

THE DEVELOPMENT OF A CATALYTIC PROCESS FOR THE
HYDROTREATMENT OF HALOARENES

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Abstract

The abatement of halogenated compounds released from various processes into the environment is now recognized as a pressing environmental issue. Catalytic hydrodehalogenation (HDH) has emerged as a potential technology that can facilitate waste transformation and reuse. In this thesis, a comprehensive study of the critical reaction/catalyst variables is considered for the HDH of a range of haloarenes (chloro- and bromo-phenols and chlorobenzenes) using (commercial) Pd/Al₂O₃ and (laboratory synthesised) Au supported on α -Fe₂O₃ and Fe₃O₄. Aqueous phase ($T = 303$ K) HDH is demonstrated to be structure sensitive where smaller Pd particles are intrinsically more active and metal/support interactions have a major impact on reaction selectivity (notably at pH = 3). HDH follows an electrophilic aromatic substitution mechanism: the rate of C–Br bond(s) scission is an order of magnitude greater relative to C–Cl (due to the lower bond dissociation energy). The presence of a second halogen substituent has a deactivating effect (by lowering electron density in the aromatic ring). Solvent (water, organic and water/organic mixtures) effects have been established where, in absence of mass transport limitations, reaction in water delivers significantly higher HDH rates and selectivity is unaffected by solvent composition. A mathematical analysis demonstrates that these effects are principally (*ca.* 80 % contribution) the result of the variations in solvent dielectric constant where the molar volume represents a secondary consideration. The advantages of a shift from batch to continuous HDH are established in terms of: (i) more efficient gas to liquid H₂ transfer; (ii) enhanced HDH rates; (iii) prolonged catalyst lifetime. The potential of HDH as a means of waste transformation to a commercial product is demonstrated in the gas phase ($T = 423$ K) hydroconversion of 2,4-dichlorophenol into cyclohexanone (over Pd) and 4-chlorophenol (over iron-oxide supported Au). In both cases, a contribution due to spillover hydrogen is established. A comprehensive programme of (Au) catalysts synthesis and characterization, in terms of TPR, H₂ chemisorption/TPD, XRD, DRS UV-Vis, SEM/TEM and BET/pore volume measurements is provided and correlated with HDH kinetics. The results presented in this thesis demonstrate the feasibility and flexibility (in terms of operation, rate/selectivity control and product reuse) of catalytic HDH as a progressive means of haloarene waste treatment.

Dedication

To

Emilio Gómez Gutiérrez

Victoriano Quero Castro

Julia Díaz Sastre

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Glossary

Roman Letters

<i>Symbol</i>	<i>Physical Meaning</i>	<i>Units</i>
a_ε	Fitting parameter	$\text{mmol}_{2,4\text{-DCP}} \text{g}_{\text{Pd}}^{-1} \text{min}^{-1}$ $\text{mmol}_X \text{g}_{\text{Pd}}^{-1} \text{min}^{-1}$
a_g	Gas/liquid interfacial area per unit volume of liquid	$\text{m}^2 \text{m}^{-3}$
$a_{\bar{v}}$	Fitting parameter	$\text{mmol}_{2,4\text{-DCP}} \text{mol}_{\text{Solvent}}^{b_{\bar{v}}} \text{g}_{\text{Pd}}^{-1} \text{min}^{-1} \text{cm}^{-(3+b_{\bar{v}})}$ $\text{mmol}_X \text{mol}_{\text{solvent}}^{b_{\bar{v}}} \text{g}_{\text{Pd}}^{-1} \text{min}^{-1} \text{dm}^{-(3+b_{\bar{v}})}$
a_T	Fitting parameter	$\text{mmol}_{2,4\text{-DCP}} \text{cm}^{(3+b_T)} \text{g}_{\text{Pd}}^{-1} \text{min}^{-1} \text{mol}_{\text{solvent}}^{-b_T}$ $\text{mmol}_X \text{dm}^{(3+b_T)} \text{g}_{\text{Pd}}^{-1} \text{min}^{-1} \text{mol}_{\text{solvent}}^{-b_T}$
b_ε	HDH/HDC rate dependence factor on solvent dielectric constant	dimensionless
$b_{\bar{v}}$	HDH/HDC rate dependence factor on solvent molar volume	dimensionless
b_T	HDH/HDC rate dependence factor on both solvent dielectric constant and molar volume	dimensionless
C_{HX}	Concentration of inorganic halogen	$\text{mol}_{\text{HX}} \text{dm}^{-3}, \text{mmol}_{\text{HX}} \text{dm}^{-3}$
$(C_{\text{H}_2})_{\text{bulk}}$	H ₂ concentration in the bulk liquid	$\text{mmol}_{\text{H}_2} \text{dm}^{-3}$
$(C_{\text{H}_2})_{\text{saturation}}$	H ₂ saturation concentration	$\text{mmol}_{\text{H}_2} \text{dm}^{-3}$
C_i	Concentration of compound i	$\text{mol}_i \text{dm}^{-3}, \text{mmol}_i \text{dm}^{-3}$
$C_{i,0}$	Initial concentration of compound i	$\text{mol}_i \text{dm}^{-3}, \text{mmol}_i \text{dm}^{-3}$
$C_i(t)$	Concentration of compound i at time t	$\text{mol}_i \text{dm}^{-3}$
C_X	Concentration of organic halogen	$\text{mol}_X \text{dm}^{-3}, \text{mmol}_X \text{dm}^{-3}$
$C_{X,0}$	Initial concentration of organic halogen	$\text{mol}_X \text{dm}^{-3}, \text{mmol}_X \text{dm}^{-3}$
Ca	Carberry number	dimensionless
D	Metal dispersion	dimensionless
$D_{\text{Eff},i}$	Effective diffusivity of compound i	$\text{m}^2 \text{s}^{-1}$
D_i	Diffusivity of compound i	$\text{m}^2 \text{s}^{-1}$
d	Catalyst particle diameter	μm
d_{Chem}	Metal particle size estimated from H ₂ chemisorption analysis	nm
d_i	Diameter of the i^{th} metal particle	nm
d_{TEM}	Surface area weighted metal particle size estimated from TEM analysis	nm
$\Delta\bar{H}$	Enthalpy of vaporization	kJ mol^{-1}

Symbol	Physical Meaning	Units
$\Delta\bar{H}_{T_b}$	Boiling point enthalpy of vaporization	kJ mol^{-1}
Δt	Integral time	h
$EC_{50,i}$	Median effective concentration of compound i	mg dm^{-3}
F	Molar flow of 2,4-DCP	$\text{mol}_{2,4\text{-DCP}} \text{h}^{-1}$
F_{Cl}	Molar flow of organic chlorine	$\text{mol}_{Cl} \text{h}^{-1}$
F_{OH}	Molar flow of (chloro-)phenol	$\text{mol}_{OH} \text{h}^{-1}$
$f_{H_2}^0$	Fugacity of H_2 gas	MPa
$f_{H_2}^L$	Fugacity of H_2	MPa
g	Volume fraction of the solvent	dimensionless
K	Ratio of 2-CP consumption and formation constants	dimensionless
K_j	Equilibrium constant of step j	dimensionless, atm^{-1} , atm^{-2}
k	Pseudo first order 2,4-DCP consumption rate constant	$\text{mol}_{2,4\text{-DCP}} \text{h}^{-1} \text{mol}_{Au}^{-1}$
k_j	Pseudo first order rate constant for reaction step j	min^{-1}
k_L	liquid film mass transfer coefficient	m min^{-1}
k_X	Pseudo first order HDH rate constant	min^{-1}
k'	Specific pseudo first order 2,4-DCP consumption rate constant	$\text{mol}_{2,4\text{-DCP}} \text{h}^{-1} \text{m}_{Au}^{-2}$
k'_{Cl}	Specific HDC rate constant	$\text{mol}_{Cl} \text{h}^{-1} \text{m}_{Au}^{-2}$
L	Fitting parameter	dimensionless
M	Fitting parameter	dimensionless
M_M	Atomic mass of metal M	dimensionless
m	Catalyst concentration	g dm^{-3}
m_{Pd}	Catalyst Pd loading	$\text{g}_{Pd} \text{g}^{-1}$
N_{H_2}	H_2 mass transfer rate	$\text{mmol}_{H_2} \text{min}^{-1} \text{dm}^{-3}$
n_{Cl}	Number of moles of organic chlorine	mmol_{Cl}
$n_{2,4\text{-DCP}}$	Number of moles of 2,4-DCP	$\text{mol}_{2,4\text{DCP}}$
n_{HCl}	Number of moles of inorganic chlorine	mmol_{HCl}
n_i	Number of metal particles of diameter d_i	dimensionless
n_M	Number of moles of metal M	mol_M
P	Pressure	atm
P_i	Partial pressure of compound i	atm
P/P_0	Relative pressure	dimensionless
pH_{acid}	pH maintained at acid conditions	dimensionless
pH_{basic}	pH maintained at basic conditions	dimensionless
$pH_{l/s}$	pH at the bulk liquid/catalyst surface interface	dimensionless
pH_{pzc}	pH of the point of zero charge	dimensionless
pK	Acid-base equilibria dissociation constant	dimensionless
R	Universal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$

Symbol	Physical Meaning	Units
r	Pore radius	Å
$(R_{C6ONE})_0$	Initial C6ONE production rate	$\text{mol}_{C6ONE} \text{mol}_{Pd}^{-1} \text{h}^{-1}$
$(R'_{C6ONE})_0$	Specific initial C6ONE production rate	$\text{mol}_{C6ONE} \text{m}_{Pd}^{-2} \text{h}^{-1}$
(R_{2-CP})	2-CP production rate	$\text{mmol}_{2-CP} \text{g}_{Pd}^{-1} \text{min}^{-1}$
$(-R_{2,4-DCP})$	2,4-DCP consumption rate	$\text{mmol}_{2,4-DCP} \text{g}_{Pd}^{-1} \text{min}^{-1}$
$(-R_{2,4-DCP})_0$	Initial 2,4-DCP consumption rate	$\text{mmol}_{2,4-DCP} \text{g}_{Pd}^{-1} \text{min}^{-1}$
$(-R'_{2,4-DCP})_0$	Specific initial 2,4-DCP consumption rate	$\text{mmol}_{2,4-DCP} \text{m}_{Pd}^{-2} \text{min}^{-1}$
$(-R_{2,4-DCP})_0^E$	Excess initial 2,4-DCP consumption rate in a water+organic solvent mixture	$\text{mmol}_{2,4-DCP} \text{g}_{Pd}^{-1} \text{min}^{-1}$
$(-R_{2,4-DCP})_0^{Predicted}$	Initial 2,4-DCP consumption rate in a water+organic solvent mixture, as predicted assuming an ideal mixing rule	$\text{mmol}_{2,4-DCP} \text{g}_{Pd}^{-1} \text{min}^{-1}$
$(R_{HDC})_0$	Initial HDC rate	$\text{mmol}_{Cl} \text{g}_{Pd}^{-1} \text{min}^{-1}$
$(R'_{HDC})_0$	Specific initial HDC rate	$\text{mmol}_{Cl} \text{m}_{Pd}^{-2} \text{min}^{-1}$
$(R_{HDH})_0$	Initial HDH rate	$\text{mmol}_X \text{g}_{Pd}^{-1} \text{min}^{-1}$
$(-R_i)_0$	Consumption rate of compound i	$\text{mol g}^{-1} \text{s}^{-1}$
S_i	Reaction selectivity with respect to product i	dimensionless
$S_{i,0}$	Initial reaction selectivity with respect to product i	dimensionless
S_M	Specific surface area of metal M	$\text{m}_M^2 \text{g}_M^{-1}$
T	Temperature	K
$T.U. \text{ Mixture } (t)$	Toxicity units of the reaction mixture at time t	dimensionless
t	Reaction time, contact time	min
V_{N_2}	Volume of N_2 adsorbed during pore volume measurements	cm^3_{STP}
W	Catalyst mass	g
W_{Pd}	Pd concentration	$\text{g}_{Pd} \text{dm}^{-3}$
X_i	Fractional conversion of compound i	dimensionless
$X_{i,0}$	Initial fractional conversion of compound i	dimensionless
$X_{i,5h}$	Fractional conversion of compound i after 5 h time-on-stream hydroprocessing	dimensionless
x_i	Molar fraction of compound i	dimensionless
$x_{i,0}$	Initial molar fraction of compound i	dimensionless
x_X	Fractional degree of HDH	dimensionless
Y_i	Yield of compound i	dimensionless
$Y_{i,0}$	Initial yield of compound i	dimensionless

Greek Letters

<i>Symbol</i>	<i>Physical Meaning</i>	<i>Units</i>
α	Fitting parameter	dimensionless
β	Heating rate	K min ⁻¹
δ	Solubility parameter for the solvent	kJ ^{1/2} m ^{-3/2}
δ_{H_2}	Solubility parameter for H ₂	kJ ^{1/2} m ^{-3/2}
ε	Dielectric constant	dimensionless
ε_c	Corrected dielectric constant of a water+organic solvent mixture	dimensionless
$\varepsilon_{catalyst}$	Catalyst porosity	dimensionless
ε_m	Dielectric constant of a water+organic solvent mixture	dimensionless
ε_i	Dielectric constant of compound <i>i</i>	dimensionless
ε^E	Excess dielectric constant of a water+organic solvent mixture	dimensionless
η	Effectiveness factor	dimensionless
η_S	Dynamic viscosity of solvent <i>S</i>	mPa s ⁻¹
\bar{v}	Molar volume	cm ³ mol ⁻¹
\bar{v}_c	Corrected molar volume of a water+organic solvent mixture	cm ³ mol ⁻¹
\bar{v}_i	Molar volume of compound <i>i</i>	cm ³ mol _{<i>i</i>} ⁻¹
\bar{v}^E	Excess molar volume of a water+organic solvent mixture	cm ³ mol ⁻¹
ρ	Catalyst bulk density	kg m ⁻³
ρ_M	Density of metal <i>M</i>	g _M cm _M ⁻³
τ	Catalyst tortuosity	dimensionless
Φ	Weisz-Prater number	dimensionless
ϕ	Thiele modulus	dimensionless
Ψ	HDH/HDC fractional dependence on the solvent dielectric constant	dimensionless

Nomenclature

<i>Acronym</i>	<i>Meaning</i>
BET	Brunauer-Emmet-Teller
BP	Bromophenol
CB	Chlorobenzene
CFC	ChloroFluoro Carbon
C6OH	Cyclohexanol
C6ONE	Cyclohexanone
CP	Chlorophenol
CSTR	Continuous Stirred-Tank Reactor
CTC	Carbon Tetrachloride
DBP	Dibromophenol
DCB	Dichlorobenzene
DCP	Dichlorophenol
DRS UV-Vis	Diffuse Reflectance Spectroscopy in the Ultraviolet-Visible region
EDX	Energy Dispersive X-ray
EPA	Environmental Protection Agency
EXAFS	Extended X-ray Atomic Fine Structure
FID	Flame Ionization Detector
FTIR	Fourier Transform InfraRed spectroscopy
GHSV	Gas Hourly Space Velocity
HDC	Hydrodechlorination
HDH	Hydrodehalogenation
IARC	International Agency for Research Cancer
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
JCPDS-ICDD	Joint Committee on Powder Diffraction Standards – International Center for Diffraction Data
PCDD / PCDF	Polychlorodibenzodioxins / Polychlorodibenzofurans
PhOH	Phenol
SEM	Scanning Electron Microscopy
TCD	Thermal Conductivity Detector
TCP	Trichlorophenol
TEM	Transmission Electron Microscopy
TPD	Temperature-Programmed Desorption
TPR	Temperature-Programmed Reduction
TSCA	Toxic Substance Control Act
UTW	Ultra-Thin Window
WHO	World Health Organisation
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

List of Publications by the Candidate

- 1) S. Gómez-Quero, F. Cárdenas-Lizana, M. A. Keane, Effect of Metal Dispersion on the Liquid Phase Hydrodechlorination of 2,4-Dichlorophenol over Pd/Al₂O₃, *Ind. Eng. Chem. Res.*, 47, 6841 (2008).
- 2) S. Gómez-Quero, F. Cárdenas-Lizana, M. A. Keane, Solvent Effects in the Liquid Phase Hydrodechlorination of 2,4-Dichlorophenol over Pd/Al₂O₃, *AIChE J.*, Accepted.
- 3) S. Gómez-Quero, E. Díaz, F. Cárdenas-Lizana, M. A. Keane, Solvent Effects in the Catalytic Hydrotreatment of Haloaromatics over Pd/Al₂O₃ in Water Organic Mixtures, *Chem. Eng. Sci.*, submitted for publication.
- 4) S. Gómez-Quero, F. Cárdenas-Lizana, M. A. Keane, Liquid Phase Catalytic Hydrodechlorination of 2,4-Dichlorophenol over Pd/Al₂O₃: Batch vs. Continuous Operation, manuscript ready for submission.
- 5) S. Gómez-Quero, F. Cárdenas-Lizana, M. A. Keane, Gas Phase Hydrotreatment of Chlorophenols as an Alternative Route to Cyclohexanone, manuscript ready for submission.
- 6) S. Gómez-Quero, F. Cárdenas-Lizana, M. A. Keane, Selective Hydrodechlorination of 2,4-Dichlorophenol over Iron Oxide Supported Au, manuscript ready for submission.
- 7) S. Gómez-Quero, F. Cárdenas-Lizana, M. A. Keane, Au/Fe₃O₄: Characterization and Application in Gas Phase Hydrodechlorination, manuscript ready for submission.

List of Presentations by the Candidate

- 1) “Solvent and Particle Size on the Hydrodechlorination of 2,4-Dichlorophenol over Pd/Al₂O₃”, 5th International Conference in Environmental Catalysis; University of Belfast, August 2008.
- 2) “Solvent Effects in Catalytic Hydrodechlorination”, SURCAT Ecosse Conference; University of Aberdeen, May 2008.
- 3) “Solvent and Particle Size Effects in Liquid Phase Catalytic Hydrodechlorination”, Mechanical and Chemical Engineering Department Seminar Series; Heriot-Watt University (Edinburgh), February 2008.
- 4) “Metal Dispersion in 2,4-Dichlorophenol Catalytic Hydrodechlorination”, SURCAT Ecosse Conference; University of St. Andrews, May 2007.
- 5) “Metal Dispersion in 2,4-Dichlorophenol Catalytic Hydrodechlorination”, ScotCHEM Materials Conference; Heriot-Watt University (Edinburgh), March 2007.

List of Posters by the Candidate

- 1) “The Hydrotreatment of Chlorophenols: An Alternative Route to Cyclohexanone”, IChemE Conference on Applied Catalysis: Towards Sustainable Chemical Industry; University of Bath, November 2008.
- 2) “Catalytic Hydrodechlorination of Chlorophenols over Palladium”, 9th UK Particle Technology Forum; Heriot-Watt University (Edinburgh), June 2008.
- 3) “Catalytic Hydrodechlorination of Chlorophenols over Palladium”, 1st Year PhD Progress Meeting; Heriot-Watt University (Edinburgh), October 2006.

Chapter 1

Introduction and Scope of the Thesis

This Chapter presents a short overview of the environmental implications associated with the release of halogenated compounds and available methods of control/disposal, highlighting the significance of catalytic hydrodehalogenation as a progressive approach to environmental remediation. The objectives of this PhD research are defined and the approach taken is described.

1.1 Halogenated Compounds

Halogen-containing organics (particularly chlorinated compounds) have long been used in the chemical industry for the manufacture of fine chemicals, notably personal care formulations and microorganism/plant/insect control (see **Table 1.1**). Lack of stringent production controls has resulted in the release of these compounds into the environment as a result of uncontrolled emissions and/or accidental spills [1,2]. Due to their low biodegradability and deleterious ecological and environmental effects (see **Table 1.2**), they are now identified as high priority pollutants in terms of treatment [2-4] and heavily legislated by the EPA Toxic Substance Control Act (TSCA), the International Agency for Research Cancer (IARC) and the World Health Organization (WHO) [5,6].

Table 1.1: Typical products manufactured using halogenated compounds as starting materials or additives.

Category	Products	Refs.
Health/personal care	Pharmaceuticals	[7,8]
	Deodorants	
	Mouthwashes and toothpastes	
	Fragrances	
Microorganism control	Biocides	[7-13]
	Antiseptics	
	Fungicides	
	Molluscicides	
	Antimicrobial finishing of textiles and paper	
Plant/insect control	Herbicides	[7,8,14-16]
	Algae control in water circulating systems	
	Repellents for plant-feeding insects	
Other	Preservative for metal working lubricants	[1,7,8,14,17]
	Flame retardant additives in unsaturated polyester and epoxy resins	
	Fire extinguishing agents	
	Solvents for oil, waxes, resins, greases and rubbers	
	Wood preservation	

Table 1.2: Impact of halogenated chemicals on human health and the environment.

Category	Effect	Refs.
Health ^a	Irritation of skin, eyes and lung	[4,6-8,11,14,18,19]
	Kidney/liver damage	
	Cardiovascular effects	
	Carcinogenic	
	Neuropathies and behavioral disturbances	
Death		
Environment ^b	Global warming	[4,6,8,20-23]
	O ₃ depletion	
	Contamination of agriculture	
	Animal disease	

^adetailed information can be found in refs. [4] (for a range of compounds) and [17] and [8] for specific chlorinated and brominated organics, respectively

^bconcise examples can be found in refs [20] and [23] for dioxin(s) and chlorobenzene(s) presence/effects in the Great Lakes (USA) and UK rivers, respectively

Several methods of halogenated waste control/disposal have been considered and are summarised in **Table 1.3**. Cumulative methods are typically inexpensive and are the preferred option for the treatment of individual compounds when present in high concentrations ($> 2 \text{ g dm}^{-3}$ [24]). This approach serves to concentrate the pollutant(s). Oxidative methods generate CO_2 , H_2O and the corresponding hydrogen halide (HX , $\text{X} = \text{Cl, Br, I}$) [2,25] and are the most widely used due to their proven efficiency (*e.g.* incineration [26]). Nevertheless, oxidative treatments present decided drawbacks in terms of (i) the requirement of expensive reactants (*e.g.* photo-oxidation [27,28]) and/or equipment (*e.g.* sono- [29,30] and electrochemical [31,32] oxidation) and (ii) the potential production of even more toxic by-products as a result of incomplete combustion (*e.g.* incineration [33,34]). Bioremediation, either aerobic (oxidative) or anaerobic (reductive), can be successfully used for the treatment of a wide range of compounds (halogenated dioxins, benzenes and phenols) but only at low concentrations (*e.g.* $< 6 \times 10^{-3} \text{ mol}_{\text{Cl}} \text{ dm}^{-3}$ in the case of chlorinated compounds [35,36]). Furthermore, effective practical application of bioremediation can be hampered by the requirement of careful control of the moisture content and the inclusion of C/N/P nutrients [37]. In order to minimise environmental effects and ensure conservation of resources, the ideal abatement option should be the recovery/reuse of raw material [4,38]. This is facilitated by the last reductive method included in **Table 1.3** and the focus of this thesis: catalytic hydrodehalogenation.

Table 1.3: Short overview of principal methods for halogenated waste control/disposal.

Nature	Method	Resume	Refs.
Cumulative	Adsorption	Pollutant capture from a gas/liquid stream onto a solid (typically activated carbon or resins)	[39-41]
	Absorption	Pollutant capture from a gas stream into a liquid stream where it can react.	[42,43]
	Air stripping	Pollutant capture from a liquid stream into air	[43-45]
	Permeation	Concentration from a liquid stream into another by membrane separation	[46,47]
Oxidative	Incineration	Pollutant combustion at high temperatures ($T \geq 1200$ K)	[26,33,34]
	Wet air oxidation	Treatment of a liquid stream containing the pollutant with O_2 at $T \geq 433$ K and $P \geq 2$ atm	[48-50]
	Advanced	Pollutant oxidation by $OH\cdot$ radicals generated by chemical redox processes (Fe, H_2O_2 , O_3), UV radiation, ultrasound or high voltages	[27-32,51]
	Aerobic biodegradation	Treatment with microorganisms in the presence of air	[35-37]
Reductive	Anaerobic biodegradation	Treatment with microorganisms in the absence of oxygen	[37,52]
	Hydrodehalogenation	Transformation of the C-X bond into C-H using a range of reducing agents: (notably, inorganic salts, formic acid, secondary alcohols or H_2)	^a

^aliterature review provided in section 1.2

1.2 Catalytic Hydrodehalogenation

Hydrodehalogenation (HDH) involves the H_2 -mediated cleavage of the carbon-halogen bond to form an alkane (*via* an electrophilic mechanism [53,54], see **Table 1.3**), with the release of the corresponding HX [54-56]. A distinction should be made between HDH and dehydrohalogenation, the latter involving internal halogen elimination with the production of an alkene [57,58]. HDH is a thermodynamically favourable and exothermic process [59,60] where the use of a catalyst results in an appreciable enhancement of HDH rate. This feature of catalytic HDH will be reviewed, analysed and discussed throughout this thesis. The main body of work dealing with catalytic HDH research has been developed over the past decade where Pd has been identified as the most effective metal due to its H_2 chemisorptive ability [61,62] and resistance to HX-induced deactivation [63,64]. The effect of process variables relating to the catalyst (support [65-68], metal particle size [67-77] and electronic state [78,79]) and reaction conditions (temperature/pressure [70,80-87], solvent/carrier [82-86,88-97], contact time [70,78,81,95,98]) has now been studied. Nevertheless, there is still no general consensus regarding the role of such variables as metal dispersion and solvent.

Moreover, few published studies have included detailed kinetic measurements with an explicit analysis of mass transport phenomena. Indeed, there is a dearth of studies that have provided any clear correlation of catalyst performance with catalyst structure/surface chemistry. This lack of fundamental information has limited the actual deployment of catalytic HDH in environmental pollution control.

1.3 Scope and Organization of the Thesis

The objective of this research is to carry out a systematic and comprehensive study of critical variables that can underpin catalytic HDH and to demonstrate the potential of this approach as a progressive haloarene waste abatement technology.

The liquid phase catalytic hydrodechlorination of 2,4-dichlorophenol over Pd/Al₂O₃ has been taken as starting point because it is a relatively well characterized system and total dechlorination can be achieved under mild conditions ($P = 1$ atm; $T = 303$ K; [99-104]). The effect of variations in Pd dispersion is first established in **Chapter 2** where the Pd particle size is adjusted by means of controlled thermal sintering at different temperatures (423 - 1273 K) and heating rates (1 - 50 K min⁻¹); the action of bulk (unsupported) Pd is also considered for comparative purposes. The effect of the solvent is next considered in **Chapters 3 and 4** using water and organic (alcohols, cyclohexane, *n*-hexane, benzene and THF) solvents and extending the study to a range of mono- and di-chlorophenols, bromophenols and chlorobenzenes. Since the vast majority of liquid phase HDH studies have been carried out in batch (discontinuous) operation, the feasibility and advantages of a shift to continuous HDH is addressed in **Chapter 5**. Finally, the feasibility of product recovery/reuse from catalytic HDH is examined in **Chapters 6, 7 and 8**, focusing on the gas phase production of cyclohexanone and 4-chlorophenol over Pd and iron oxide supported Au, respectively. A detailed catalyst characterization program (in terms of TPR, H₂ chemisorption/TPD, BET/pore volume, XRD, SEM/TEM and DRS UV-Vis) has been performed in each instance to link critical catalyst structural features with the observed catalytic response(s). A comprehensive assessment of mass transfer limitations has ensured operation under a kinetically controlled regime. In short, this thesis is a compilation of fundamental HDH studies with the practical deliverable of halogenated waste control/disposal/recovery.

1.4 References

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