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Review

A review of catalytic approaches to waste minimization: case study — liquid-phase catalytic treatment of chlorophenols

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Abstract: Effective waste management must address waste reduction, reuse, recovery/recycle and, as the least progressive option, waste treatment. Catalysis can serve as an integral green processing tool, ensuring lower operating pressures/temperatures with a reduction in energy requirements while providing alternative cleaner synthesis routes and facilitating waste conversion to reusable material. The case study chosen to illustrate the role that catalysis has to play in waste minimization deals with the conversion of toxic chlorophenols in wastewater. The presence of chloro-organic emissions is of increasing concern with mounting evidence of adverse ecological and public health impacts. A critical overview of the existing treatment technologies is provided with an analysis of the available literature on catalytic dechlorination. The efficacy of Pd/Al_2O_3 to promote the hydrogen-mediated dechlorination of mono- and dichlorophenols is demonstrated, taking account of both the physical and chemical contributions in this three-phase (solid catalyst and liquid/gaseous reactants) system. Hydrodechlorination activity and selectivity trends are discussed in terms of chloro-isomer structure, the influence of temperature is discussed, the role of base (NaOH) addition is examined and the feasibility of catalyst reuse is addressed.
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Keywords: waste minimization; chlorophenols; catalytic hydrodechlorination; palladium on alumina; detoxification; recycle

INTRODUCTION: CATALYSIS AND WASTE MINIMIZATION

It is now accepted that a progressive approach to chemical processing must embrace the 'four Rs', ie reduction, reuse, recycling and (energy) recovery.[1] The ultimate goal is the achievement of zero waste, the development of novel low energy cleaner manufacturing technologies that support pollution avoidance/prevention at source, ie what has become known as 'green' processing. The term 'waste', in the context of commercial chemical processes, encompasses material that was not used for its intended purpose or unwanted material produced as a consequence of a secondary process. In the chemical industry, waste is either considered inert or contaminated. Inert waste can be recycled or released into the environment whereas contaminated waste, the subject of this review, must be treated before the components can be recycled/released. The accepted waste minimization 'hierarchy' is illustrated in Fig 1, which identifies the route to responsible waste management—disposal only comes into play when all possible reduction/reuse/recycle/treatment options have been exhausted. Catalysis is an integral component in any green processing technology, serving as an important tool to support sustainable development. Heterogeneous catalysis (solid catalyst used to promote the conversion of reactants in the liquid and/or gas phases), in particular, has always had an environmental dimension as the deployment of catalysts ensures lower operating temperatures and/or pressures with a resultant reduction in fuel usage/waste production. The emergence of 'environmental catalysis' as a discipline has focused on the development of catalysts to either decompose environmentally unacceptable compounds or provide alternative catalytic syntheses of important compounds without the formation of environmentally unacceptable by-products. Catalysts play key roles in: (a) the production of clean fuels; (b) the conversion of waste and green raw materials into energy; (c) clean combustion in terms of controlling NO_x and soot production and

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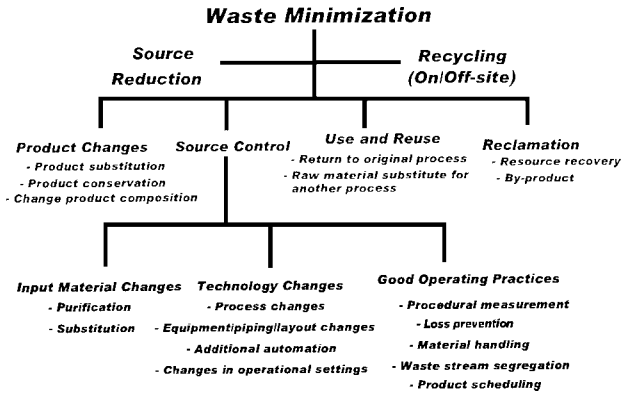

Figure 1. The hierarchy of waste minimization.

reducing greenhouse gas emissions; (d) selective polymer synthesis; (e) H_2 and syngas production; and (f) fuel cell development. The catalytic strategy considered in this review is directed at a low-temperature transformation of toxic chloroarene waste into benign reusable raw material. Where a manufacturing process is energy intensive, a controlled recycle/reuse is an effective means of decreasing overall negative environmental impacts.[2] The study of the causes, effects and control of pollution remains a fast-moving field of research, characterized by changes of emphasis and often of perception. Authoritative scientific data with a solid interpretative basis are essential to ensure significant progress in terms of environmental pollution control. It is estimated that over 90% of hazardous waste is aqueous[3] and, for that reason, this review deals with heterogeneous catalysis in aqueous media. Water is the most fundamental of resources and, without it, as the cliché has it, life could not exist on land. The fate and overall impact of any pollutant that enters the aquatic environment are difficult, if not impossible, to assess given the prevailing complex interrelated bio-processes/cycles. It is therefore essential to prevent any toxic release at source and severely limit any possibility of polluted groundwater release, so minimizing the environmental burden. The past decade has seen a plethora of scientific publications that address the issue of catalysis from the perspective of 'green' synthesis/environmental pollution control. Rather than entering into an enumeration of this burgeoning literature, the author has chosen to examine the role of catalysis in treating chloroaromatic waste. The review will be focused further to examine one case study for illustrative purposes—the catalytic hydrodechlorination (HDC) of chlorophenols, setting out the advantages of the catalytic approach with a critical assessment of the existing literature. The applicability of this approach is evaluated by examining the HDC of aqueous chlorophenolic solutions using alumina-supported Pd as catalyst, addressing the physical vs chemical constraints in this three-phase reaction system with consideration of the critical catalyst structural characteristics, pertinent reaction selectivity patterns and the issue of catalyst deactivation/catalyst reuse.

ENVIRONMENTAL IMPLICATIONS OF CHLOROPHENOL WASTE

Chloroaromatics are well established as persistent toxic compounds for which the environment has little assimilative capacity.[4,5] Indeed, the lethal effects of chlorine-containing compounds have been well recognized for some time, from the use of asphyxiating gases in World War I (eg phosgene and mustard gas), through defoliants (Agent Orange) in the Vietnam War to the application of the powerful insecticide DDT. The release of chlorinated organic compounds into the natural environment proceeded unabated until the late 1960s, as a result of the upsurge in industrial processes based on halogenated raw materials. The introduction of stringent legislation has served to curtail those emissions from commercial operations that lead to the contamination of water, land and air.[1] In addition to the legislative demands, the economic pressures faced by the commercial sector in the 21st century include loss of potentially valuable resources through waste, escalating disposal charges and increasing raw material/energy costs. Chlorophenols (CPs) are commercially important chemicals, used as end products and intermediates in the manufacture of herbicides, dyes and plant growth regulators.[6–8] Aromatic chlorination reactions are notoriously non-selective with limited control over the ultimate product composition. The development of a low waste-producing process that generates organohalogen products necessitates the inclusion of a robust waste processing/detoxification component where the energy requirements of such a downstream process must be weighed against the possibility of recycle and the high value of the final product. The effectiveness of distillation as a means of treating effluent stream(s) from the chlorinator is limited, even when coupled with a crystallization step.[9] The presence of chlorinated compounds in effluent discharges is of increasing concern owing to the mounting evidence of adverse stratospheric ozone, ecological and public health impacts.[10] Waste associated with chlorination processes is typically xenobiotic and, having no analogous compounds in nature, there is no natural means of ameliorating the negative environmental impact. Chlorobenzenes are sparingly soluble in water and soil contamination is the predominant environmental impact.[11] CPs are significantly more soluble in water (1000 mg 2-chlorophenol dm^{-3} at 298 K[12]) with recorded[13] LC_{50} (lethal concentration, 50%) values spanning the range 2–20 mg dm^{-3} and have been listed for some time by the US Environmental Protection Agency[14–16] and European regulatory authorities[17] as 'priority pollutants', specifically targeted in terms of emission control. CPs are poorly biodegradable with a half-life in aerobic waters that can exceed 3 months and can exceed some years in organic sediments.[18] The ecological impact is dependent on the nature and concentration of the discharge and the rate of transport/dispersion, which is controlled by advection

(mass movement) and mixing or diffusion (without net movement of water). It has been reported that the low 2,4-dichlorophenol (2,4-DCP) biodegradation rate ($<15\,mg\,g^{-1}\,h^{-1}$) results in an unabated transport through wastewater treatment stations.[19] CPs have been isolated in both surface and ground waters far removed from the presumed point of entry.[20,21] The existing guidelines set the permissible CP level (depending on Cl content) in surface water[22] at $0.06-4.4\,mg\,dm^{-3}$ and the permissible concentration in drinking water at $10\,\mu g\,dm^{-3}$.[17]

There is now an urgent need for efficient methods of dechlorination that are suitable for eliminating CPs from both concentrated industrial effluents and diluted polluted groundwater. The existing control strategies involve some form of 'end-of-pipe' treatment, eg adsorption, incineration and catalytic/chemical oxidation. Incineration requires high temperatures (1200–1500 K) and excess oxygen[23,24] where products of incomplete combustion, polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs) are far more toxic than the chlorinated feed.[25] The primary incinerator design measures cannot guarantee compliance with present (ca $0.1\,mg\,m^{-3}$) or future legislated PCDD/PCDF emissions.[26] Indeed, Addink and Altwicker[27] have recently demonstrated that the combustion of *o*-dichlorobenzene generates a chlorinated soot that exhibits high reactivity with regard to PCDD/PCDF formation. Chlorinated dioxins and furans are regarded as the most severe environmental contaminants with toxicities that are orders of magnitude greater than those of strychnine and sodium cyanide; immune system damage, reproductive effects/birth defects, cancer and neurological effects have been established for short-term exposure to low concentrations.[28,29] Phase transfer/physical separation often precedes an ultimate destructive waste treatment and typically involves adsorption on activated carbon.[11,30–33] Adsorption offers a means of concentration rather than transformation and, where the adsorbate is a mixture of chlorinated isomers, selective recovery/recycle of a target isomer is certainly problematic, if not impossible. Catalytic combustion is preferable to incineration (lower energy demands/NO_x emissions)[34] but generates unwanted CO_2 and products such as CO, Cl_2 and $COCl_2$ that are difficult to trap. Catalyst deactivation is an issue, given the costs associated with precious metal oxidation catalysts.[35,36] In any case, the irreversible loss of raw material that results from combustion runs counter to the progressive concept of low waste technologies. Application of photolysis, ozonation and supercritical oxidation to the treatment of recalcitrant organics falls within what is regarded as advanced oxidation technologies[17,37–41] but the efficiency of each technique is unproven and all are hampered by practical considerations in terms of high energy demands.[42] Ultrasonic irradiation[43,44] and electrochemical dechlorination[45,46] have also been considered in the literature and are remediation strategies that show promise, especially at low contaminant concentrations. Biotreatment is effective when dealing with biodegradable compounds but CPs are very resistant to biodegradation;[47–49] solutions >200 ppm cannot be treated effectively by direct biological methods.[50,51] Catalytic HDC is an emerging 'green' chloro-waste treatment approach that involves hydrogen cleavage of one or more C–Cl bonds, lowering toxicity and generating reusable raw material. Indeed, catalytic HDC can be employed as a pretreatment step to detoxify concentrated chlorinated streams prior to biodegradation. Cyclohexanol, the ultimate product from a combined HDC and hydrogenation of chlorophenols, is classified as non-toxic ($LC_{50} = 2060\,mg\,dm^{-3}$) and is of commercial significance as an intermediate in polyamide production.[52] Bengtson *et al*[53] have demonstrated the viability of coupling a semipermeable membrane to a chemical reactor as a means of simultaneously concentrating and reacting 4-CP in aqueous solution. The advantages of catalytic HDC compared with traditional oxidation methods (and even biological treatment) include: (i) low-temperature non-destructive transformation with no directly associated NO_x/SO_x emissions; (ii) no dioxin/furan formation; and (iii) selective Cl removal to generate recyclable (isomeric) products. The author has already highlighted[54] the appreciable environmental and economic advantages associated with a move to catalytic hydroprocessing as a means of waste minimization/recovery.

OVERVIEW OF CATALYTIC HYDRODECHLORINATION (HDC)

Whereas there is a wealth of published data concerning hydrodenitrogenation, hydrodesulfurization and hydrodeoxygenation,[55] HDC is only now becoming the focus of significant catalysis research, largely as a result of the environmental remediation implications. Thermal (non-catalytic) dehalogenation has been successfully applied to a range of halogenated compounds but elevated temperatures (up to 1173 K) are required to achieve near-complete (ca 99.95%) dehalogenation to HX.[56,57] A thermodynamic analysis of gas-phase HDC reactions has shown that HCl formation is strongly favored[58,59] and the presence of a metal catalyst reduces considerably the operating temperature, providing a lower energy pathway for the reaction to occur.[60] A distinction should be drawn between HDC and dehydrochlorination; the latter involves the internal elimination of HCl and is applicable to the dechlorination of aliphatic chloro compounds[61] where an external H_2 source is not necessary but can serve to limit catalyst deactivation.[62] As this dechlorination route is not applicable to aromatic systems, consideration of catalytic aspects of dehydrochlorination falls outside the intended remit of this review. Catalytic hydrodehalogenation is established for homogeneous systems where the catalyst and reactants are in the same (liquid) phase[63,64]

and although high turnovers have been achieved this approach, important in organic synthesis, it is not suitable for environmental protection purposes owing to the involvement of additional chemicals (such as solvents/hydrogen donors) and the, often difficult, product/solvent/catalyst separation steps. It is, nevertheless, worth flagging the reported application[65] of transition metal coenzymes such as vitamin B_{12} (Co), F_{430} (Ni) and hematin (Fe) to promote homogeneous hydrodehalogenation reactions.

Although the catalytic dehalogenation of aliphatic halides[66,67] and CFCs[68,69] has been the subject of recent notable mechanistic studies, chloroarene HDC has not yet received the same rigorous treatment. Chlorine removal from an aromatic reactant has been proposed to be both more[70–72] and less[73] facile than dechlorination of aliphatics. To date, chlorobenzene has been the most widely adopted model aromatic to assess catalytic HDC, principally in the gas phase,[74–80] but liquid-phase[81–83] transformations have also been considered. HDC has been successfully promoted using Pd,[77,78,84] Pt,[85] Rh[77,86] and Ni[59,60,74,80,87–91] catalysts. Based on three comprehensive reviews of the available hydrodehalogenation literature,[70,92,93] it is clear that Pd is the most active dechlorination metal. The first comprehensive report[94] of the liquid-phase HDC of chlorophenols to phenol over (carbon) supported Pd appeared in 1992 and this has since been supplemented by results pertaining to reaction over Pd, Pd–Fe, Rh–Pt and Rh catalysts.[83,95–99] The catalytic HDC of 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) has been investigated in the liquid phase, but because of the relatively low solubility of CPs in water, a complete kinetic analysis of HDC in aqueous solution has been limited to 4-CP as one of the more soluble (ca 2.7 g per 100 cm^3 water at 293 K) of the isomers.[95,98] It is accepted that catalytic HDC, in common with most hydrogenolysis reactions, exhibits structure sensitivity[65] where the electronic structure of the active metal sites can govern catalyst performance.[100] In the transformation of haloarenes, the nature of both the surface reactive adsorbed species and catalytically active metal center is still, however, open to question. One critical issue associated with liquid-phase HDC is the appreciable catalyst deactivation caused by the HCl by-product.[70] Owing to the weak acidity of CPs, the addition of base can serve to increase solubility in addition to limiting HCl poisoning.[95] With base addition, catalyst deactivation is largely governed by HCl solubility/transport and the nature of the basic species in the catalyst matrix. Hoke *et al*[94] have reported higher HDC rates and enhanced catalyst stability in an ethanol–water mixture when compared with pure ethanol. In marked contrast, Shindler *et al*[98] obtained a constant HDC of 4-CP in water over Pd supported on carbon cloths for up to 3 h without the addition of any base. 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.[101] 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 the metal support remains unclear. A full characterization of the catalyst pre- and post-HDC is necessary, which, when coupled with activity/selectivity data, can inform catalyst development. Nevertheless, the available data, albeit limited, support catalytic HDC as a viable detoxification process: monochlorophenols in aqueous media can be completely converted into less toxic cyclohexanone and/or cyclohexanol over Ru/C[95] and Pd/C[94,95,102,103] under ambient conditions.

The author and co-workers have demonstrated, in previous studies of liquid-phase HDC systems,[103–106] a high degree of control in terms of reaction selectivity with raw material recycle. In the case study chosen in this review for illustrative purposes, commercial Pd/Al_2O_3 is the catalytic agent, a system that has been employed to a limited extent in the liquid-phase HDC of chloroaliphatic[93,107,108] and -aromatic[83,93,105,109] reactants. Hydrogen gas, rather than a hydrogen donor (eg Na + ROH, $LiAlH_4$, $NaHH_4$, hydrazine), has been used as the reductive agent to simplify reactant/product/catalyst separation and catalyst reuse while facilitating a meaningful evaluation of the intrinsic chloroarene HDC reactivity. The latter necessitates the establishment of reaction conditions free of physical transport limitations. As model chloroarene reactants, the author has chosen the three monochlorophenol isomers (2-CP, 3-CP and 4-CP) and sterically constrained (2,4-DCP) and unconstrained (3,5-DCP) dichlorophenol isomers: each of these reactants is classified as a high-priority pollutant. HDC activity/selectivity is probed as a function of reaction time and temperature (303–343 K), pH effects are addressed and the possibility of catalyst reuse is considered.

CASE STUDY — LIQUID PHASE CATALYTIC HYDRODECHLORINATION OF CHLOROPHENOLS

The catalyst

A commercial (Aldrich Chemical) alumina-supported Pd catalyst was employed: the critical physico-chemical characteristics are given in Table 1. The Pd loading was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Vista-PRO, Varian) from a diluted extract of aqua regia.

Table 1. Physico-chemical characteristics of the Pd/Al_2O_3 catalyst

Pd content (%, w/w)	9.2
BET surface area ($m^2\,g^{-1}$)	172
pH at the point of zero charge	7.7
H_2 uptake ($\mu mol\,g^{-1}$)	119
Average Pd particle size (nm)	3.5
Specific Pd surface area ($m^2\,g_{Pd}^{-1}$)	251

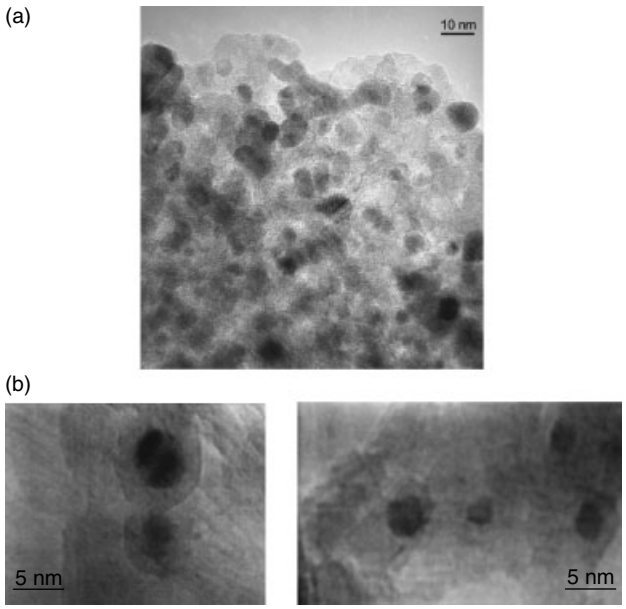

Figure 2. Representative TEM images of the Pd/Al_2O_3 catalyst showing (a) a general overview of Pd dispersion and (b) Pd particle morphology.

BET surface area/H_2 chemisorption measurements were conducted using a CHEM-BET 3000 system (Quantachrome Instruments); H_2 uptake/BET values were reproducible to within ±5%. Representative TEM images of the catalyst are shown in Fig 2, where the nature of the Pd dispersion can be assessed; selected area electron diffraction (SAED) confirmed the presence of metallic Pd. The Pd particle diameters spanned the range <2–15 nm to give, on the basis of a measurement of over 600 individual particles, an average particle size of 3.5 nm. There is some evidence of faceted Pd particles (see Fig 2(b)), which is suggestive of a strong Pd–support interaction that can be attributed to electron transfer from the alumina support.[110] The room temperature H_2 adsorption (recorded in Table 1) was measured at an H_2 partial pressure of 0.004 atm. There was no detectable H_2 uptake on the alumina carrier alone and the tabulated H_2 uptake represents a surface dissociatively chemisorbed species associated with the supported Pd phase. Moreover, it is well established that Pd can absorb H_2 to form a Pd hydride at ambient temperature where the H_2 partial pressure exceeds 0.0224 atm.[111] Surface hydride, chemisorbed hydrogen on the supported Pd and 'spillover' hydrogen, ie migration of atomic hydrogen to the support after H_2 dissociation on Pd,[112] can all contribute to the catalytic HDC performance. The pH associated with the point of zero charge (pH_{pzc}) is an important surface characteristic in liquid-phase heterogeneous reaction systems where solution pH is an important variable. The pH_{pzc} parameter is defined as the pH value at which the accessible surface of the wetted catalyst particle possesses neither a net positive nor negative charge.[113] In the case of Pd/Al_2O_3, the pH_{pzc}, determined using the potentiometric mass titration technique,[113] equals 7.7 (see Table 1), which fits into the pH_{pzc} 7–9 range quoted in the literature for γ-Al_2O_3.[114] At a pH < pH_{pzc}, the catalyst surface will bear a positive charge, which favors interaction with anionic species. Conversely, when pH > pH_{pzc}, the surface will exhibit a higher affinity for cationic species in solution. The experimentally determined pH_{pzc} suggests a weak basicity, diagnostic of the amphoteric nature of the support. 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.[115]

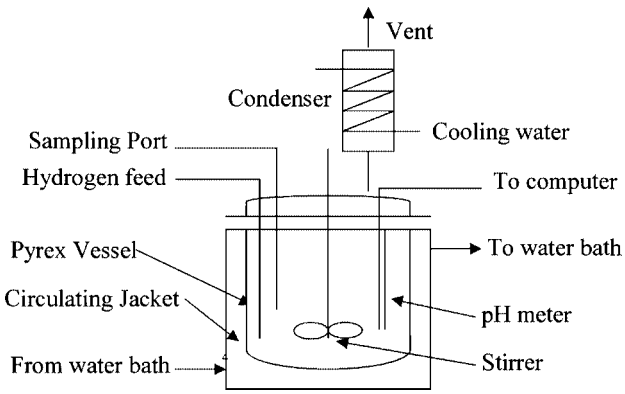

Figure 3. Schematic diagram of the three-phase slurry-type reactor.

The catalytic procedure

Catalytic HDC was performed in a three-phase slurry-type reactor; a simple schematic is provided in Fig 3. The corrosive nature of the chloroarene reactants and HCl product necessitated inert materials of construction to avoid the introduction of any impurities as a result of corrosive leaching; the reaction media only came into contact with a glass and/or PTFE surface. A 100 cm^3 volume reactor Pyrex vessel, fitted with a recirculating oil jacket, was employed where the temperature was measured and controlled (to within ±0.1 K) using a thermal probe situated within the reactor vessel. Agitation was provided by an overhead stirrer motor attached to a custom-built glass impeller; the stirring speed can be adjusted in the range 0–2000 rpm. The hydrogen flow rate was carefully controlled by a mass flow controller and adjusted from 20 to 150 cm^3 min^{-1}; the hydrogen inlet was positioned relative to the impeller to facilitate three-phase contact/mixing. The solution pH was continually monitored using a pencil electrode coupled to a data logging and collection system with a computer interface to permit a graphical representation of transient pH changes. A non-invasive liquid sampling system through in-line PTFE filters allowed the controlled syringe removal of aliquots (0.1 cm^3) of reactant/product(s) with no loss of catalyst from the system. At the beginning of each reaction, 100 cm^3 of stock aqueous chloroarene solution with NaOH ($[Cl]/[OH^-] = 1$ mol/mol) were charged with catalyst; the reaction was also conducted in the absence of base. The suspension was agitated in an He flow (50 cm^3 min^{-1}) and the temperature

was allowed to stabilize. A reaction temperature of 330 K was used as a basis for assessing physical vs chemical control effects but HDC performance was evaluated over the interval 303–343 K; there was no significant loss (<0.5%, v/v) of liquid reactor contents. Hydrogen was then introduced (time $t = 0$ for reaction) and the pH of the reaction mixture was monitored over the entire reaction. Samples of the reactant mixture were taken periodically for analysis by capillary gas chromatography (GC). Upon completion of the reaction, the H_2 flow was replaced with an He purge. The catalyst and reactant/product mixture was either drained from the system with the subsequent introduction of a fresh charge of catalyst/reactant or the reactant/product liquor was separated from the catalyst, which was retained in the reactor. A series of in-line fine particulate (1 μm pore PTFE) filters ensured that there was no inadvertent catalyst loss from the vessel. The catalyst was then washed repeatedly with deionized water (with pH analysis of the washings) until the wash water was near neutral. The final water sample was tested by GC to ensure that there was no significant organic component (<0.2 mmol dm^{-3}). The catalyst was maintained in a flow of dry He until a second reactant charge was introduced.

As a general (and important) observation, the conversion of each CP and DCP reactant was highly selective in terms of dechlorination. Aromatic ring reduction (to generate cyclohexanone/cyclohexanol) was only observed once dechlorination approached completion (>95% HDC). It is well established that the rate of heterogeneous liquid/solid/gas reactions can be controlled by the external diffusion of reactant(s) and product(s) to and from the catalytically active sites.[116,117] In terms of heat transfer effects, temperature gradients arising from heat transfer limitations are not as prevalent under liquid-phase conditions when compared with gas-phase operation. The relatively high thermal conductivity of the liquid phase, an order of magnitude higher when compared with gases,[118] coupled with the small heat of reaction per unit slurry volume, means that there is little temperature difference between particle and liquid. In the slurry-type reactor used in this study, the overall rate of chloroarene consumption is governed by a series of reaction and mass-transfer steps that proceed simultaneously:[103,119] (a) H_2 diffusion through the gas film at the gas/liquid interface; (b) H_2 diffusion through the liquid film at the gas/liquid interface; (c) chloroarene and H_2 diffusion through the liquid film at the liquid/solid interface; (d) reaction and diffusion at the catalyst surface; and (e) the reverse transport of products into bulk solution. In order to evaluate the intrinsic catalytic activity and chloroarene reactivity, it is essential to ascertain the extent to which the physical processes control the overall conversion. To this end, four experimental diagnostic criteria were employed, taking the HDC of 3-CP as a representative case.

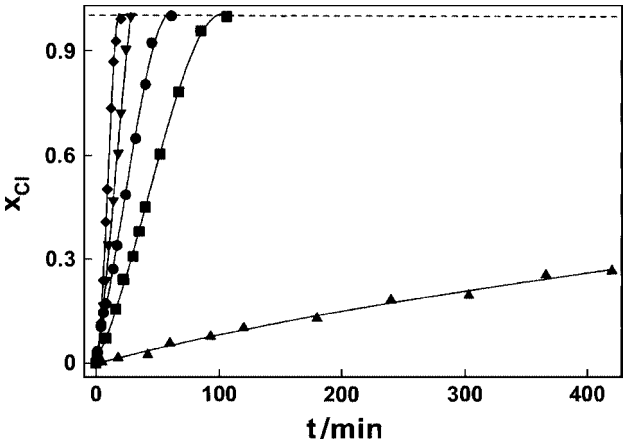

Figure 4. Variation of fractional 3-CP HDC (x_{Cl}) with time in the absence of any agitation (▲) and with increasing stirring speed: (■) 300; (●) 600; (▼) 750; (♦) 1000 rpm. [Catalyst] = 1 g dm^{-3}; [Cl] = 9.2×10^{-2} mol dm^{-3}; H_2 flow rate = 60 cm^3 min^{-1}; $[OH^-]/[Cl] = 1$. The dashed line represents complete dechlorination.

Variation of stirring speed

Effective mixing serves to extend the liquid/gas/solid interface and limit the transport constraints of H_2 from the gas phase to the bulk liquid phase and the haloarene from the bulk liquid phase to the catalyst surface. The influence of stirring speed on the fractional dechlorination of 3-CP (x_{Cl}) is shown in Fig 4, where agitation had a profound effect on the extent of HDC, particularly when compared with the inert mixture in which HDC was severely limited. The temporal 3-CP consumption increased as the stirring speed was raised from 100 to 750 rpm, diagnostic of a transport contribution, but remained largely unchanged at higher stirring speeds. A stirring speed of 750 rpm was taken to be the minimum agitation needed to circumvent segregation of both fluid and solid catalyst and was accordingly employed for subsequent measurements to avoid overly turbulent/vortex conditions and catalyst particle attrition.

Variation of hydrogen flow rate

Transfer of hydrogen in the liquid phase takes place from the bubbles emerging from the gas inlet that are entrapped in the liquid phase by the action of the impeller. Hydrogen mass transfer limitations can be minimized by increasing the inlet H_2 flow rate, which enhances the gas hold-up in the three-phase slurry, increasing the total area of the gas/liquid interface.[120] Taking 750 rpm stirring as optimum, 3-CP HDC was insensitive to any increase in H_2 feed rate above 60 cm^3 min^{-1} and a flow rate of 80 cm^3 min^{-1} was accordingly adopted as standard.

Variation of catalyst mass

An increase in catalyst mass is accompanied by a proportional increase in HDC rate where the supply of reactant(s) to the catalyst surface is not transport limited. The effect of altering catalyst mass at a fixed initial [3-CP] is shown in Fig 5, where it can be seen

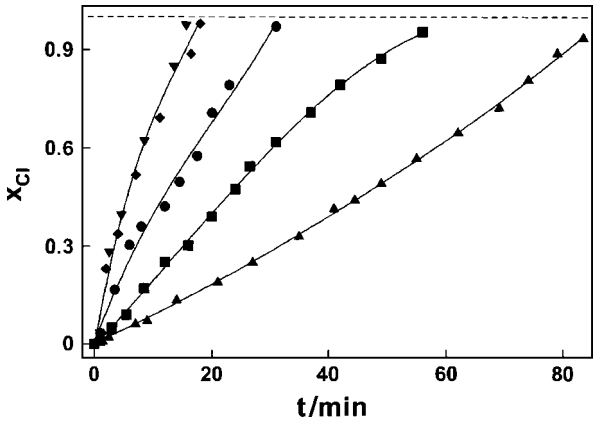

Figure 5. Fractional 3-CP HDC (x_{Cl}) as a function of time at a fixed initial [3-CP] (9.2×10^{-2} mol dm^{-3}) and varying catalyst mass: Cl:Pd = (▲) 700; (■) 390; (●) 200; (♦) 33; (▼) 20 mol/mol. Stirring speed = 750 rpm; H_2 flow rate = 80 cm^3 min^{-1}; [OH^-]/[Cl] = 1. The dashed line represents complete dechlorination.

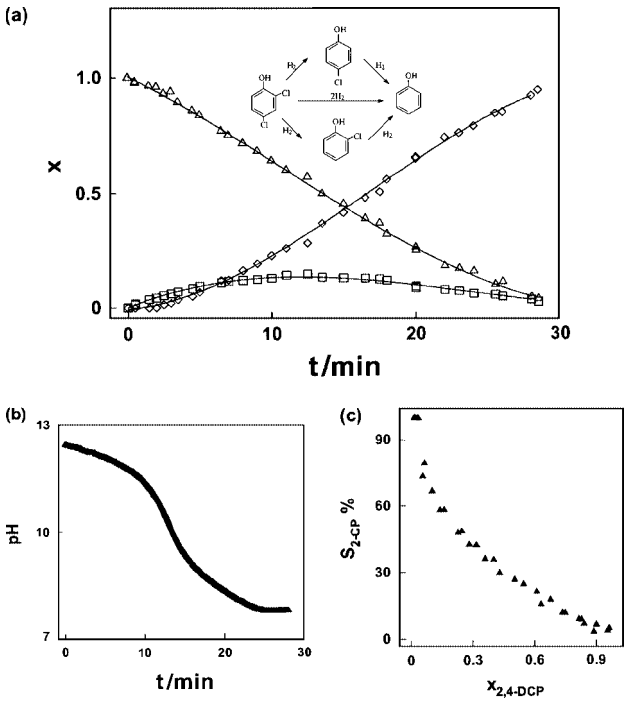

Figure 6. Temporal 2,4-DCP HDC response in terms of (a) liquid mole fraction (x) of (△) 2,4-DCP, (□) 2-CP and (◇) phenol, (b) solution pH changes and (c) 2-CP selectivity (S_{2-CP}) as a function of fractional 2,4-DCP conversion ($x_{2,4-DCP}$). Stirring speed = 750 rpm; H_2 flow rate = 80 cm^3 min^{-1}; [catalyst] = 0.5 g dm^{-3}; [OH^-]/[Cl] = 1.

that the temporal [3-CP] variations coincide where the catalyst mass exceeded that which corresponds to Cl/Pd ≈33 mol/mol. A point is therefore reached at which a further increase in catalyst mass has little effect on the apparent rate and the system operates under transport retardation.

Variation of catalyst particle size

Liquid/solid transport contributions are strongly influenced by catalyst particle size. Under conditions of minimal gas/liquid transport resistance, as established above, the 3-CP HDC rate declined by a factor of ca 2 with increase in the average catalyst particle size from 60 to 140 μm but was unaffected by particle size variations from 30 to 60 μm, where the reaction can be considered to largely fall within the kinetic controlled region.

CATALYTIC ACTIVITY AND SELECTIVITY

Adopting the process conditions identified above as necessary to ensure chemical/catalytic control, the temporal response in terms of reactant/product distribution, solution pH and selectivity resulting from the HDC of 2,4-DCP is shown in Fig 6; repeated runs using different samples from the same batch of catalyst delivered a product composition that did not deviate by more than ±6%. The selectivity (as a percentage) with respect to 2-CP (S_{2-CP}) in the HDC of 2,4-DCP is defined as the mole % 2-CP in terms of the total moles of product(s) formed, ie

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

where $[\text{2,4-DCP}]_0$ represents the starting 2,4-DCP concentration. The HDC of 2,4-DCP can proceed in a stepwise and/or concerted fashion with 2-CP and 4-CP as partially dechlorinated products, as shown in Fig 6(a). It is immediately evident that low-temperature HDC is feasible and, under the stated experimental conditions, complete dechlorination was achieved within 30 min. The Gibbs free energy (ΔG) associated with the HDC of saturated 2,4-DCP, 2-CP and 4-CP aqueous solutions (pH = 7, T = 298 K and H_2 partial pressure = 0.1 MPa) lie in the range −65 to −130 kJ mol^{-1}.[121] It is instructive to note that the mole fraction of 4-CP in the product mixture was below the detection limits (<0.4%, ca 0.4 mmol dm^{-3}) but 2-CP served as a reactive HDC intermediate. The temporal pH of the bulk solution is shown in Fig 6(b), where a switch from strongly to weakly basic conditions is evident. The pH profile coincides with the 2,4-DCP time-dependent consumption and associated HCl release. The mole fraction of 2-CP in solution exhibited a time-dependent maximum (Fig 6(a)) and 2-CP selectivity (S_{2-CP}) declined continuously with increasing fractional 2,4-DCP conversion ($x_{2,4-DCP}$), as illustrated in Fig 6(c). Such an anti-sympathetic relationship is to be expected in a stepwise dechlorination process. The isolation of partially dechlorinated products has been reported elsewhere for diverse polychloroarene HDC processes.[76,80,81,92,122] In contrast to the conversion of 2,4-DCP, HDC of 3,5-DCP under the same reaction conditions generated phenol as by far the predominant HDC product and 3-CP was formed in only trace quantities (S_{3-CP} < 2%), ie a concerted HDC is favored. The selectivity trends point to a far more facile removal of Cl that is positioned *meta* and *para* to the—OH ring substituent when compared with the *ortho*-positioned Cl, suggestive of steric hindrance effects. The initial HDC rate

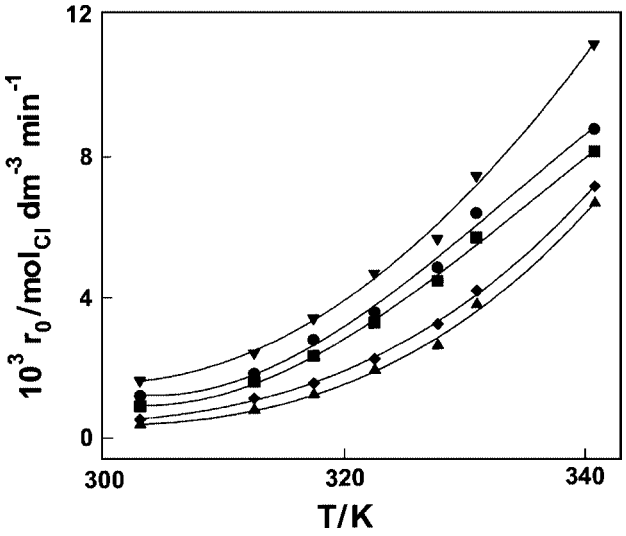

Figure 7. Initial HDC rate (r_0) of (■) 2-CP, (●) 3-CP, (▼) 4-CP, (▲) 2,4-DCP and (♦) 3,5-DCP as a function of temperature. Stirring speed = 750 rpm; H_2 flow rate = 80 cm^3 min^{-1}; [catalyst] = 0.5 g dm^{-3}; $[OH^-]/[Cl]$ = 1.

(r_0), defined as the initial rate of Cl removal and calculated from pseudo-first-order linear regression of the temporal HCl product concentration profiles, is plotted in Fig 7 as a function of temperature for the three mono- and two dichlorophenol reactants. The following sequence of increasing HDC activity holds over the entire temperature range: 2,4-DCP < 3,5-DCP < 2-CP < 3-CP < 4-CP. The HDC rate for monochlorophenols was consistently higher than that for the two DCP isomers. There is persuasive evidence in the literature[123,124] that haloarene activation on the catalyst surface involves dissociative adsorption with the formation of a surface σ-complex via the aromatic ring carbon with the highest electron density. The presence of a second Cl substituent (in DCP) serves to reduce the electron density associated with the ring carbons, which must act to lower haloarene reactivity.[123] Moreover, steric hindrance due to the close proximity of the *ortho*-substituent, in the case of 2-CP and 2,4-DCP, appears to inhibit or restrict catalytic HDC performance.

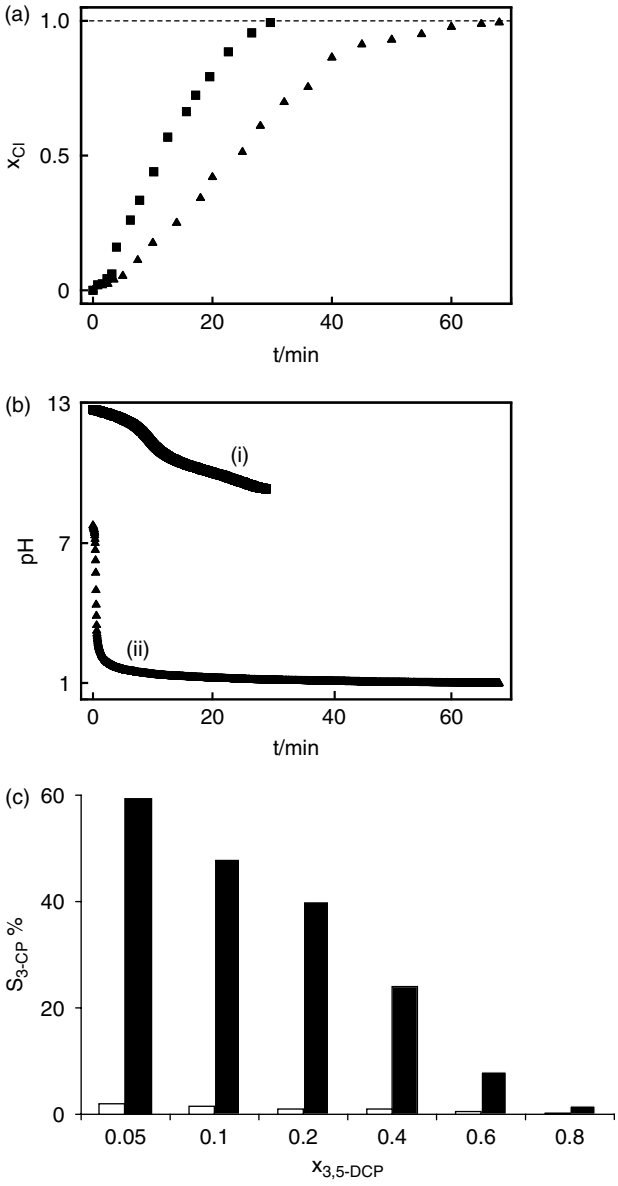

Figure 8. (a) Fractional dechlorination (x_{Cl}) of 3,5-DCP HDC and (b) solution pH as a function of time in the (■, i) presence and (▲, ii) absence of base and (c) 3-CP selectivity (S_{3-CP}) at selected 3,5-DCP conversions ($x_{3,5-DCP}$), with (open bars) and without (solid bars) base addition. Stirring speed = 750 rpm; H_2 flow rate = 80 cm^3 min^{-1}; [catalyst] = 0.5 g dm^{-3}. The dashed line in (a) represents complete dechlorination.

ROLE OF BASE ADDITION AND CATALYST REUSE

The addition of a base to the reaction solution can serve both to increase the solubility of the weakly acidic chlorophenols and to limit HCl poisoning.[95] The fractional dechlorination of 3,5-DCP, as a representative case, is plotted as a function of time in Fig 8(a), where it can be seen that the inclusion of NaOH served to promote HDC: rate increases of up to a factor of 2 were recorded owing to the presence of the base. In the absence of base, the solution pH switches from near neutral to strongly acidic and the addition of NaOH ensured that the pH did not fall below 7 over the course of the reaction (see Fig 8(b)). From consideration of pK_a values,[106] the nature of the reactant/product(s) in bulk solution switches from chlorophenolate/phenolate anions to the chlorophenolic/phenolic form on moving from a basic to an acidic medium. The surface charge of Pd/Al_2O_3, with an associated pH_{pzc} = 7.7 (Table 1), 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. When pH ≤ 5 (conditions which prevail in the absence of base), the chlorophenolic species dominates and interaction with a positively charged alumina surface is unfavorable. Consequently, the HDC rate is lower than that obtained in the presence of NaOH. HDC selectivity was also influenced by

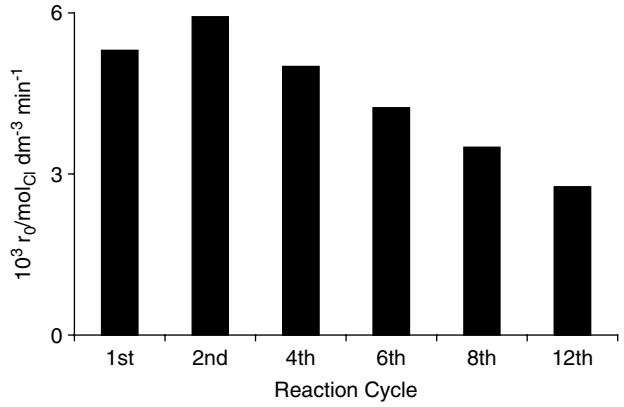

Figure 9. Initial 3-CP HDC rate (r_0) as a function of catalyst reuse. Stirring speed = 750 rpm; H_2 flow rate = 80 cm^3 min^{-1}; [catalyst] = 0.5 g dm^{-3}; $[OH^-]/[Cl] = 1$.

base addition in that partial dechlorination of 3,5-DCP to 3-CP was significant in the absence of base, as shown in Fig 8(c). The feasibility of catalyst reuse was considered and the results are given in Fig 9 for 3-CP HDC. The initial 3-CP HDC rate declined with extended catalyst use, dropping by almost 50% after the 12th reaction cycle. This loss of activity can be attributed to a combination of Pd leaching (up to 40% loss of the initial Pd content was recorded), alteration to Pd particle dispersion, support structural breakdown, HCl poisoning and some unavoidable loss of catalyst during product/catalyst separation and catalyst washing. The possibility of minimizing this activity loss through variations in Pd loading/particle size, nature of the support (possible metal/support stabilizing interaction(s)) and base addition represents new research directions that are now under way in this laboratory. It is nonetheless worth flagging the increase in initial HDC rate recorded for the first catalyst reuse. The latter can be due to a beneficial restructuring of the catalyst that occurs over the first reaction cycle, an effect that is counterbalanced in subsequent reaction cycles by one or more of the detrimental effects noted above. Such an increase in HDC rate observed in the second reaction cycle is not without precedent in that Zhang and Beard[125] have reported that pretreatment of Pt/Al_2O_3 with NH_4Cl served to enhance the hydrogen-mediated dechlorination of CCl_4, an effect that they attributed to metal particle restructuring.

SUMMATION — A LOOK TO THE FUTURE

While the multiple applications of man-made halogen-containing compounds are of considerable societal benefit, uncontrolled production of halogenated compounds has led to waste and emissions with deleterious effects on the environment. Although global environmental systems are extremely resilient, there is a limit to the pollution burden that can be sustained. Unabated entry of chlorinated compounds into the environment will undoubtedly result in dramatic adverse effects on human health, agricultural productivity and natural ecosystems. Metal-mediated HDC has a decided role to play in detoxifying chlorinated waste and facilitating raw material recycle, as has been demonstrated in the case study of liquid-phase HDC of mono- and dichlorophenols over Pd/Al_2O_3. The following pertinent features of catalytic HDC have emerged from the case study:

(a) Under conditions of minimal mass transport constraints, high HDC activity (complete dechlorination at a starting Cl/Pd $\leq$ 200 at $t \leq$ 30 min) and selectivity are achieved at near ambient temperature.
(b) Chlorophenol reactivity is dependent on both geometric and electronic effects.
(c) Bulk solution pH has a considerable impact on activity/selectivity—addition of base lessens any inhibition due to HCl poisoning and results in a more effective electrostatic catalyst–reactant interaction.
(d) Product composition (partial vs complete dechlorination) is dependent on the reaction conditions, ie time, temperature and pH, where catalytic control can be exerted to deliver a desired level of HDC.
(e) Catalyst reuse is feasible, albeit HDC performance ultimately declines with successive reaction cycles.

Future work should be directed at extending the limited database of hydrogen-mediated liquid-phase haloaromatic (and haloaliphatic) single- and multi-component dehalogenation to consider an array of metal catalysts (that are known to promote hydrogenolysis) over a range of reaction conditions with a particular emphasis on the possibility of pH adjustment as a means of process control. Reactor design for operation in batch, semi-batch and continuous modes and the options in terms of the hydrogenolysis agent (direct use of H_2 or an indirect source, ie H_2 donor) are important considerations. There is little in the way of published catalyst characterization pre- and post-reaction, something which must be rectified in order to establish an explicit link between catalyst structure and dehalogenation performance as an essential prerequisite for process optimization. In terms of ultimate application, two progressive possibilities arise, both requiring appreciable basic research/feasibility input:

(i) Development of a hybrid catalytic hydrodehalogenation/biocatalytic process where hydrodehalogenation over synthetic metal catalysts serves to dehalogenate a concentrated waste stream (with product recycle) and the diluted halogen-containing stream can then be subjected to biological degradation to generate an aqueous stream suitable for discharge.
(ii) Coupling of a semi-permeable membrane to a three-phase catalytic hydrodehalogenation unit to facilitate removal of the dehalogenated product and introduction of halogenated feed—further

advances should encompass the development of a catalytically active membrane with view to selectivity enhancement.

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