

# Gas phase catalytic dehydrochlorination and hydrodechlorination of aliphatic and aromatic systems

George Tavoularis, Mark A. Keane \*

*Department of Chemical Engineering, The University of Leeds, Leeds, LS2 9JT, UK*

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## Abstract

The gas phase dechlorination of cyclohexyl chloride and chlorobenzene, over the temperature range  $423 \text{ K} \leq T \leq 573 \text{ K}$ , promoted using a silica supported nickel catalyst in the presence of hydrogen has been studied. Chlorine removal from the chloroalkane is shown to occur by dehydrochlorination via an E1 type elimination mechanism to yield cyclohexene and HCl as the products. The reaction was found to exhibit zero order behaviour with respect to hydrogen partial pressure, a temperature dependent reaction order (varying from 0.4 to 0.7) with respect to the chloroalkane and an apparent activation energy equal to  $115 \text{ kJ mol}^{-1}$ . Turnover of the cyclohexyl chloride reactant was subject to a short term loss of catalytic activity due to a surface poisoning by the HCl that was produced where the presence of hydrogen served to displace the inorganic halide and extend the productive lifetime of the catalyst. A steady state conversion of chlorobenzene was however readily achieved where dechlorination in hydrogen occurs via an electrophilic hydrodechlorination mechanism. Bromine removal from cyclohexyl bromide and bromobenzene is also considered for comparative purposes. The ease of halogen removal and process selectivity are discussed in terms of thermodynamic limitations and reactant/catalyst interactions. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The disposal of chlorinated organic waste is now recognised as a serious environmental problem [1,2]. The treatment technologies that are presently in general use are destructive in nature and typically involve incineration or chemical degradation processes. As such methodologies are energy demanding and can result in the generation of toxic products [3,4], they do not constitute the best practicable envi-

ronmental option. Catalytic hydroprocessing is now emerging as a viable alternative for handling halogenated waste where the hazardous material is transformed into recyclable products in a closed system with no (or significantly reduced) toxic emissions [5,6]. Moreover, the hydrodehalogenation step may serve as a potentially viable synthetic route in addition to being a means of recycle. While there is a wealth of kinetic data concerning hydrodenitrogenation, hydrodesulphurisation and hydrodeoxygenation reactions [7], catalytic hydrodechlorination is, by comparison, as yet poorly characterised. Nevertheless, if one compares review articles

\* Corresponding author. Tel.: +44-113-2332428; Fax: +44-113-2332405; E-mail: chemaak@leeds.ac.uk

dating from 1980 [8] and 1996 [9], it is immediately evident that research in this area is developing rapidly. The aim of the work reported herein is to compare directly, under standard conditions, the dehalogenation of halogenated benzyl and cyclohexyl compounds on a molecular basis in order to assess the influence of aromaticity on the ease of halogen removal. This report represents, to the best of the authors' knowledge, the only comprehensive comparative study that deals with dehalogenation of aliphatic and aromatic compounds using the same catalyst.

Thermodynamic analyses of gas phase hydrodechlorination reactions have shown that HCl formation is strongly favoured and the presence of a metal catalyst reduces considerably the operating temperature, providing a lower energy pathway for the reaction to occur [10]. The energetics for the thermal dechlorination of aliphatic and aromatic systems are very similar [5]. In catalytic applications, chlorine removal from an aromatic reactant has however been shown to be both more [11,12] and less [8] facile than that observed for an aliphatic feed. In homogeneous systems [13], dehalogenation can proceed via concerted ( $S_{N2}$ ) and sequential ( $S_{N1}$ ) nucleophilic substitution or  $\beta$ -elimination. The mechanisms in heterogeneous catalysed reactions have not been irrefutably established and the reaction has been viewed in terms of both nucleophilic [14,15] and electrophilic [16] attack. In addition, a number of kinetic models have been proposed [14,17–19] to account for the observed rate data and attempts have been made to identify the nature of the adsorbed species and the catalytically active site(s) [10,12,16,18]; the pertinent features of these reports will be compared herein with the data generated in this study. This paper sets out to identify, from a kinetic and mechanistic viewpoint, the effect of an aliphatic (cyclohexyl ring) or aromatic (benzene ring) host in determining gas phase dechlorination (and, to a lesser extent, debromination) promoted by Ni/SiO<sub>2</sub> in the presence of hydrogen. The ultimate goal of

this work is to assess the viability of such a methodology as a generic approach for treating concentrated halogenated gas streams.

## 2. Experimental

### 2.1. Catalyst preparation and activation

A 1.5% w/w Ni/SiO<sub>2</sub> catalyst was prepared by homogeneous precipitation/deposition and characterised as described in detail elsewhere [20]. All the catalytic reactions were carried out under atmospheric pressure in a fixed bed glass reactor (i.d. = 15 mm) over the temperature range  $423 \text{ K} \leq T \leq 573 \text{ K}$ . The hydrated sample, sieved in the 150–200  $\mu\text{m}$  mesh range, was activated in situ by heating in a  $100 \text{ cm}^3 \text{ min}^{-1}$  stream (monitored using a Humonics Model 529 digital flow meter) of dry hydrogen (99.9%) at a fixed rate of  $5 \text{ K min}^{-1}$  (controlled using a Eurotherm 91e temperature programmer) to a final temperature of  $673 \pm 1 \text{ K}$  which was maintained for 18 h. Under these activation conditions, the catalyst is estimated [20] to support  $1.1 \times 10^{20}$  exposed nickel metal atoms per gram of solid. Preliminary analyses of the fresh and used Ni/SiO<sub>2</sub> by XRD and TEM did not reveal any appreciable loss of nickel from the silica support or modification to the particle size distribution.

### 2.2. Catalytic procedure

The catalytic reactor has been described previously in some detail [21,22] but the particular features pertinent to this study are given below. A Model 100 (kd Scientific) microprocessor controlled infusion pump was used to deliver the halogenated feed via a glass/teflon air-tight syringe and teflon line at a fixed, calibrated, rate and the vapour was carried through the catalyst bed in a stream of purified hydrogen. Undiluted cyclohexyl chloride (Aldrich, 99%), cyclohexyl bromide (Aldrich, 98%), chlorobenzene

(Aldrich 99 + %) and bromobenzene (Aldrich, 99 + %) served as the feedstock where the concentration was in the overall range  $2 \times 10^{-3}$ – $13 \times 10^{-3}$  mol h<sup>-1</sup>; all the halogenated reactants were used without further purification. In a series of blank experiments, passage of the halogenated feed in a stream of hydrogen through the empty reactor, i.e., in the absence of the catalyst, did not result in any detectable conversion. Some conversion of cyclohexyl chloride was observed in the presence of silica alone but it was less than 3% of that generated by the nickel catalyst under the same reaction conditions. The catalytic measurements were made at an overall space velocity of 375–2250 h<sup>-1</sup> and at  $W/F$  values in the range 33–198 g mol<sup>-1</sup> h where  $W$  is the weight of activated catalyst and  $F$  is the molar flow rate of the hydrocarbon. Mass diffusion contributions under these conditions were found to be negligible when using the approach proposed by Ruthven [23] which delivered effectiveness factors ( $\eta$ ) > 0.99. Heat transport effects can also be disregarded when applying the criteria set down by Mears [24]. The reaction order with respect to hydrogen was determined by dilution in helium to vary the hydrogen partial pressure in the range 0.34–0.94 atm; the reaction order with respect to cyclohexyl chloride was likewise evaluated by varying the partial pressure in the range 0.02–0.10 atm.

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 split/splitless injector and a flame ionization detector, employing a DB-1 50 m  $\times$  0.20 i.d., 0.33  $\mu$ m capillary column (J&W Scientific). Data acquisition and analysis were performed using the JCL 6000 (for Windows) chromatography data system and the overall level of hydrodechlorination was converted to mol% conversion using detailed calibration plots for each feedstock. Molar percentage selectivity ( $S$ ) in terms of product  $x$  is defined as  $m_x/m_{\text{tot}} \times 100$  where  $m_{\text{tot}}$  is the total number of moles of product. A chlorine (in

the form of HCl product) mass balance was performed by passing the effluent gas through an aqueous NaOH ( $3.5$ – $8.0 \times 10^{-3}$  mol dm<sup>-3</sup>, kept under constant agitation at  $\geq 300$  rpm) trap and monitoring continuously the pH change by means of a Hanna HI Programmable Printing pH Bench-Meter. Qualitative analysis for the presence of chlorine (or bromine) gas was made by analysis of the trap for the formation of hydrates at  $T > 283$  K [25]. The test was negative in every instance, regardless of the nature of the organic reactant and/or the carrier gas confirming that cleavage of the C–Cl (or C–Br) bond in aromatic and aliphatic reactants yields HCl (or HBr) as the only inorganic product. At the end of each catalytic run the catalyst was normally heated in flowing dry hydrogen at 5 K min<sup>-1</sup> to 673 K and maintained at this temperature for at least 12 h. In many cases the reaction was repeated under identical conditions where rate reproducibility was better than  $\pm 7\%$ .

### 3. Results and discussion

#### 3.1. Time-on-stream profiles

The hydrogen treatment of cyclohexyl chloride over the temperature range  $423 \text{ K} \leq T \leq 523 \text{ K}$  generated cyclohexene as by far the predominant product ( $S > 97\%$ ) with cyclohexane as the secondary product while benzene was detected in trace quantities ( $< 0.5$  mol%) at temperatures in excess of 473 K. The same catalyst proved to be 100% selective in the hydrodechlorination of chlorobenzene ( $473 \text{ K} \leq T \leq 573 \text{ K}$ ), generating benzene as the sole product, i.e., the aromatic ring remained intact in every instance. Reactivity of the aromatic and aliphatic halogenated feed is compared in terms of the turnover frequencies (TOF), the number of molecules of reactant converted per exposed metal atom. The variation of the TOF of cyclohexyl chloride as a function of reaction time is illustrated in Fig. 1 for three representative temperatures. It is immediately evident that conver-

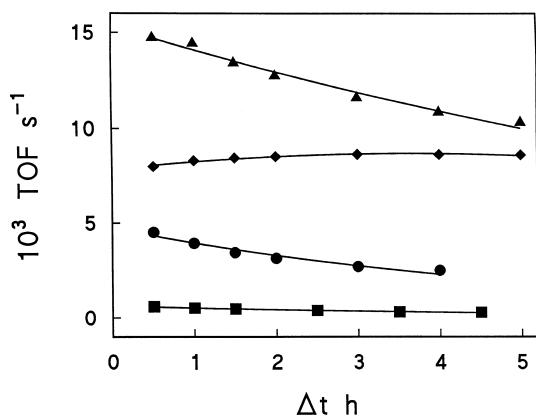


Fig. 1. Variation with reaction time of the TOF of chlorobenzene at 573 K (◆) and cyclohexyl chloride at 423 K (■), 448 K (●) and 473 K (▲).

sion is time dependent and there was a decided drop in activity over the 5 h period. The nature of this short term deactivation was quantified by extrapolation to initial activity ( $\text{TOF}_{\text{initial}}$ ) using the empirical relationship:

$$\text{TOF} = \text{TOF}_{\text{initial}} \exp(-\alpha \Delta t) \quad (1)$$

where the coefficient  $\alpha$  can be considered to reflect the time dependency of TOF: the lines included in Fig. 1 represent the fit of Eq. (1) to the experimental chloroalkane TOF data. The variation of chlorobenzene hydrodechlorination rate with time at a selected temperature is also included in Fig. 1 for comparative purposes. The time-on-stream profile in this case is characterised by an initial induction period wherein there is a discernible increase in rate with time followed by the attainment of a steady state conversion after at most 3 h. Catalyst deactivation in a variety of dechlorination processes utilising supported rhodium [10], platinum [26] and unsupported nickel [19] catalysts has been ascribed to a poisoning of the surface metal by the HCl that is produced in the reaction. Chlorine coverage of the catalyst surface under reaction conditions was probed indirectly by monitoring (via pH changes in an aqueous NaOH trap) HCl desorption after completion of the catalytic step. Representative desorption data generated after the catalyst was used to hy-

droprocess a concentrated stream of gaseous cyclohexyl chloride and chlorobenzene are recorded in Fig. 2. Hydrogen chloride desorption was monitored over three treatment steps: (a) constant hydrogen flow for 40 min at the reaction temperature; (b) temperature ramping to 673 K; (c) prolonged hydrogen flow at 673 K. Repeated and careful experimentation permit us to positively attribute the chlorine component that is monitored to HCl that is desorbed from the catalyst. The total concentration of HCl desorbed is similar for both cyclohexyl chloride and chlorobenzene reactions and the actual concentrations that were recorded, in a series of experiments (over a range of process conditions), represent a coverage of the surface nickel metal sites in the range 1.6 to 3.2. A buildup of surface chlorine can be considered to coincide with the slight initial increase in chlorobenzene dechlorination activity, the induction period illustrated in Fig. 1, where the active catalyst surface under steady state reaction conditions must be taken to be highly chlorinated.

The divergence in behaviour with regard to conversion vs. time for the chlorobenzene and cyclohexyl chloride feed cannot then be simply attributed to differences in the concentration of adsorbed HCl as the surface conditions which prevail during both processes involve a virtual

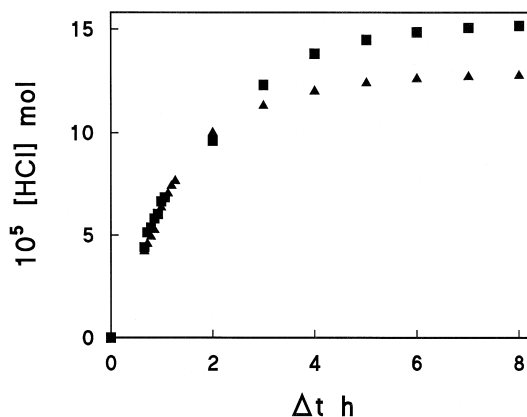


Fig. 2. Concentration of HCl desorbed after processing  $4.1 \times 10^{-2}$  moles of chlorobenzene at 573 K (■) and  $5.0 \times 10^{-2}$  moles of cyclohexyl chloride at 473 K (▲).

saturation by HCl. Rather, the nature of reactant and/or product interactions with the catalyst must be taken into account. Given that cyclohexene is the principal product resulting from the hydroprocessing of cyclohexyl chloride, the ‘catalytically significant’ reactant/catalyst interaction must be through the chlorine substituent. Concurrent desorption of cyclohexene from the surface must accompany HCl elimination where cyclohexene does not serve, to any great extent, as a reactive intermediate for an additional hydrogenation step [21] to produce cyclohexane. The HCl that is generated does however interact with the catalyst as we have established in our pH measurements. Both Coq et al. [17] and Estelle et al. [19] have attempted to quantify catalyst poisoning in terms of an initial toxicity which relates the quotient  $\text{TOF}/\text{TOF}_{\text{initial}}$  to the concentration of HCl that is produced [27]. The corresponding linear relationships generated in this study for the hydroprocessing of cyclohexyl chloride at three reaction temperatures are shown in Fig. 3. It is immediately evident that the dependence of rate loss on HCl produced was lowered as the reaction temperature was increased where the latter action also brought about an increase in the overall TOF values (as shown in Fig. 1). The concentration of HCl produced corresponding in

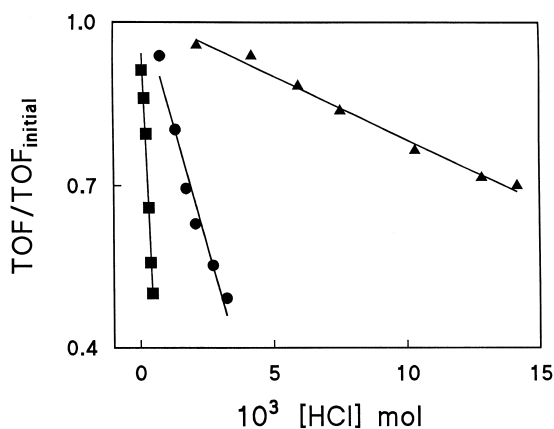


Fig. 3. Linear relationships between the ratio of time dependent to initial TOF and the concentration of HCl that is produced in the hydroprocessing of cyclohexyl chloride at 423 K (■), 448 K (●) and 473 K (▲).

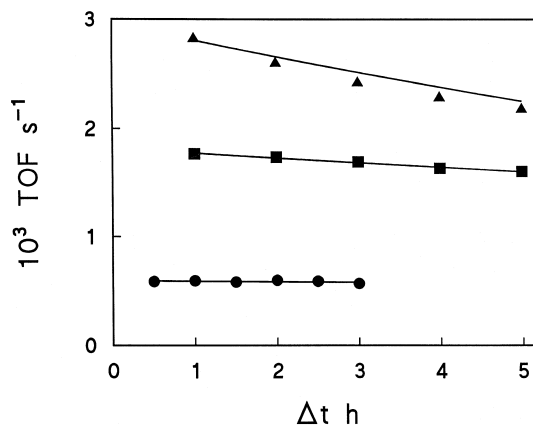


Fig. 4. TOF of ( $5 \times 10^{-3} \text{ mol h}^{-1}$ ) cyclohexyl chloride at 448 K as a function of time with (▲) and without (■) catalyst regeneration at 673 K and after five successive cycles of catalyst regeneration at 573 K (●).

a drop of  $\text{TOF}_{\text{initial}}$  by 50% (at a feed rate of  $1.3 \times 10^{-3} \text{ mol C}_6\text{H}_{11}\text{Cl h}^{-1}$ ) increased with increasing temperature from  $4.5 \times 10^{-4}$  moles (423 K) to  $3.0 \times 10^{-3}$  moles (448 K) and  $2.2 \times 10^{-2}$  moles (473 K). Such a limiting of rate inhibition induced by a temperature increase suggests the involvement of sorption phenomena which we shall consider in due course. The short term loss of activity depicted in Fig. 1 can however lead to longer term deactivation if the catalyst is not regenerated as is illustrated by the representative time-on-stream profiles given in Fig. 4. Repeating the reaction (after contacting the catalyst with a prolonged flow of hydrogen) under the same reaction conditions resulted in an appreciably lower turnover of reactant. The rate profile is again characterised by a drop in conversion albeit the dependence on time was not as great as that observed for the initial run, i.e.,  $\alpha = 2 \times 10^{-5} \text{ s}^{-2}$  for the first cycle as opposed to  $7 \times 10^{-6} \text{ s}^{-2}$  for the second. Regeneration of the catalyst to achieve full restoration of catalytic activity was only achieved with prolonged hydrogen treatment at 673 K. It should be noted that a constant TOF of chlorobenzene was maintained without the need for any regeneration step. Such observations are indicative of both a reversible and irreversible deactivation component in the hydroprocessing

of the chloroalkane. Heating the catalyst in hydrogen to the lower temperature of 573 K did not serve to regenerate the initial catalytic activity and repeated cycles of regeneration at 573 K were accompanied by a steady decrease in TOF, by a factor of 0.90 after the first cycle, a factor of 0.55 after the second and 0.29 after the third, diagnostic of a cumulative catalyst deactivation. Indeed, after five such cycles, the value of  $\text{TOF}_{\text{initial}}$  was appreciably lowered and the residual activity is shown in Fig. 4.

### 3.2. Reaction kinetics

The kinetics for the hydrogen treatment of cyclohexyl chloride resulting in dechlorination may be represented by the empirical power equation given below which does not include any contribution due to possible inhibition by the reaction products:

$$\text{TOF} = kP_{\text{C}_6\text{H}_{11}\text{Cl}}^m P_{\text{H}_2}^n \quad (2)$$

where  $k$  represents the rate constant and  $m$  and  $n$  the orders of the reaction with respect to the cyclohexyl chloride and hydrogen partial pressures, respectively. The reaction orders were determined by means of logarithmic plots where, for instance at constant reaction temperature and partial pressure of hydrogen:

$$\log \text{TOF}_{\text{initial}} = \log(kP_{\text{H}_2}^n) + m \log P_{\text{C}_6\text{H}_{11}\text{Cl}} \quad (3)$$

and representative logarithmic plots depicting the variation of  $\text{TOF}_{\text{initial}}$  with the partial pressure of cyclohexyl chloride at 423 K, 448 K and 473 K are shown in Fig. 5. The computed reaction order with respect to cyclohexyl chloride partial pressure increased with increasing temperature from 0.4 to 0.7, indicative of a temperature induced loss of surface reactive chloroalkane. The hydrodechlorination of chlorobenzene over the same catalyst was also characterised by a shift in the reaction order from 0.3 to 0.6 but over the more elevated temperature interval  $473 \text{ K} \leq T \leq 573 \text{ K}$  [28]. Such reaction dependences suggest that the reactive adsorbed form of chlorobenzene interacts

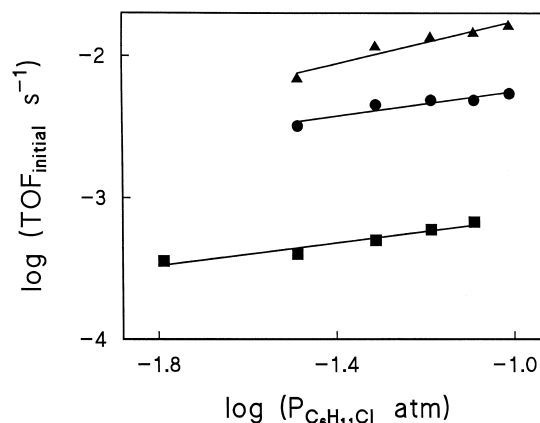


Fig. 5. Initial TOF of cyclohexyl chloride as a function of cyclohexyl chloride partial pressure at 423 K (■), 448 K (●) and 473 K (▲).

with the catalyst surface to a greater extent than is the case for cyclohexyl chloride. Halogens are known to act as electron acceptors with respect to transition metals [29] with the result that the degree of interaction for a particular chlorinated compound should depend on electronic effects, i.e., the greater the electron affinity of the halogenated reactant, the greater should be the strength of adsorption. If both chlorobenzene and cyclohexyl chloride adsorb on the catalyst solely through the chlorine component, the degree of interaction with the catalyst will, by inference, increase with increasing ionisation potential (IP) of the isolated gaseous halogenated molecule. The IP of cyclohexyl chloride is however greater than that of chlorobenzene [30] which suggests the additional involvement of the aromatic nucleus in fixing chlorobenzene to the surface. Benzene has been shown elsewhere [31] to adsorb on nickel supported systems via  $\pi$ -bond interactions in which the ring lies parallel to the active surface while cyclohexane interactions are far weaker. A combined 'two-point' interaction is then considered to hold chlorobenzene more strongly to the catalyst than is the case for the single chlorine-catalyst attachment assumed for the cyclohexyl chloride reaction. As the aromatic nucleus was not attacked in the hydrogen treatment of

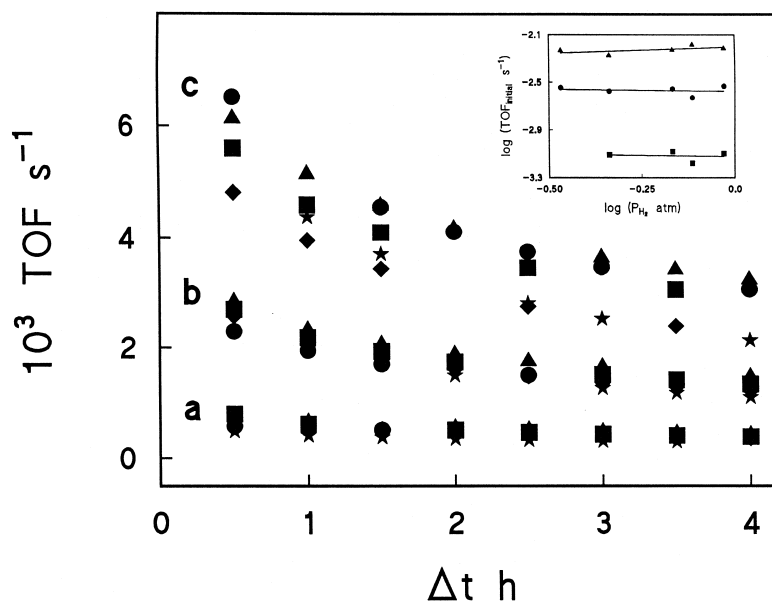


Fig. 6. Variation of cyclohexyl chloride TOF as a function of time-on-stream at (a) 423 K, (b) 448 K and (c) 473 K where  $P_{\text{H}_2} = 0.94$  atm ( $\blacktriangle$ ), 0.77 atm ( $\bullet$ ), 0.68 atm ( $\blacksquare$ ), 0.46 atm ( $\blacklozenge$ ) and 0.34 atm ( $\blackstar$ ). Inset: initial TOF of cyclohexyl chloride as a function of  $P_{\text{H}_2}$  at 473 K ( $\blacksquare$ ), 523 K ( $\bullet$ ) and 573 K ( $\blacktriangle$ ).

chlorobenzene, we must assume that the resonance energy of the benzene ring is not significantly lowered in the activation step.

The effect of varying the partial pressure of hydrogen (from 0.3 to 0.9 atm) on the TOF of the chloroalkane is considered in Fig. 6, in the first instance in terms of time-on-stream. Each profile is superimposable at the lower reaction temperatures ( $\leq 448$  K) and while there is a decided scatter of data at 473 K, the observed rate was not strongly influenced by variations in the partial pressure of hydrogen. This is borne out by the data presented in the inset to Fig. 6 which establish an essentially zero order dependence of initial rate on hydrogen partial pressure. Moreover, conversion of cyclohexyl chloride to cyclohexene was found to proceed in the absence of hydrogen where helium was used as the carrier gas and representative comparative catalytic data generated in hydrogen and helium gas streams are presented in Fig. 7. The reaction does not therefore require an external source of hydrogen and, as such, the process is really a dehydrochlorination. The initial TOFs, when

evaluated using Eq. (1), are close for both  $\text{He}/\text{Ni}^0$  and  $\text{H}_2/\text{Ni}^0$  systems but catalyst deactivation was more marked in the former case where the initial activity was cut by up to 60% after 4 h on stream. Dechlorination was also promoted by unreduced  $\text{NiO}-\text{SiO}_2$  in a helium stream but the drop in conversion was more extreme when compared with the two other

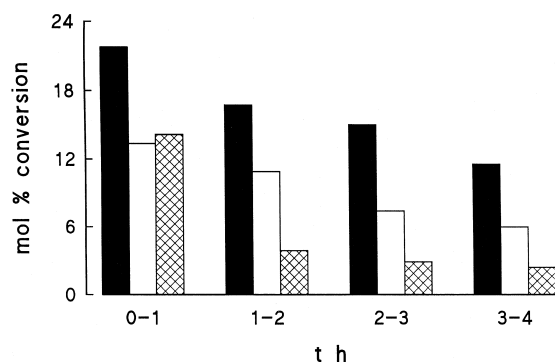


Fig. 7. The variation of cyclohexyl chloride conversion (at 448 K) in hourly increments for the reaction in hydrogen (solid bars) and helium (open bars) over supported zero valent nickel metal and for the reaction in helium over supported NiO (cross-hatched bars).

systems. In contrast, removal of chlorine from chlorobenzene only proceeded in a hydrogen flow in the presence of nickel metal which represents a clear example of catalytic hydro-dechlorination.

### 3.3. Reaction mechanism(s)

The conversion of the chloroalkane to the alkene involves internal elimination of HCl where the catalyst activates the reactant while the presence of hydrogen/nickel metal serves to maintain/prolong catalytic activity. The possibility of thermodynamic limitations was considered by estimating the pertinent gas phase constants using the NIST database [32]. The resultant calculations yielded equilibrium constants in the form of temperature dependences ( $300 \text{ K} \leq T \leq 600 \text{ K}$ ) for the conversion of cyclohexyl chloride to cyclohexene:

$$K_{\text{C}_6\text{H}_{10}} = \frac{(P_{\text{C}_6\text{H}_{10}})(P_{\text{HCl}})}{(P_{\text{C}_6\text{H}_{11}\text{Cl}})} = 17.4 \times \exp\left(\frac{-7991}{T}\right) \quad (4)$$

and cyclohexane:

$$K_{\text{C}_6\text{H}_{12}} = \frac{(P_{\text{C}_6\text{H}_{12}})(P_{\text{HCl}})}{(P_{\text{C}_6\text{H}_{11}\text{Cl}})(P_{\text{H}_2})} = 0.2 \times \exp\left(\frac{6366}{T}\right). \quad (5)$$

At 423 K, the equilibrium constant for the gas phase reaction of hydrogen and cyclohexyl chloride to yield cyclohexane ( $4.2 \times 10^6$ ) is greater by more than seven orders of magnitude than that calculated (0.23 atm) for the formation of cyclohexene. In gas phase homogeneous systems operating under equilibrium conditions, thermodynamics predict that cyclohexane is by far the preferred product. In complete contrast, Ni/SiO<sub>2</sub> exclusively promotes (where  $T \leq 473 \text{ K}$ ) dehydrochlorination to cyclohexene. Within the experimental and pressure regime used in this study, catalytic dehydrochlorination to cyclohexene only approaches equilibrium values

at the highest reaction temperatures that were studied and the various responses to alterations in reaction variables (where  $T \leq 473 \text{ K}$ ) can be positively attributed to surface reaction phenomena. While the Ni/SiO<sub>2</sub> catalyst promotes the hydrogen cleavage of chlorine from an aromatic host, the same system does not effectively promote hydrogenolytic cleavage from an aliphatic host but rather the internal elimination of HCl. The TOFs of cyclohexyl chloride and chlorobenzene are plotted as a function of reaction temperature in Fig. 8. It is immediately evident that supported nickel promotes the overall turnover of the halogenated alkane to a far greater extent than the aromatic reactant. From a consideration of the equilibrium constants calculated from literature values [33], the levels of chlorobenzene conversion reported here are far removed from thermodynamic limitations so the data presented are again due to catalytic action. There is some discordancy regarding the reported reactivity of the C–Cl bond where chlorine removal has been shown to be more [12,34,35] and less facile [36,37] from aromatic compared with aliphatic compounds. In this study, the rate of conversion of cyclohexyl chloride exceeds that of chlorobenzene by a factor of up to 18 while the reaction is initiated at temperatures ca. 50 K lower than that observed for the aromatic feed. Such differences in rate and temperature dependence will have a signifi-

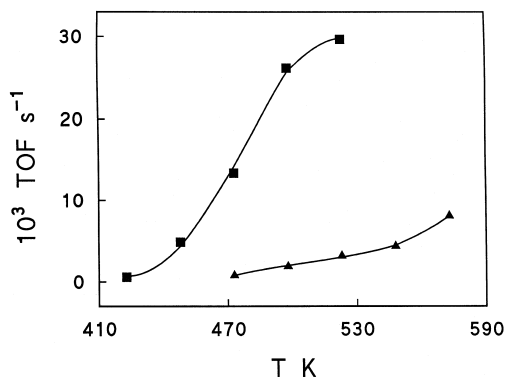


Fig. 8. Steady state TOF of chlorobenzene (▲) and initial TOF of cyclohexyl chloride (■) as a function of reaction temperature.



cant bearing on the design of reactors for hydrogen treatment of mixed chlorinated aliphatic/aromatic waste streams. Using the computed reaction orders (from the data presented in Figs. 5 and 6) the temperature dependence of the rate constants for the cyclohexyl chloride reaction yields an apparent activation energy (where  $448 \text{ K} \leq T \leq 473 \text{ K}$ ) equal to  $115 \text{ kJ mol}^{-1}$  which is considerably higher than the value of  $73 \text{ kJ mol}^{-1}$  (where  $473 \text{ K} \leq T \leq 573 \text{ K}$ ) measured for the hydrodechlorination of chlorobenzene over the same catalyst [28]. It should however be noted that the energetics for both catalytic reactions are still much lower than the 175–185  $\text{kJ mol}^{-1}$  range quoted for the pyrolysis of  $\text{CH}_3\text{Cl}$  and  $\text{C}_6\text{H}_5\text{Cl}$  [38]. The catalyst promoted removal of HCl from the chloroalkane occurs via a dehydrochlorination step and the rate shows a high temperature dependence. The removal of HCl from chlorobenzene occurs via a hydrodechlorination step which requires both an external source of hydrogen and higher reaction temperatures to initiate the process but once promoted the process exhibits a lower temperature dependence which translates into a net lower activation energy.

The conversion of an alkyl halide to an alkene is well established in organic chemistry where the reagent required for the elimination of a molecule of acid is a strong base. The function of the hydroxide ion, supplied by the base, is to pull a hydrogen away from the carbon which, with the separation of a halide ion, results in  $\text{C}=\text{C}$  bond formation. Conventional organic chemistry distinguishes between a bimolecular (E2) elimination involving a single step and a unimolecular (E1) elimination which involves

one molecule in the rate determining step. In the E2 mechanism the base pulls a hydrogen ion away from the carbon and simultaneously the halide separates. In the E1 mechanism the alkyl halide dissociates into halide and carbonium ions and the carbonium ion loses a hydrogen ion to the base in the second step. It is perhaps unfeasible to apply the principles of solution chemistry directly to gas phase heterogeneous catalysis where the reactant(s) interact with the catalyst surface to generate reactive species that are quite distinct from those involved in homogeneous reaction systems. Nevertheless, the catalytic reaction may be viewed in terms of an E1 elimination mechanism, as depicted in Fig. 9, where the chlorine component interacts with the catalyst with electron withdrawal, weakening the  $\text{C}-\text{Cl}$  bond and inducing intermediate carbocation formation. The adsorbed chlorine species may then serve as a base for the removal of the hydrogen atom in a fast step followed by  $\text{C}=\text{C}$  bond formation and desorption of cyclohexene from the catalyst surface.

The formation of cyclohexane from cyclohexyl chloride would certainly be viewed from an organic chemistry standpoint as a standard nucleophilic substitution reaction but hydrodechlorination appears to be the more likely route in this catalytic application. In fact, hydrogenolysis of methyl-substituted [21,22] and oxygenated [39] aromatics, again over the same catalyst, was only observed to an appreciable degree at temperatures in excess of 473 K. The isolation of cyclohexane in the cyclohexyl chloride product feed at  $T > 473 \text{ K}$  can then be ascribed to a commencement of hydrogenolysis. The possibility of a nickel promoted hydrogenation

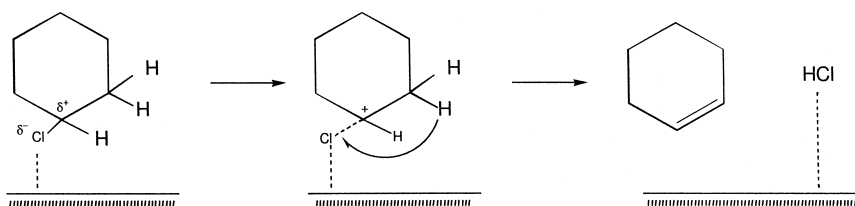


Fig. 9. Proposed reaction scheme for the surface catalyzed dehydrochlorination of cyclohexyl chloride.

tion of surface cyclohexene (prior to desorption) cannot however be ruled out. In an uncatalysed system, mixtures of cyclohexene and cyclohexane should result; the presence of Ni/SiO<sub>2</sub> elevates reaction rate and introduces a high degree of process selectivity. The data generated in this report support the contention that the C–Cl bond in the cyclohexane is less susceptible to hydrogen cleavage than the C–Cl linkage in an aromatic compound. The former reactant is however readily converted via internal HCl elimination by dehydrochlorination. The idea that the C–Cl bond is more or less reactive or that chlorine in an alkane, olefin or arene is more or less easily removed will depend on the nature of reaction (and the mechanism) involved.

### 3.4. Dechlorination vs. debromination

The effect of varying the nature of the halogen on catalytic dehalogenation activity was also considered taking cyclohexyl bromide as the second model aliphatic reactant. Representative time-on-stream profiles are presented in Fig. 10 and compared directly with the corresponding chloride system. Hydrogen treatment of cyclohexyl bromide was again 100% selective (at  $T \leq 473$  K) in generating cyclohexene via dehydrobromination. In terms of the carbon–halogen bond strength, bromo-compounds are expected to be more reactive than the chloro-counterparts [36]. The data plotted in Fig. 10 bears this out where the rate of dehydrobromination was consistently greater than the rate of dehydrochlorination. The TOF values were also observed to decline with reaction time where the relative loss of activity was again greater at the lower temperatures, i.e.,  $\alpha$  decreased from  $5 \times 10^{-5} \text{ s}^{-2}$  at 423 K to  $9 \times 10^{-6} \text{ s}^{-2}$  at 473 K. In complete contrast, the rate of bromine removal from the aromatic host was appreciably lower than that recorded for chlorine: initial dehydrohalogenation and steady state hydrodehalogenation specific activities are summarised in Table 1. It has been shown else-

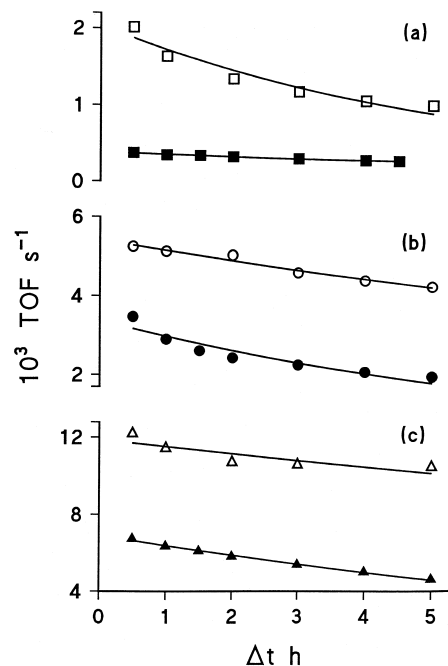


Fig. 10. TOF of cyclohexyl chloride (solid symbols) and cyclohexyl bromide (open symbols) as a function of reaction time at (a) 423 K, (b) 448 K and (c) 473 K.

where that catalytic hydrodechlorination in aromatic systems is an electrophilic reaction and is promoted by electron donating ring substituents [28,40]. The lower rate of hydrodebromination observed in this study is at odds with a greater conversion of bromobenzene reported for Pd/C [15] and sulphided Co–Mo/Al<sub>2</sub>O<sub>3</sub> and Ni–Mo/Al<sub>2</sub>O<sub>3</sub> [41]. Steady state hydrodebromination activity was nevertheless readily achieved and the aromatic ring again remained intact. It is reasonable to assume that the same active sites are responsible for promoting the hydrodehalogenation of both model compounds. As chlorine has a higher electron affinity (3.615 eV) than bromine (3.364 eV) [30] the chlorinated reactant can be considered to interact more strongly than the brominated reactant with the catalyst. The higher rates of hydrodechlorination can then be attributed to a greater activation of the Cl–C bond for attack by hydrogen. Implicit in the assumed mechanism, illustrated in Fig. 11 for the conversion of chlorobenzene,

Table 1

Variation with reaction temperature of the steady state hydrodehalogenation and initial dehydrohalogenation TOFs for model chlorinated and brominated aromatic and aliphatic systems

| T (K) | $10^3$ TOF $s^{-1}$ |                       |                    |                       |
|-------|---------------------|-----------------------|--------------------|-----------------------|
|       | $C_6H_5Cl$<br>feed  | $C_6H_{11}Cl$<br>feed | $C_6H_5Br$<br>feed | $C_6H_{11}Br$<br>feed |
| 423   | –                   | 0.4                   | –                  | 2.0                   |
| 448   | –                   | 3.4                   | –                  | 5.4                   |
| 473   | 0.8                 | 7.0                   | 0.3                | 11.9                  |
| 498   | 1.9                 | –                     | 0.4                | –                     |
| 523   | 3.2                 | –                     | 0.5                | –                     |
| 548   | 4.4                 | –                     | 1.4                | –                     |
| 573   | 8.1                 | –                     | 2.3                | –                     |

is the notion that the halogen atom carries a negative charge and an intermediate carbonium ion is formed via addition of surface dissociated hydrogen. The adsorbed phenyl carbonium ion intermediate undergoes additional hydrogen attack and benzene desorbs from the surface without any further reaction. In the case of dehydrohalogenation of the alkyl halide, the reactant molecules do not need to be activated for external hydrogen attack and the higher rate of HBr elimination is consistent with C–halogen bond strengths.

### 3.5. The nature of catalyst deactivation

The observed decrease in dehydrohalogenation rate can be ascribed to an occlusion of the active sites by either the hydrogen halide and/or the cyclohexene that is produced. The possible contribution of strong cyclohexene adsorption in determining the progress of the reaction was probed, in this study, by monitoring the conversion of cyclohexyl chloride in the presence and

Table 2

Initial TOFs of a range of cyclohexyl chloride/cyclohexene ( $8.2 \times 10^{-3}$  mol  $h^{-1}$  at 448 K) feedstock combinations involving hydrogenation and dehydrochlorination steps

| Feedstock                 | $10^3$ TOF <sub>initial</sub> $s^{-1}$ |
|---------------------------|--|
| $C_6H_{10} + CH_3OH$      | 7.7 <sup>a</sup>                       |
| $C_6H_{11}Cl$ undiluted   | 3.8 <sup>b</sup>                       |
| $C_6H_{11}Cl + C_6H_{10}$ | 4.1 <sup>b</sup>                       |
| $C_6H_{11}Cl + CH_3OH$    | 2.8 <sup>b</sup>                       |

<sup>a</sup>Hydrogenation to cyclohexane with trace amounts (< 1 mol%) of benzene formed (by dehydrogenation).

<sup>b</sup>Dehydrochlorination to cyclohexene.

absence of cyclohexene in the feed stream, using methanol as a diluent which does not undergo a hydrogenation step. The results of these tests are given in Table 2. It is immediately evident that the overall TOF of cyclohexene (predominantly to cyclohexane) far exceeds that of cyclohexyl chloride. In addition, the TOF of undiluted cyclohexyl chloride was significantly higher compared with the methanolic feedstock. This effect may be rationalised in terms of the E1 type mechanism that has been tentatively proposed for this catalyst system where the polar methanol molecules inhibit the dissociation of the alkyl halide and consequently lowers the overall dehydrochlorination rate. The observed TOF<sub>initial</sub> of cyclohexyl chloride was roughly the same in the presence or absence of cyclohexene in the reaction mixture. Given the appreciably higher TOF of cyclohexene (in methanol), this finding is in keeping with a very limited direct interaction of cyclohexene with the active surface when in the presence of cyclohexyl chloride. In addition, passage of cyclohexene in hydrogen over a chlorinated (after prolonged catalytic dechlorination) surface did

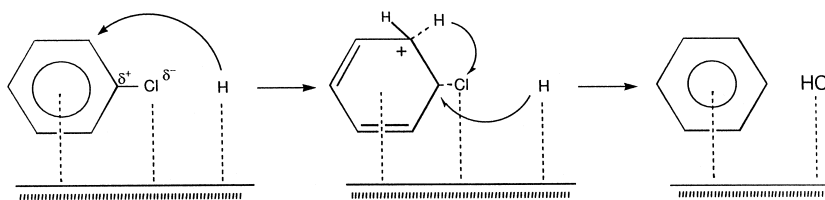


Fig. 11. Proposed reaction scheme for the surface catalysed hydrodechlorination of chlorobenzene.

not result in the generation of cyclohexyl chloride. Cyclohexene clearly does not then serve as a reactive intermediate while a surface site occlusion by cyclohexene is not the source of the observed (see Figs. 1, 4, 6 and 10) drop in dehydrochlorination activity. Catalyst poisoning by HCl is then the obvious cause of decreasing TOF and given the appreciably higher IP (12.74 eV), HCl must interact strongly with the active site(s) and is not fully displaced by in-coming cyclohexyl chloride reactant. The effect of HCl poisoning is more pronounced at lower temperatures, as shown in Fig. 3, which is indicative of a higher relative occupancy of the active sites, in other words a greater degree of competition with the chlorinated reactant. The suppression of catalyst deactivation due to the presence of hydrogen as opposed to helium (see Fig. 7) must be due to a displacement of the hydrogen halide by dissociated hydrogen which acts to 'clean' the surface. It is known that chlorine containing poisons readily desorb from a nickel surface in the presence of hydrogen at temperatures in the range 400–800 K [42]. In the hydroprocessing of the chloroalkane over Ni/SiO<sub>2</sub>, hydrogen treatment at 673 K is required for effective catalyst regeneration.

The absence of any short term deactivation in the hydroprocessing of the haloarene can be attributed to a negligible competition with the hydrogen halide product for adsorption sites. The stronger, two-point interaction of the aromatic with the surface more effectively displaces any adsorbed halogenated product than is the case with the aliphatic feed. It is interesting to note that while the fresh catalyst generated high and stable benzene hydrogenation rates to cyclohexane [21,22], once the catalyst was contacted with chlorinated reactant it exhibited no benzene hydrogenation activity while the rates of the far more facile cyclohexene hydrogenation [43] were considerably lower. Such an effect suggests quite different surface requirements for the promotion of aromatic reduction as opposed to aromatic hydrodechlorination. Exposure to the chlorinated reactant may alter

the nature of the aromatic and/or hydrogen activation step presumably by altering the electronic structure of the adsorption site(s). It is known that chlorine interaction with transition metals alters the dissociation energetics for adsorbed gases [29] and such an effect may disrupt the supply of the active hydrogen consumed in aromatic hydrogenation. Implicit in this argument is the fact that active hydrogen used in addition reactions is different to that used in bond cleavage reactions. Work is now underway to probe the freshly activated and used catalyst surface, employing H<sub>2</sub> TPD and XPS in the first instance, in order to gain some insight into the factors that govern catalytic hydrogen addition as opposed to hydrogen cleavage.

#### 4. Conclusions

In the gas phase catalytic hydrogen treatment of halogenated aromatic and aliphatic reactants, the data presented in this paper support the following conclusions.

(i) Halogen removal from an aliphatic and an aromatic host occurs predominantly via (E1 elimination) dehydrohalogenation and (electrophilic) hydrodehalogenation routes, respectively.

(ii) Dehydrochlorination (and dehydrobromination) is (are) subject to a short term loss of catalytic activity due to a surface poisoning by the hydrogen halide product while a steady state hydrodehalogenation of the aromatic feed is readily achieved as a result of stronger interaction(s) with the catalyst.

(iii) In the absence of thermodynamic limitations, chlorine removal from cyclohexyl chloride is characterized by a temperature dependent reaction order with respect to the chloroalkane and a zero order dependence on hydrogen partial pressure. The activation energy for the dechlorination of cyclohexyl chloride is far higher than that recorded for the dechlorination of chlorobenzene but chlorine removal from the aliphatic host occurs at an appreciably greater

rate and is initiated at temperatures at least 50 K lower.

(iv) The rate of dehydrobromination exceeds that of dehydrochlorination due to the lower C–Br bond strength but the rate of hydrode-bromination is less than that of hydrodechlorination as a result of the greater activation of the C–Cl bond for hydrogen attack via interaction with the catalyst.

(v) The interaction of chlorine with the catalyst has a severely detrimental effect on catalytic hydrogenation where only very facile (such as cyclohexene to cyclohexane) hydrogenation steps can be promoted to any extent.

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