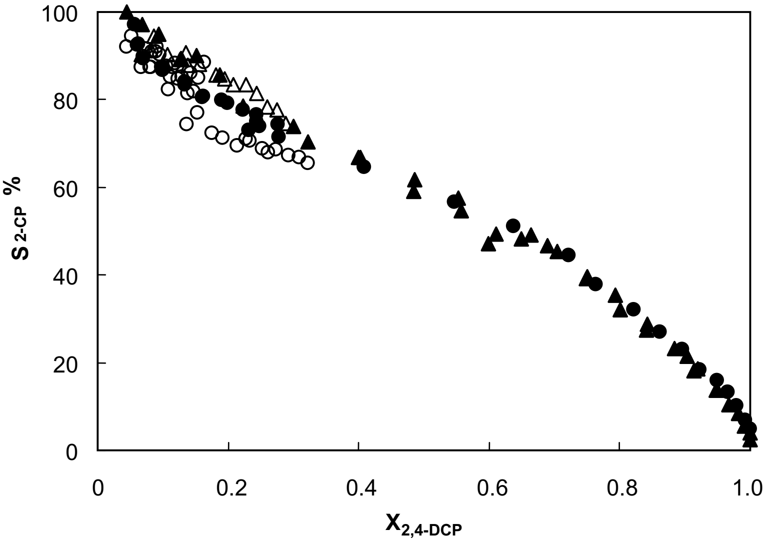

Fig. 3. Selectivity with respect to 2-CP ($S_{2\text{-CP}}$, %) as a function of 2,4-DCP conversion ($X_{2,4\text{-DCP}}$) at 303 K over 1% (w/w) Pd/C (●, ○) and 1% (w/w) Pd/Al_2O_3 (▲, △). *Note*: HDC data were collected from runs using fresh (●, ▲) and reused catalysts (○, △).

selectivity with respect to 2-CP over Pd/Al_2O_3 was slightly higher than that delivered by Pd/C, which may suggest some structure sensitivity in terms of HDC selectivity.

3.2. Characterization of fresh and used catalysts

3.2.1. Pd content and BET surface area

The bulk Pd content of the fresh and used catalysts (measured by ICP-OES) and the N_2 BET surface areas are listed in Table 3. It can be seen from the analysis of the Pd content of the used catalysts that there was no Pd loss during the reaction over Pd/Al_2O_3, while Pd leaching from Pd/C represents less than 15% of the initial amount. The Pd content in the reaction solution was analyzed and revealed corresponding trace quantities of Pd in solution. It has been reported that a 0.5% (w/w) Pd/C suffered a 20% Pd loss during a 20 h HDC of polychlorinated biphenyls (PCB) without base [33] and a 25% metal loss from 4.2% (w/w) Pd/C (with a ca. 20% drop in surface area) in a 4-CP HDC aging experiment with NH_4OH and 50/50 (v/v) ethanol/water solvent [15]. Our results are consistent with the literature and the addition of NaOH serves to prevent Pd leaching by the HCl that is produced. The loss of Pd from Pd/C is however significant when compared with Pd/Al_2O_3 and is suggestive of weaker metal/support interactions in the case of the carbon substrate. Strong interaction between supported transition metals and Al_2O_3 as carrier has been

Table 3
Pd content, BET surface area, hydrogen uptake and catalytic activities of the catalysts before and after (120 min) 2,4-DCP at 303 K

	1% (w/w) Pd/C		1% (w/w) Pd/Al_2O_3	
	Fresh	Used	Fresh	Used
BET surface area ($m^2\,g_{cat}^{-1}$)	1037	550	160	162
Pd content (%, w/w)	1.01	0.88	1.17	1.26
Hydrogen uptake ($\mu mol\,g_{cat}^{-1}$)	8.5	2.8	21	13
Initial rate of 2,4-DCP consumption ($mmol\,g_{Pd}^{-1}\,min^{-1}$)	317	24	274	174
Initial HDC rate ($mmol\,g_{Pd}^{-1}\,min^{-1}$)	337	24	299	190

Note: The initial 2,4-DCP consumption and HDC rates with respect to Pd mass are calculated from the Pd contents determined by ICP.

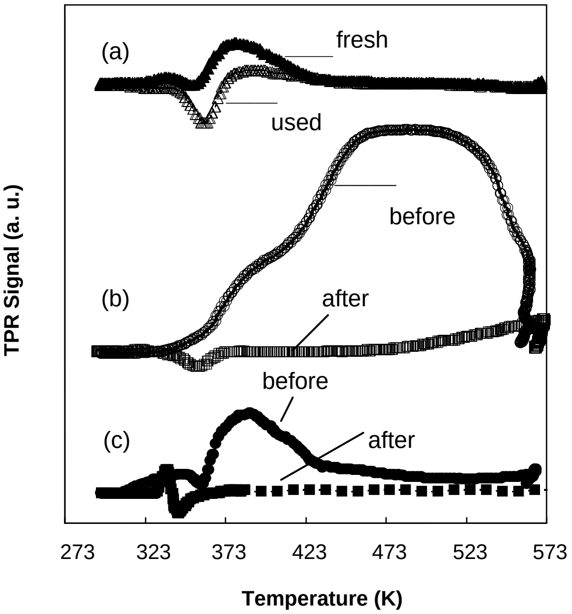

Fig. 4. TPR profiles for the fresh and used catalysts: (a) fresh (▲) and used (△) 1% (w/w) Pd/Al_2O_3; (b) used 1% (w/w) Pd/C before (○) and after (□) TPR–chemisorption–TPD cycle; (c) fresh 1% (w/w) Pd/C before (●) and after (■)TPR–chemisorption–TPD cycle.

demonstrated elsewhere [34] leading to an enhanced metal dispersion whereas there is limited binding of metals to activated carbon [35]. Nevertheless, Pd leaching cannot be the major source of the observed catalyst deactivation. Comparing the BET results for the used samples with the fresh catalysts, the surface area of Pd/Al_2O_3 was unchanged after reaction. However, the total apparent surface area of Pd/C showed a 50% loss. This decrease of surface area must be due to an occlusion of the meso/micro-pores of the activated carbon. Such an effect is to be expected given the CP uptake capacity of activated carbon when used as an adsorbent, which is in the range of 0.3–5 mmol g^{-1} [8,20]. Subjecting the same used Pd/C sample to a TPR treatment resulted in a return of the BET area to the original value (1046 $m^2\ g_{cat}{}^{-1}$), i.e. the occluded species were removed in a reductive atmosphere at $T \leq 573$ K.

3.2.2. Temperature programmed reduction (TPR)

The TPR profiles for the fresh and used catalysts are shown in Fig. 4. The catalysts as supplied (fresh samples) are passivated reduced samples. The positive peak at ca. 383 K, common to both fresh samples, corresponds to a reduction of the oxidized Pd species. The negative peak at ca. 355 K represents a Pd hydride phase change with a resultant hydrogen release [36,37]. The capability of Pd hydride formation may be linked to catalyst activity in that the hydride can serve as a source of active hydrogen during HDC reaction [36,38]. All the samples showed this Pd hydride phase change with the exception of the used Pd/C catalyst in the initial TPR (Fig. 4(b)) where the negative peak at ca. 355 K is obscured by the broad intense peak that spans the temperature range 340–560 K. The latter can be attributed to a decomposition of the species blocking the substrate pores that lower the BET value. The same sample, after a second TPR (following the TPR–chemisorption–TPD cycle) exhibited evidence of the hydride phase change. Relating this to the BET surface area results, the initial TPR recovered the exposed surface area and any loss of activity due to pore blockage should then be reversible.

3.2.3. Hydrogen chemisorption and temperature programmed desorption (TPD)

Extracting a measure of metal dispersion from hydrogen chemisorption values is problematic due to the uncertain H_2/metal uptake stoichiometry, the possibility of hydrogen spillover and the dependence of Pd hydride formation on Pd particle size [38]. However, it has been reported that the hydrogen that adsorbs on Pd and on the carbon substrate can be linked to two distinct desorption peaks at ca. 383 and 593 K, respectively [39]. This suggests that a chemisorption–desorption cycle below 593 K may be used to measure the reversible hydrogen adsorption on the supported Pd particles and a good agreement of the Pd dispersion values calculated from hydrogen titration with those obtained from TEM analysis has been observed elsewhere [35,40]. The H_2 TPD profiles (up to 723 K) for the fresh Pd/C and Pd/Al_2O_3 catalysts are shown in Fig. 5 where two hydrogen desorption peaks associated with Pd/C were observed at ca. 440 and 723 K. The first peak can be linked to hydrogen on Pd and the second (tentatively) to hydrogen spillover on carbon. The H_2 TPD for Pd/Al_2O_3 was characterized by a broad peak that spans the range 323–723 K and may represent hydrogen desorption as a continuum from the metal, metal/support

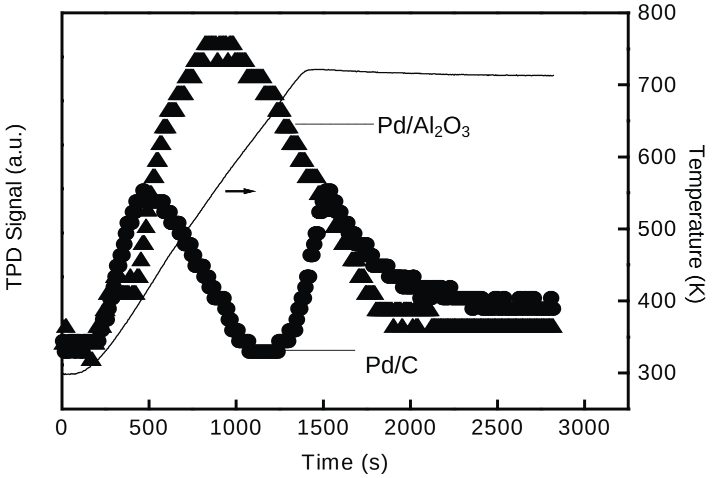

Fig. 5. TPD profiles (up to 723 K) for the fresh 1% (w/w) Pd/C (●) and fresh 1% (w/w) Pd/Al_2O_3 (▲) TPR to 723 K, at 20 K min^{-1}.

interface and support. Taking the second TPD peak for Pd/C to represent hydrogen desorption from carbon, this hydrogen loss is only initiated at $T > 640$ K, well above maximum temperature (573 K) employed in our TPR–chemisorption–TPD cycles. This means that the hydrogen uptake values listed in Table 3 can be related to the hydrogen associated with the supported Pd particles. The catalytic activities of the used sample, given in Table 3, refer to reaction after a TPR–chemisorption–TPD–TPR cycles. There is a clear correlation between the hydrogen uptake and initial HDC rates for the fresh and used Pd/Al_2O_3 catalysts. The significantly higher uptake of H_2 on Pd/Al_2O_3 is indicative of a greater dispersion of Pd on Al_2O_3 compared with activated carbon and can be attributed to the strong interaction between Pd and Al_2O_3 as noted previously [35,41,42]. The higher Pd dispersion on Al_2O_3 is not accompanied by a higher specific HDC activity compared with Pd/C. The latter may be influenced by a contribution due to hydrogen spillover as proposed elsewhere [18,43] where the possibility of structure sensitivity has yet to be established conclusively in the literature.

The H_2 TPD profiles (up to 573 K) associated with the fresh and used catalyst samples can be compared in Fig. 6. The low temperature (383 K) desorption peak for fresh Pd/C is not in evidence in the used sample (Fig. 6(a)) which is characterized by a peak at 573 K. The interaction of Cl with transition metals is known to lower the metal electron density and impact on hydrogen uptake/release characteristics [44,45]. The higher temperature desorption peak for the used Pd/C may represent a change in H/Pd surface energetics after reaction but a possible contribution due to the vaporization of residual organics still remaining on the surface after TPR cannot be ruled out. In marked contrast, the TPD profiles for the fresh and used Pd/Al_2O_3 largely overlap with the possible development of a higher temperature shoulder to the main peak for the used sample. The divergence in H_2 TPD for the fresh/used Pd/C and Pd/Al_2O_3 samples is significant, particularly when linked to the appreciable deactivation suffered by Pd/C. Estelle et al. [46] concluded that HDC activity is more sensitive to hydrogen adsorption–desorption characteristics than to the nature of the reactive haloarene. The significant loss of Pd/C activity is reflected in the disruption to the H_2 TPD where Cl/Pd interactions must induce perturbations in the Pd particle electronic structure which have a negative impact on the supply of surface reactive hydrogen, an effect that is lessened somewhat by stronger Pd/support interactions (in the case of Pd/Al_2O_3).

Comparing activated carbon with Al_2O_3 as supports, the former presents a higher surface area, a “local” hydrophobic environment at the liquid/solid interface and a greater facility for direct interaction with the chloroarene [47]. Poisoning by reactant/product

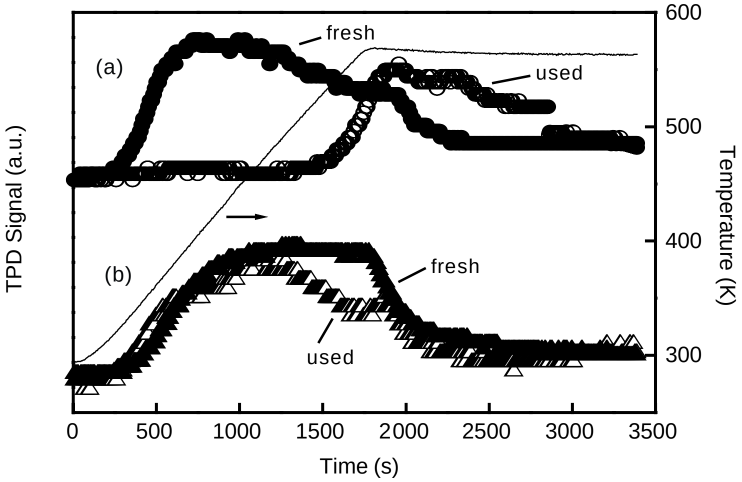

Fig. 6. TPD profiles (up to 573 K) of (a) fresh (●) and used (○) 1% (w/w) Pd/C and (b) fresh (▲) and used (△) 1% (w/w) Pd/Al_2O_3: TPR to 573 K, at 10 K min^{-1}.

accumulation at the surface is reversible [29,48] and the available surface area was restored in this study by TPR. However, the used Pd/C delivered a dramatically lower HDC that was not recovered after TPR–chemisorption–TPD–TPR cycles (see Table 3), i.e. the decomposition of the occluded organic species and the recovery of total surface area did not serve to rebuild the HDC activity. This irreversible loss of activity cannot be accounted for on the basis of the limited leaching of Pd into solution but must be due to a chemical poisoning resulting from strong Cl–Pd interactions. Both Pd catalysts suffered this decline in activity but the hydrophobic nature of the activated carbon substrate can serve to compound this deactivation. Taking the reported pK_a values of 2,4-DCP, 2-CP and phenol as 7.85, 8.11 and 10.0, respectively [49], the chloro-phenolate anions are initially the reactive species in solution and can serve as proton scavengers during HDC [22,28]. As HDC proceeds with a concomitant decrease of the pH in the bulk solution (from an initial value of 12.5–ca. 8) [22], the involvement of (chloro-)phenolic/substrate interactions come into play with an accompanying pore blockage. With a further decrease of the local pH in the catalyst matrix, (chloro-)phenolic interactions predominate and the hydrophobic environment at the liquid/support interface inhibits HCl transport away from the surface which must make for a more severe poisoning effect.

4. Conclusions

The liquid phase HDC (273–303 K) of 2,4-DCP over 1% (w/w) Pd/C and 1% (w/w) Pd/Al_2O_3 catalysts yields 2-CP as the only intermediate partially dechlorinated product which reacts further to give phenol; there is evidence of cyclohexanone formation in the case of Pd/Al_2O_3 prior to the completion of dechlorination. The initial (raw) 2,4-DCP HDC activities are similar (per gram of catalyst) for both samples where the reaction is operated under kinetic control (with catalyst particles $\leq 45\,\mu m$). Catalyst reuse was accompanied by a loss of HDC activity that was significantly more marked in the case of Pd/C. The selectivity/activity relationship in terms of partial dechlorination was essentially the same for both fresh and used catalysts. BET analysis revealed a loss of ca. 50% of the total Pd/C surface area during HDC due to pore blockage, an effect that was reversed by a subsequent TPR. ICP analysis of the Pd content in the catalysts and bulk solution demonstrates that Pd leaching is not a significant contributor to activity decline but there was a definite Pd loss (ca. 10%) from the activated carbon substrate. Hydrogen TPD from the fresh and used catalysts has revealed a marked change in the surface hydrogen associated with Pd/C after HDC, a feature that can be linked to the loss of activity. Based on the pre- and post-characterization data, the most plausible cause of deactivation for both Pd/C and Pd/Al_2O_3 in liquid phase HDC is chemical poisoning through Cl–Pd interactions(s) where Al_2O_3 serves to stabilize the supported Pd to a greater extent.

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References

[1] P.M. Armenante, D. Kafkewitz, G.A. Lewandowski, C.-J. Jou, Water Res. 33 (3) (1999) 681–692.

[2] P.H. Pritchard, E.J. O'Neill, C.M. Spain, D.J. Ahern, Appl. Environ. Microbiol. 53 (1987) 1833–1838.

[3] U.S. EPA, The Inventory of Sources of Dioxin in the United States, EPA/600/P-98/002Aa, 1998.

[4] U.S. EPA, Chemical Advisory and Notice of Potential Risk: Skin exposure to molten 2,4-Dichlorophenol (2,4-DCP) can cause rapid death, Advisory No. 8EHQ-14302, 2000.

[5] C.C. Wang, C.M. Lee, C.H. Kuan, Chemosphere 41 (2000) 447–452.

[6] S. Sabhi, J. Kiwi, Water Res. 35 (8) (2001) 1994–2002.

[7] P. Pitter, J. Chudoba, Biodegradability of Organic Substances in the Aqueous Environment, CRC Press, Boca Raton, FL, USA, 1991.

[8] A.A.M. Daifullah, B.S. Girgis, Water Res. 32 (1998) 1169–1177.

[9] F. Caturla, J.M. Marti-Matinez, M. Molina-Sobio, J. Colloid Interface Sci. 124 (1988) 528–534.

[10] M.D. Erickson, S.E. Swanson, J.D. Flora, G.D. Hinshaw, Environ. Sci. Technol. 23 (1989) 462–470.

[11] J. Qin, Q. Zhang, K.T. Chuang, Appl. Catal. B: Environ. 29 (2001) 115.

[12] A. Svenson, L.O. Kjeller, C. Rappe, Chemosphere 19 (1989) 585–587.

[13] E.-J. Shin, M.A. Keane, Chem. Eng. Sci. 54 (1999) 1109–1120.

[14] P.N. Rylander, Catalytic Hydrogenation over Platinum Metals, Academic Press, New York, 1967, pp. 405–411.

[15] J.B. Hoke, G.A. Gramiccioni, E.N. Balko, Appl. Catal. B: Environ. 1 (1992) 285–296.

[16] V. Felis, P. Fouilloux, C.D. Bellefon, D. Schweich, Rec. Prog. Gen. Proc. 13 (1999) 303–309.

[17] Yu Matatov-Meytal, M. Sheintuch, Catal. Today 75 (2002) 63–67.

[18] G. Bengtson, H. Scheel, J. Theis, D. Fritsch, Chem. Eng. J. 85 (2002) 303–311.

[19] V. Felis, C.D. Bellefon, P. Fouilloux, D. Schweich, Appl. Catal. B: Environ. 20 (1999) 91–100.

[20] Yu Shindler, Yu Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 40 (2001) 3301–3315.

[21] F. Murena, F. Gioia, Catal. Today 75 (2002) 57–61.

[22] G. Yuan, M.A. Keane, Chem. Eng. Sci. 58 (2003) 257–267.

[23] G. Yuan, M.A. Keane, Catal. Commun. 4 (2003) 195–201.

[24] F.J. Urbano, J.M. Marinas, J. Mol. Catal. A: Chem. 173 (2001) 329–345.

[25] E.-J. Shin, A. Spiller, G. Tavoularis, M.A. Keane, Phys. Chem. Chem. Phys. 1 (1999) 3173–3181.

[26] S. Ordonez, F.V. Diez, H. Sastre, Appl. Catal. B: Environ. 31 (2001) 112–122.

[27] D.J. Moon, M.J. Chung, K.Y. Park, S.I. Hong, App. Catal. A: Gen. 168 (1998) 159–170.

[28] V. Felis, C.D. Bellefon, P. Fouilloux, D. Schweich, Appl. Catal. B: Environ. 20 (1999) 91–100.

[29] Yu Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 37 (2) (1998) 309–326.

[30] L. Gomez-Sainero, A. Cortes, X.L. Seoane, A. Arcoya, Ind. Eng. Chem. Res. 39 (2000) 2849–2854.

[31] M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, F. Lafont, A. Marinas, J.M. Marinas, F.J. Urbano, J. Mol. Catal. A: Chem. 184 (2002) 237–245.

[32] E.V. Golubina, E.S. Lokteva, V.V. Lunin, A.O. Turakulova, V.I. Simagina, I.V. Stoyanova, Appl. Catal. A: Gen. 241 (2003) 123–132.

[33] P. Forni, L. Prati, M. Rossi, Appl. Catal. B: Environ. 14 (1997) 49–53.

[34] M.I. Zaki, Stud. Surf. Sci. Catal. 100 (1996) 569–577.

[35] R.T.K. Baker, E.B. Prestridge, R.L. Garten, J. Catal. 59 (1979) 293–302.

[36] N.K. Nag, J. Phys. Chem. B 105 (2001) 5945–5949.

[37] V.H. Sandoval, C.E. Gigola, Appl. Catal. A: Gen. 148 (1996) 81–96.

[38] N. Krishnankutty, M.A. Vannice, J. Catal. 155 (1995) 312–326.

[39] T. Ouchaib, B. Moraweck, J. Massardier, A. Renouprez, Catal. Today 7 (1990) 191–198.

[40] N. Martin, S. Fuentes, Carbon 26 (1988) 795–803.

[41] B. Ealet, E. Gillet, Surf. Sci. 281 (1993) 91–101.

[42] H. Dropsch, M. Baerns, Appl. Catal. A: Gen. 158 (1997) 163–183.

[43] L. Gomez-Sainero, X.L. Seoane, J.L. Fierro, A. Arcoya, J. Catal. 209 (2002) 279–288.

[44] C. Hoang-Van, Y. Kachaya, S.J. Teichner, Y. Arnaud, J.A. Dalmon, Appl. Catal. 46 (1989) 281–296.

[45] T. Halchev, E. Ruckenstein, J. Catal. 73 (1982) 171–186.

[46] J. Estelle, J. Ruz, Y. Cesteros, R. Fernandez, P. Salagre, F. Medina, J.-E. Sueiras, J. Chem. Soc., Faraday Trans. 92 (1996) 2811–2816.

[47] C. Park, M.A. Keane, In, Interfacial applications in environmental engineering, M.A. Keane (Ed.), Marcel Dekker, New York, 2002, pp. 165–192.

[48] Y. Ukisu, S. Kameoka, T. Miyadera, Appl. Catal. B: Environ. 27 (2000) 97–104.

[49] J.C. Liu, P.S. Chang, Water Sci. Technol. 35 (7) (1997) 123–130.