



Detoxifying chlorine rich gas streams using solid supported nickel catalysts

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Abstract

Catalytic hydrogen treatment is presented as a viable low energy means of treating/detoxifying concentrated chlorinated gas streams to generate recyclable raw materials. Nickel (1.5% w/w and 15.2%) loaded silica and nickel (2.2% w/w) exchanged Y zeolite catalysts have been used to hydrotreat a range of chlorophenols (CPs), dichlorophenols (DCPs), trichlorophenols (TCPs) and pentachlorophenol (PCP) over the temperature interval $473\text{ K} \leq T \leq 573\text{ K}$. In every instance the nickel catalysts were 100% selective in cleaving the chlorine component from the ring, leaving the aromatic nucleus and hydroxyl substituent intact. The effects of varying process time and temperature are considered in terms of phenol yield and the ultimate partitioning of chlorine in the parent organic and product inorganic hosts. Chlorine removal rates, hydrodechlorination selectivity and apparent activation energies are also provided. Prolonged exposure of the catalysts to the concentrated chlorine gas streams resulted in an irreversible loss of activity which is related to the total concentration of chlorine that had been hydroprocessed. Hydrodechlorination proceeds via irreversible stepwise and/or concerted routes as is illustrated for the treatment of 2,3,5-TCP. Increasing the nickel content was found to raise the overall detoxification efficiency while the use of a zeolite support introduced spatial constraints which had a strong bearing on process selectivity. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorinated organic compounds have long been regarded as a major source of environmental pollution [1] with the result that more severe and restrictive directives

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have and continue to be introduced to reduce such emissions [2]. Incineration which has largely been the favoured methodology to handle toxic organic compounds is a difficult task to perform in a technically and environmentally acceptable way when dealing with chlorinated organics [3]. As a direct result of the thermal stability of these compounds, complete combustion occurs at such high temperatures ($T > 1700$ K) as to be economically prohibitive while the formation of hazardous by-products can result from incomplete incineration [4]. Both a high destruction and removal efficiency ($\geq 99.9999\%$) are required for incineration plants while strict limitations are now in place for disposal in landfills [5]. In recent years, catalytic hydrodechlorination has received attention as one of the most promising innovative technologies for the handling rather than disposal of toxic waste streams containing chlorinated organic compounds, converting the toxic organic chlorides into the corresponding hydrocarbons under moderate condition [4,6–8]. The HCl that is produced is easily separated and the hydrocarbon(s) can be recycled as a means of waste minimisation, avoiding the production of greenhouse effect gases [7]. As the replacement of each chlorine by hydrogen in polychlorinated compounds represents a decrease in toxicity of the parent organic, catalytic hydrodechlorination can be termed a detoxification process.

Chlorophenols are widely recognised as toxic chemicals resistant to biodegradation and enter the environment as industrial effluent from a range of organic source material, most notable in waste from herbicide or biocide production plants [2,9]. The methods which have been proposed for the treatment of chlorophenol containing waters and waste streams are, in the main, oxidative in nature and include supercritical [10], wet air [11] and photocatalytic [12] oxidation. To date, catalytic hydrodechlorination of monochlorophenol isomers in the liquid phase over carbon supported palladium [9] and in the gas phase over nickel based systems [13,14] have been studied. Initial rates for the liquid phase [9] and limited data for the gas phase [15] hydroprocessing of dichlorophenols are also available in the literature. There is now a genuine need for fundamental kinetic measurements of the hydrogen treatment of mono- and poly-chlorinated phenols in order to develop a database from which the generic features of the dechlorination process may emerge as an aid to process optimisation. In this paper we describe a catalytic approach for treating chlorine rich gas streams using silica and zeolite supported nickel. Taking the highly toxic pentachlorophenol and representative tri-, di- and mono-chlorophenols as feedstock the effects of varying a range of process conditions on detoxification efficiency have been considered as the first step to process development.

2. Experimental methods and procedures

A 1.5% and a 15.2% w/w Ni/SiO₂ were prepared by homogeneous precipitation/deposition [16] and the catalytic action of each was compared with a 2.2% w/w NiNa-Y zeolite prepared by ion exchange [17]. The hydrated samples, sieved in the 150–200 μm mesh range, were reduced, without a precalcination step, by heating in a 100 $\text{cm}^3 \text{min}^{-1}$ stream of dry hydrogen (99.9%) at 5 K min^{-1} to a final temperature of

673 ± 1 K which was maintained for 18 h. Catalyst characterization is described in some detail elsewhere [16–18]. All the catalytic reactions were carried out, in situ, under atmospheric pressure in a fixed bed glass reactor (i.d. = 15 mm) over the temperature range 473 K ≤ T ≤ 573 K. The catalytic procedure has been described previously [19], but some pertinent details are given below. A Merck-Hitachi LC-6000A pump was used to deliver the organic feed at a fixed rate which had been carefully calibrated and the vapour was carried through the catalyst bed in a stream of purified hydrogen. Single isomer methanolic solutions (methanol/aromatic mol ratio = 4) of 2-, 3- and 4-chlorophenol (CP), 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dichlorophenol (DCP), 2,3,5-, 2,3,6-, 2,4,5- and 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) were used as feedstock. Catalytic activity and selectivity were compared in each case at a constant inlet feed rate of 7.4 × 10⁻³ mol h⁻¹. The catalytic measurements were made at an overall space velocity of 1270 h⁻¹ and at a W/F value equal to 67 g mol⁻¹ h where W is the weight of activated catalyst and F is the molar flow rate of aromatic. Conversions have been shown elsewhere [20] to be proportional to W/F in the range 17–134 g mol⁻¹ h. At the end of each catalytic run the catalyst was regenerated by heating in flowing dry hydrogen at 5 K min⁻¹ to 673 K and maintained at this temperature for at least 12 h. The reactor effluent was frozen in a liquid nitrogen trap for subsequent analysis which was made using an AI Cambridge GC94 chromatograph equipped with a flame ionization detector and employing a DB-1 50 m × 0.20 i.d., 0.33 μm capillary column (J&W Scientific). Catalytic action is discussed in this paper in terms of percentage conversion, percentage selectivity and percentage yield where, taking the example of the dechlorination of a chlorophenol to phenol

$$\text{C}_6\text{H}_4\text{OHCl conversion (\%)} = \frac{[\text{C}_6\text{H}_4\text{OHCl}]_i - [\text{C}_6\text{H}_4\text{OHCl}]_o}{[\text{C}_6\text{H}_4\text{OHCl}]_i} \times 100 \quad (1)$$

$$\text{C}_6\text{H}_5\text{OH selectivity (\%)} = \frac{[\text{C}_6\text{H}_5\text{OH}]_o}{[\text{C}_6\text{H}_4\text{OHCl}]_i - [\text{C}_6\text{H}_4\text{OHCl}]_o} \times 100 \quad (2)$$

$$\text{C}_6\text{H}_5\text{OH yield (\%)} = \frac{[\text{C}_6\text{H}_5\text{OH}]_o}{[\text{C}_6\text{H}_4\text{OHCl}]_i} \times 100 \quad (3)$$

where [] denotes organic concentration and subscripts i and o refer to the concentration of organic entering and exiting the reactor, respectively. A chlorine mass balance was achieved by analysis of an aqueous NaOH trap through which the effluent gas was passed [21]; qualitative analysis for the presence of chlorine gas was negative and confirmed that HCl was the only inorganic product. All the reactants were AnalaR grade and were used without further purification.

3. Results and discussion

The pertinent physical characteristics of the catalyst precursors and activated material are given in Table 1 where the lower and higher nickel loaded silica samples are denoted Ni/SiO₂-A and Ni/SiO₂-B, respectively. The Ni/SiO₂-B sample supports larger metal

Table 1
Physical characteristics of the catalyst precursors and activated material

	Ni/SiO ₂ -A	Ni/SiO ₂ -B	NiNa/Y
Support	Cab-O-Sil 5 M	Cab-O-Sil 5 M	Linde LZ-52Y
<i>Precursor</i>			
Ni (w/w%) ^a	1.5	15.2	2.2
H ₂ O (w/w%)	0.6	1.2	26.6
<i>Activated catalyst</i>			
Ni ⁰ dispersion (%)	73	33	3
Ni ⁰ diameter nm	1.4	3.1	39
Exposed Ni ⁰ g ⁻¹	1.1 × 10 ²⁰	5.2 × 10 ²⁰	5.4 × 10 ¹⁸

^aBased on the hydrated catalyst.

particles than Ni/SiO₂-A and both dispersion values are in good agreement with the literature [22]. The nickel metal phase in the zeolite host is in the form of much larger crystallites when compared with the amorphous carrier as has been noted previously [18]. The product compositions resulting from the hydrogen treatment of an array of chlorophenols over Ni/SiO₂-A are given in Table 2. In every instance the catalyst was 100% selective in cleaving the C–Cl bond, leaving both the aromatic ring and hydroxyl substituent intact. Under the same reaction conditions the hydrogen treatment of phenol generated benzene via hydrogenolysis of the hydroxyl substituent (at $T > 523$ K) and cyclohexanone and cyclohexanol through a progressive hydrogenation [19]. The presence of the chlorine substituent(s) shifts the preferred reaction route from hydrogenation/hydrodeoxygenation to hydrodechlorination. The reported bond dissociation energies [23] of aromatic C–Cl (406 kJ mol⁻¹) and C–OH (469 kJ mol⁻¹) bonds indicate that aromatic deoxygenation is energetically more demanding. The isolation in the

Table 2
Reaction products resulting from the hydrogen treatment of chlorophenols (CPs), dichlorophenols (DCPs), trichlorophenols (TCPs) and pentachlorophenol (PCP) over Ni/SiO₂-A at 573 K where $W/F = 67$ g mol⁻¹ h

Reactant	Product(s)
2-CP	Phenol
3-CP	Phenol
4-CP	Phenol
2,3-DCP	2-CP, Phenol
2,4-DCP	2-CP, 4-CP, Phenol
2,5-DCP	2-CP, 3-CP, Phenol
2,6-DCP	2-CP, Phenol
3,4-DCP	3-CP, Phenol
3,5-DCP	3-CP, Phenol
2,3,5-TCP	2,3-DCP, 2-CP, Phenol
2,3,6-TCP	2,3-DCP, 2,6-DCP, 2-CP, Phenol
2,4,5-TCP	2,4-DCP, 2,5-DCP, 3,4-DCP, 2-CP, 4-CP, Phenol
2,4,6-TCP	2,4-DCP, 2,6-DCP, 2-CP, Phenol
PCP	2,3-DCP, 3,5-DCP, 2-CP, Phenol

product streams of CPs from DCPs and CPs/DCPs from TCPs and PCP is indicative of a stepwise removal of chlorine as has been proposed for the catalytic hydrodechlorination of chlorobenzenes [7,8]. Indeed, each dechlorination step is thermodynamically favourable and can be considered to be irreversible as is revealed in Table 3 which lists the equilibrium constants (at 573 K) evaluated using the NIST database [24]: as we could not access any thermochemical data for TCPs or PCP dechlorination we provide the equivalent values for the treatment of trichlorobenzene (TCB) and pentachlorobenzene (PCB) as suitable substitutes. From a qualitative standpoint, steric effects appear to play an important role in that every reactant that bears a chlorine *ortho* to the hydroxyl group generated a partially (CP or DCP) dechlorinated product which retained that particular chlorine. The nature of the products that are generated suggests that the formation of the surface reactive intermediate(s) which ultimately leads to reactant conversion must involve a direct (catalytically significant) interaction between the chlorine component and the catalyst resulting in single and multiple dechlorination steps followed by a desorption of the partially or fully dechlorinated phenol.

The conversion as a function of time of PCP and representative mono-, di- and tri-chlorophenols over Ni/SiO₂-A is illustrated in Fig. 1. With the exception of PCP which showed a decided decline in conversion after ca. 3 h on-stream, the turnover of the other chloroaromatics was essentially time invariant. Moreover, product selectivity remained largely unchanged with time as is shown in Table 4. Reaction temperature, on the other hand, had a greater bearing on product selectivity, as is illustrated in Fig. 2, taking 2,6-DCP and 2,4,6-TCP as model reactants. In both instances there is a clear cut shift in favour of more complete dechlorination of the feed at higher temperatures. In the case of 2,6-DCP (Fig. 2(a)), the drop in selective 2-CP formation was mirrored by a corresponding increase in phenol formation while 2-CP (in particular) and phenol were preferably formed at the expense of 2,4- and 2,6-DCP for the 2,4,6-TCP treatment (Fig. 2(b)). At the lowest temperature that was studied, the catalyst was 100% selective in removing only one chlorine substituent from the polychlorinated feed. Phenol formation required elevated temperatures where complete removal of the chlorine content was initiated at increasingly higher temperatures as the number of chlorine substituents increased, in the sequence CPs (> 473 K), DCPs (> 500 K), TCPs/PCP (> 550 K). The temperature dependencies of the overall chlorine removal rates is illustrated by the

Table 3
Equilibrium reaction constant (K_p) at 573 K for a number of dechlorination steps

Reaction	K_p
CP → Phenol	1.5×10^4
DCP → CP	4.2×10^{14}
DCP → Phenol	6.5×10^{18}
TCB → DCB	3.8×10^7
TCB → CB	9.5×10^{14}
TCB → Benzene	2.7×10^{21}
PCB → DCB	3.8×10^{22}
PCB → CB	2.2×10^{30}
PCB → Benzene	5.1×10^{36}

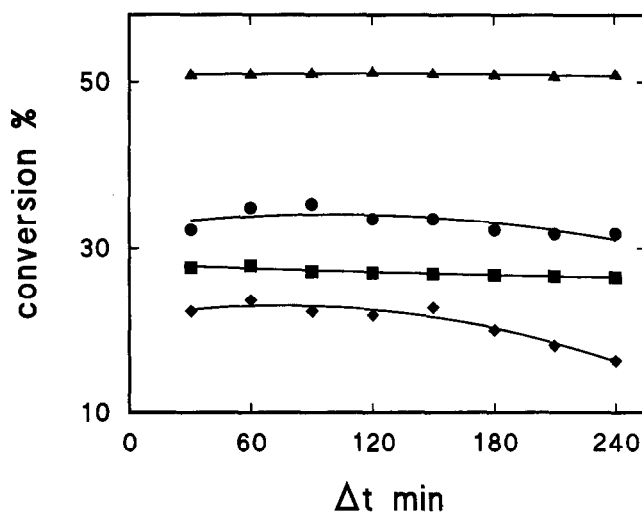


Fig. 1. Variation of the percentage conversion of PCP (◆), 2,3,6-TCP (●), 2,6-DCP (▲) and 2-CP (■) over Ni/SiO₂-A as a function of time-on-stream at 573 K.

apparent Arrhenius plots given in Fig. 3. The calculated E_{app} values increase in the order 2-CP = 2,6-DCP (40 kJ mol⁻¹) < 4-CP (55 kJ mol⁻¹) < 2,4,6-TCP (61 kJ mol⁻¹) < 3-CP (73 kJ mol⁻¹) < 3,4-DCP (113 kJ mol⁻¹). The lowest E_{app} value, recorded for both 2-CP and 2,6-DCP, suggests that, in such sterically constrained molecules, C–Cl breakage is more facile when compared with 3,4-DCP. The higher value for the latter compared with 3-CP and 4-CP suggests that the presence of the second chlorine deactivates or raises the energy barrier for hydrodechlorination, an assertion that supports an electrophilic reaction mechanism. The kinetic data for the six reactants are linked by a common Compensation Plot, shown in the inset to Fig. 3, which can be taken to diagnostic of individual reactions that proceed at comparable rates over similar temperature ranges [25], suggesting the feasibility of effectively treating chlorophenolic mixtures.

Selected reaction data for the hydrogen treatment of fourteen chlorophenolic reactants are given in Table 5 wherein it is clear that dechlorination is strongly dependent on the

Table 4

Variation in product selectivity ($S\%$) from $\Delta t = 0.5$ h to $\Delta t = 4$ h in the hydrodechlorination of PCP, 2,3,6-TCP, 2,6-DCP and 2-CP over Ni/SiO₂-A at 573 K

Reactant	$S\%$				
	2,3-DCP	2,6-DCP	3,5-DCP	2-CP	Phenol
PCP	38 → 34	–	28 → 28	17 → 14	18 → 23
2,3,6-TCP	55 → 52	4 → 5	–	16 → 21	26 → 23
2,6-DCP	–	–	–	86 → 88	15 → 12
2-CP	–	–	–	–	100 → 100

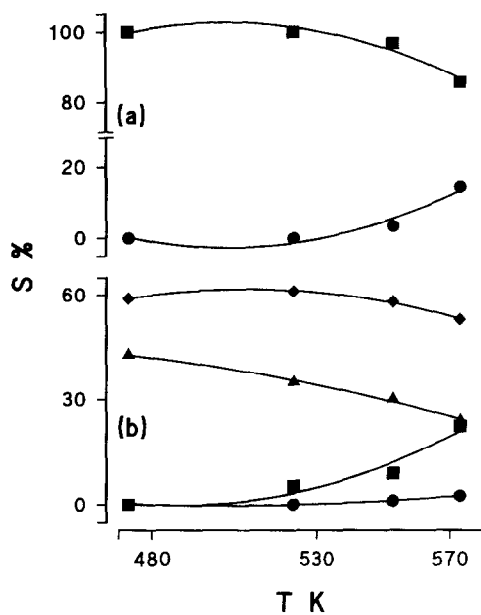


Fig. 2. Effect of temperature on selectivity in terms of the production of 2,4-DCP (◆), 2,6-DCP (▲), 2-CP (■) and phenol (●) from the hydrogen treatment of (a) 2,6-DCP and (b) 2,4,6-TCP over Ni/SiO₂-A.

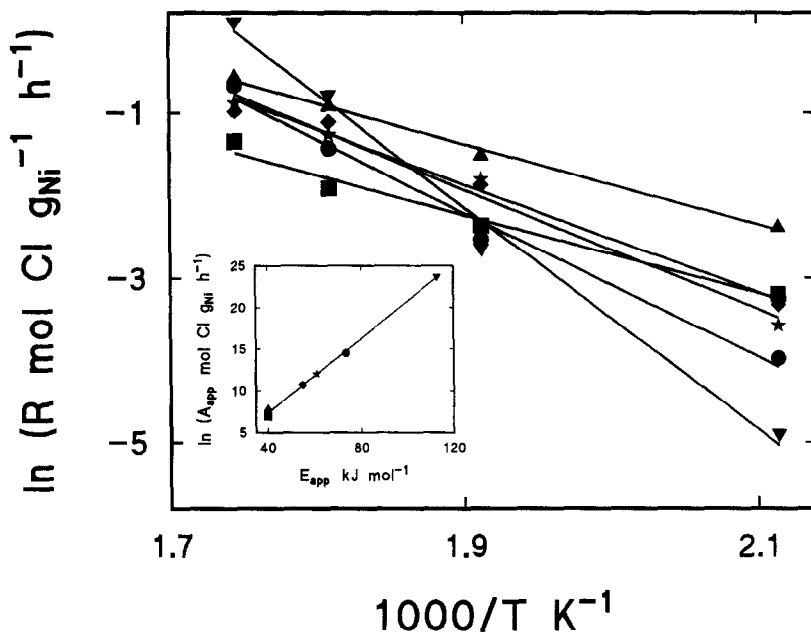


Fig. 3. Apparent Arrhenius plots that describe chlorine removal from 2,4,6-TCP (★), 2,6-DCP (▲), 3,4-DCP (▼), 2-CP (■), 3-CP (●) and 4-CP (◆) over Ni/SiO₂-A. Inset: Compensation Plot (relationship between apparent pre-exponential factor, A_{app} , and apparent activation energy, E_{app}), symbols as above.

Table 5

Chlorine removal rates, phenol yields and organic to inorganic chlorine ratios in the product stream resulting from the hydroprocessing of a range of chlorophenols over Ni/SiO₂-A at 573 K

Reactant	mol Cl g _{Ni} ⁻¹ h ⁻¹	Y _{phenol} %	Cl _{organic} /Cl _{inorganic}
2-CP	0.21	21.4	3.7
3-CP	0.34	34.4	1.9
4-CP	0.28	27.5	2.6
2,3-DCP	0.09	3.8	20.1
2,4-DCP	0.57	15.5	2.4
2,5-DCP	0.44	7.3	3.5
2,6-DCP	0.56	8.3	2.5
3,4-DCP	1.09	37.1	0.8
3,5-DCP	1.19	23.7	0.7
2,3,5-TCP	0.43	9.6	5.9
2,3,6-TCP	0.51	8.3	4.8
2,4,5-TCP	0.47	18.6	5.3
2,4,6-TCP	0.41	0.9	6.2
PCP	0.72	4.2	4.9

nature of the chlorinated feed. Chlorine removal rates were far greater for 3,4-DCP and 3,5-DCP where the halogen component is not as subject to steric hindrance due to the hydroxyl function and is consequently more susceptible to hydrogen cleavage. Treatment of PCP also yielded a high dechlorination rate while the four TCP isomers delivered virtually equal rates that were interspersed in magnitude with those generated from CP and DCP processing. Detoxification efficiency can perhaps be best quantified in terms of phenol yield and the partitioning of chlorine in the parent organic and product inorganic host. The generation of phenol may involve the concomitant splitting of all C–Cl bonds, which in the case of PCP presumes a five-point attachment to the surface, or a ‘rollover’ mechanism where each C–Cl bond cleavage is accompanied by a rollover of the molecule on the surface to initiate further attachment(s)/dechlorination(s). The phenol yield from a polychlorinated feed was highest for the less sterically constrained 3,4-DCP and 3,5-DCP reactants and lowest for the symmetrical 2,4,6-TCP which bears chlorines spaced as far apart on the ring as is possible. Complete dechlorination in the latter case must be hampered prior to desorption from the catalyst surface. The ratio Cl_{organic}/Cl_{inorganic}, i.e. the concentration of chlorine in the effluent gas stream that remains attached to an organic molecule divided by the concentration of HCl that is produced, serves as a useful index of how effective catalytic hydrodechlorination is as a detoxification methodology. The range of chlorophenolic feed considered in this study delivered a wide span of Cl_{organic}/Cl_{inorganic} ratios with the least detoxified isomer (2,3-DCP) retaining more than 2.3 times the organic chlorine than that which remained associated with the most detoxified 3,5-DCP feed. Under the stated process conditions the exiting inorganic chlorine component only exceeded the organic component in the hydroprocessing of 3,4-DCP and 3,5-DCP.

Hydrodechlorination proceeds via irreversible, simultaneous and consecutive steps. Taking the hydrogen treatment of 2,3,5-TCP as a model system, 2,3-DCP and 2-CP

represent stable partially dechlorinated intermediates in the generation of phenol according to the following sequence of steps



Pseudo-first order rate expressions have been shown previously [7,8,20] to serve as reasonable kinetic approximations where

$$\frac{-d[2,3,5\text{-TCP}]}{dW/F} = (k_1 + k_2 + k_6)[2,3,5\text{-TCP}] \quad (10)$$

$$\frac{d[2,3\text{-DCP}]}{dW/F} = k_1[2,3,5\text{-TCP}] - (k_3 + k_4)[2,3\text{-DCP}] \quad (11)$$

$$\frac{d[2\text{-CP}]}{dW/F} = k_2[2,3,5\text{-TCP}] + k_3[2,3\text{-DCP}] - k_5[2\text{-CP}] \quad (12)$$

$$\frac{d[\text{Phenol}]}{dW/F} = k_6[2,3,5\text{-TCP}] + k_4[2,3\text{-DCP}] + k_5[2\text{-CP}] \quad (13)$$

Taking a fixed inlet feed concentration, the rate constants for each unidirectional step were calculated using Eqs. (10)–(13), employing rate constants (k_3 , k_4 and k_5) that have been determined independently for the same catalyst [20,26]. The reaction pathways are shown in Fig. 4 where the rate constant ratio for stepwise to concerted attack equals 2.3, indicating the predominance of the stepwise pathway in the generation of phenol from 2,3,5-TCP.

The nickel catalysts exhibited long term deactivation due to prolonged exposure to the concentrated chlorinated gas streams. This loss of activity can be expressed as the ratio of the initial (R_{initial}) to time dependent (R_t) chlorine removal rate. Representative activity ratios for Ni/SiO₂-A are plotted in Fig. 5 as a function of the total concentration of chlorine that had been hydroprocessed. In every case there was a continual loss of hydrodechlorination activity with increasing process time. This deactivation proved to be irreversible in that catalyst regeneration in flowing hydrogen at 673 K was ineffective in restoring the original activity. The residual activity was less than 10% of the initial value after processing in excess of 1.5 mol Cl at which point the catalyst only promoted a partial dechlorination of the polychlorinated feed where phenol was not isolated in the product stream. These process conditions however represent a reactant to catalyst mass

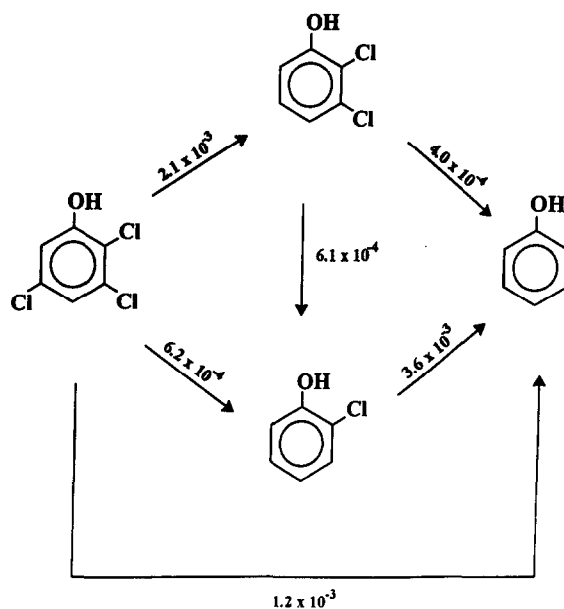


Fig. 4. Reaction pathways with the associated pseudo-first order kinetic rate constants (units = $\text{mol h}^{-1} \text{g}^{-1}$) for the hydrodechlorination of 2,3,5-TCP over Ni/SiO₂-A: $T = 573 \text{ K}$.

ratio greater than 400 and a time-on-stream in excess of 200 h which gives some indication of the extreme conditions that the catalyst had been exposed to. Previously observed losses of dechlorination activity in supported and unsupported metal catalysts

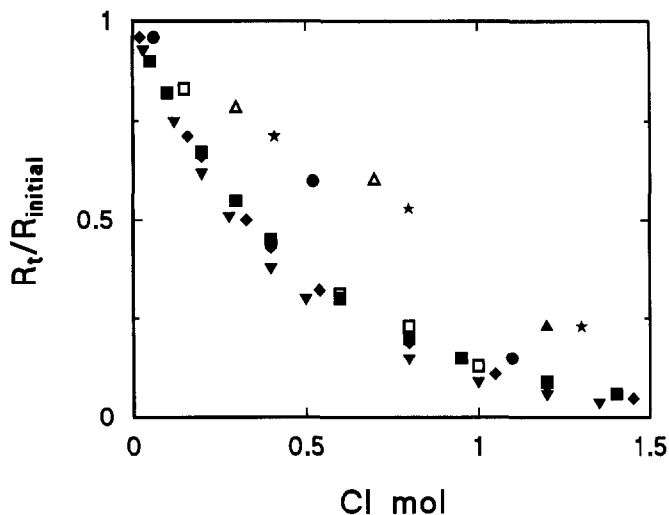


Fig. 5. The effect of the total chlorine that was hydroprocessed on the ratio of the initial (R_{initial}) to time dependent (R_t) chlorine removal rate for the treatment of 2,4,5-TCP (\square), 2,4,6-TCP (\triangle), 2,5-DCP (\bullet), 2,6-DCP (\blacktriangle), 3,5-DCP (\star), 2-CP (\blacksquare), 3-CP (\blacktriangledown) and 4-CP (\blacklozenge) over Ni/SiO₂-A at 573 K.

have been attributed to the presence of the HCl that is generated which forms an inactive surface chloride species [27,28]. Chlorine is certainly known to act as an electron acceptor with respect to transition metals [28] where prolonged exposure can result in an irreversible alteration in the electronic structure of the supported nickel which may be manifest in a less effective activation of the hydrogen and/or chloroarene reactant(s).

The effect of nickel content on the progress of dechlorination was also considered and chlorine removal as a function of time-on-stream is compared in Fig. 6 for Ni/SiO₂-A and Ni/SiO₂-B, taking 2,6-DCP and 2,4,5-TCP as model feedstock. In both cases, Ni/SiO₂-B delivered appreciably higher removal rates, i.e., 10.5×10^{-3} and 8.8×10^{-3} mol h⁻¹ compared with 3.5×10^{-3} and 2.6×10^{-3} mol h⁻¹ for the treatment of 2,6-DCP and 2,4,5-TCP, respectively. The Ni/SiO₂-B sample was also more selective in terms of phenol formation and there was a decided shift to more complete dechlorination with increasing metal loading as indicated in Table 6. The

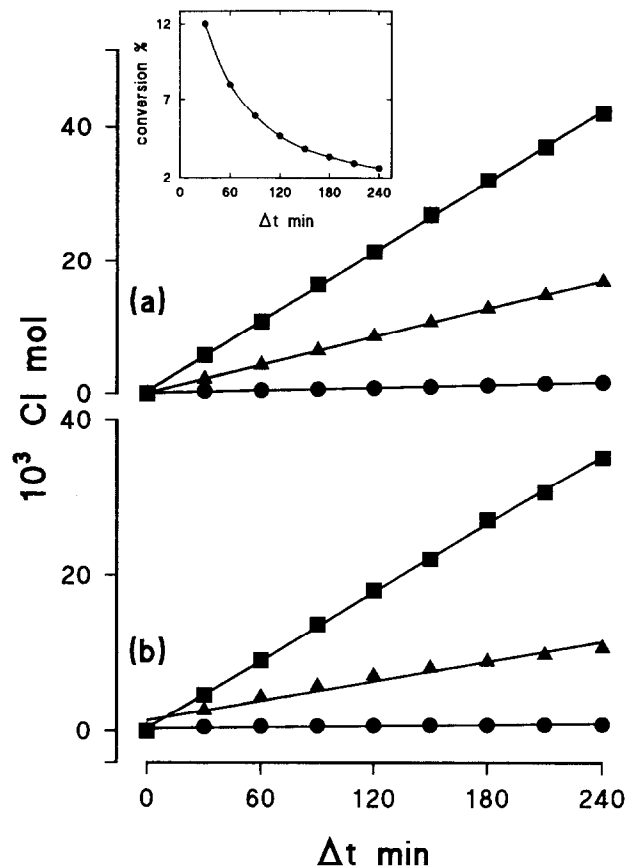


Fig. 6. Chlorine removal at 573 K as a function of time-on-stream for the hydrogen treatment of (a) 2,6-DCP and (b) 2,4,5-TCP over Ni/SiO₂-A (▲), Ni/SiO₂-B (■) and Ni/Na-Y (●). Inset: percentage conversion of 2,4,5-TCP over Ni/Na-Y as a function of time-on-stream.

Table 6

Dechlorination selectivity in the hydrogen treatment of 2,4,5-TCP and 2,6-DCP over Ni/SiO₂-A, Ni/SiO₂-B and Ni/Na-Y: $T = 573$ K; $\Delta t = 4$ h

Reaction system	10 ³ TOF s ⁻¹	S%					
		2,4-DCP	2,5-DCP	3,4-DCP	2-CP	4-CP	Phenol
<i>2,6-DCP feed</i>							
Ni/SiO ₂ -A	12.8	–	–	–	88	–	12
Ni/SiO ₂ -B	6.8	–	–	–	58	–	42
Ni/Na-Y	12.4	–	–	–	98	–	2
<i>2,4,5-TCP feed</i>							
Ni/SiO ₂ -A	7.9	5	2	29	30	3	29
Ni/SiO ₂ -B	5.7	5	3	11	37	7	38
Ni/Na-Y	9.3	–	97	–	3	–	–

chlorine partitioning was also substantially shifted in favour of the inorganic host with $Cl_{\text{organic}}/Cl_{\text{inorganic}}$ ratios of 0.4 and 1.5 for 2,6-DCP and 2,4,5-TCP which are markedly lower than the values recorded (in Table 5) for Ni/SiO₂-A. The product stream exiting the Ni/SiO₂-B reactor contained up to 2.5 times less chlorine in the organic host, representing a marked improvement in detoxification level. Work is now under way to characterize the fresh and used nickel catalysts (by TEM, H₂ TPD and XPS) in order to relate dechlorination activity/selectivity to catalyst morphology and electronic structure. The effective use of the supported nickel metal phase can however be assessed by comparing the turnover frequencies (TOFs) which are a measure of the rate of chlorine removal per exposed nickel metal atom. Although the conversion of a fixed feed concentration was higher over Ni/SiO₂-B, the lower loaded Ni/SiO₂-A delivered higher TOF values as recorded in Table 6. It should however be noted that the difference in TOF decreased as the process became more demanding, i.e., increasing chlorine concentration in the feedstock. The zeolite supported nickel catalyst generated far lower dechlorination rates (Fig. 6) but comparable TOF values (Table 6). The zeolite system, in contrast to Ni/SiO₂, was characterised by a marked loss of short term activity which is depicted in the inset to Fig. 6. Zeolite Y can be classified as a large pore aluminosilicate where access to the intracrystalline supercage metal sites is via 0.7–0.8 nm and 0.20–0.25 nm pore openings. Reduction of the nickel exchanged Y zeolite generates a nickel metal phase that exhibits a wide particle size distribution with particle growth resulting in the formation of larger metal particles supported on the external surface [18,29]. There is however an appreciable smaller particle component accommodated within the zeolite pore structure which serves to promote hydrodechlorination. The observed loss of activity can be ascribed to a pore blocking effect (which is not a factor with Ni/SiO₂) where the internal active sites become occluded, reducing their accessibility to incoming chloroaromatic reactant molecules. Such an effect has been well established and reported for closely related zeolite catalytic systems [30,31]. The porous crystalline structure of the zeolite can impose strong geometrical constraints which influence reaction selectivity. Indeed, hydroprocessing 2,6-DCP generated 2-CP as by

far the principal product while 2,4,5-TCP only yielded 2-CP and 2,5-DCP in the product stream. The finite size of the zeolite cavities must then lead to spatial constraints where complete dechlorination is unfavourable and there is a greater tendency for the partially dechlorinated 'intermediate' to desorb after the first or second chlorine removal step.

4. Conclusions

In the gas phase hydroprocessing of a range of chlorinated phenols over supported nickel catalysts, the data presented in this paper support the following conclusions:

- (i) under conditions far removed from equilibrium conversions, the catalyst system is selective in solely promoting hydrodechlorination and there is no detectable ring hydrogenation or deoxygenation products;
- (ii) the removal of chlorine from DCPs, TCPs and PCP proceeds via stepwise and/or concerted irreversible steps where steric effects influence the ultimate product composition;
- (iii) prolonged exposure of the catalyst to concentrated chlorine gas streams is accompanied by an irreversible catalyst deactivation which is manifest in lower chlorine removal rates and a suppression of complete dechlorination to phenol;
- (iv) an increase in the reaction temperature (from 473 K to 573 K) raises the overall chlorine removal rate and selectivity with respect to phenol formation;
- (v) detoxification efficiency increases with higher nickel content in the case of Ni/SiO₂;
- (vi) the use of a zeolite support imposes strong spatial limitations which favour partial dechlorination and is accompanied by short term deactivation.

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