

Effect of hydrogen pressure on detoxification of 1,2,3-trichlorobenzene by catalytic hydrodechlorination with both unsulphided and sulphided Ni–Mo/ γ -Al₂O₃ catalyst

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Abstract

A process which has large potential as a disposal method of organic toxic wastes is hydrotreating. The present work has investigated the effects of hydrogen pressure on the catalytic hydrodechlorination of 1,2,3-trichlorobenzene using the unsulphided and sulphided forms of Ni–Mo/ γ -Al₂O₃ catalyst.

All the experiments were carried out in a stirred autoclave at a constant temperature of 330 °C and at the hydrogen pressures (kept constant during each experiment) in the range $35 \leq p_{\text{H}_2} \leq 100$ bar. Hexadecane was used as reaction medium.

The experimental results allowed us to identify the reaction networks: (i) for the unsulphided form of the catalyst, there were parallel reactions to 1,2 and 1,3 dichlorobenzene. Both these species then reacting with hydrogen to form chlorobenzene, which in turn formed benzene; (ii) the sulphided form of the catalyst holds the same network but with one extra reaction from benzene to hydrocracking products.

With the help of the Langmuir–Hinshelwood theory it was possible to gain an insight into the mechanism of the single reactions which form the networks: hydrogen is adsorbed according to a Langmuir-type dissociative adsorption and the rate determining step is the surface reaction.

Finally it was demonstrated that the major dechlorination path of the reaction network is pressure independent with sulphided catalyst.

1. Introduction

It has been discussed by Gioia [1] that catalytic hydrogenation is a valid alternative for the disposal of hazardous organic waste liquids. The validity of the method

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depends on the fact that the toxicity of organic liquid wastes is caused mainly by compounds containing heteroatoms in their chemical structure. Hydroprocessing, while converting these heteroatoms into easily removable inorganics, may leave the host compound in a nontoxic recyclable form.

Hydroprocessing is a well known process largely adopted in industry for hydrotreating petroleum and has reached a stage of great reliability as far as elimination of nitrogen and sulfur from feedstock is concerned. In fact, there are plenty of research works and kinetic data concerning catalytic hydrodenitrogenation (HDN), hydrodesulfurization (HDS) and hydrodeoxygenation (HDO) processes. However, due to the fact that halogenated compounds are not contained in petroleum, little research work has been done on catalytic hydrodehalogenation (HDH); these compounds are, however, predominant in hazardous organic waste liquids.

The problem of hydrodehalogenation, even though to a limited extent, has been dealt with in the literature with reference to both thermal and catalytic processes. Indications on a few research works on the subject are reported by Gioia [1]. Many of these investigations on HDH, however, do not provide a picture of catalytic HDH as complete as that available for HDN or HDS.

Only recently the catalytic hydroprocessing of chlorobenzenes has been investigated in detail using a commercial hydrogenation catalyst. Moreau et al. [2] report on the catalytic hydrodechlorination (HDC) of chlorobenzene, with sulphided Ni–Mo/ γ -Al₂O₃ and Co–Mo/ γ -Al₂O₃ catalysts, at $T = 340^\circ\text{C}$ and $p_{\text{H}_2} = 70$ bar. Hagh and Allen [3] have studied the hydroprocessing of chlorobenzene and 1,2-dichlorobenzene in a microflow reactor in the range of temperatures from 275 to 375 °C with a sulphided Ni–Mo/ γ -Al₂O₃ catalyst. The same authors [4] have investigated, using the same type of reactor and the same catalyst, the HDC of hexachlorobenzene and all of its dechlorinated intermediates but only at one temperature of 325 °C. Gioia et al. [5] have studied the HDC of 1,2,3-trichlorobenzene on Ni–Mo/ γ -Al₂O₃ in its unsulphided form, in a stirred batch reactor, at constant hydrogen pressure (100 bar) and in the range of temperatures from 200 to 350 °C. Murena et al. [6] have extended the investigation to the sulphided form of the same catalyst, which proves much more active towards the HDC reactions.

In the present work the effect of hydrogen pressure on the kinetics of catalytic HDC of 1,2,3-trichlorobenzene, with Ni–Mo/ γ -Al₂O₃ catalyst, is investigated. The results, as far as the HDC of trichlorobenzene is concerned, provide an advancement over those of previous investigations. In fact, the kinetic behaviour of both the sulphided and unsulphided forms of the catalyst is explored, and the influence of the hydrogen pressure on the kinetic constants of the single reactions is investigated in detail, in the range 35–100 bar which is of industrial interest. Furthermore, the experimental set up has produced numerous and well resolved concentration vs. reaction time data for all identified reaction products and intermediates. These detailed concentration vs. time data have been analysed globally allowing us to identify the reaction network, and to evaluate the whole set of kinetic constants of the reactions altogether. Then the computer-simulated concentration vs. time curves, based on the kinetic model, were satisfactorily fitted to the experimental data.

The effect of the hydrogen pressure on the reactions has been interpreted on the basis of the Langmuir–Hinshelwood rate theory.

Finally the degree of detoxification has been obtained as function of the reaction time.

2. Experimental procedure

A full description of both the apparatus and the procedure is reported by Gallagher [7]. A synthetic description is as follows. The HDC runs have been carried out in a 300 ml autoclave (Autoclave Engineers) with magnetic stirrer at 1200 rpm. Pure hexadecane has been adopted as the reacting medium. It was loaded in the reactor and heated at reaction temperature. When this temperature was reached, the reactants and the catalyst in admixture with additional hexadecane were loaded in the reactor. The feeding of the catalyst slurry was carried out instantaneously by a pressurized loader connected to the reactor head. In this way the reaction takes place at a constant temperature from $t = 0$ reducing the thermal transients. During the run the hydrogen pressure was adjusted to the set value when necessary keeping the liquid solution saturated with hydrogen. Two sets of reaction runs were carried out. The first with unsulphided catalyst, the second with the catalyst in sulphided form. The materials and the range of operating variables are summarized in Table 1.

All runs were conducted at the same constant temperature. Due to the fact that the two sets of runs are for two forms of the catalyst which show quite different activities, a temperature of 330 °C was chosen which allowed us to follow equally well the kinetics of both sets of runs. The hydrogen pressure, kept constant during a run, was different for each run of the set. The pressures investigated in this work are in the range $35 \leq p_{\text{H}_2} \leq 90$ bar. The precise set of values together with the other operating conditions are indicated in Table 2.

For the second set of runs the catalyst, identical to that used in the first set was sulphided before being used in the autoclave. The sulphiding procedure was carried out in an oven at 400 °C. The catalyst was put into the oven in a gas tight vessel, with

Table 1
Materials

Reaction medium	Hexadecane, Aldrich Co.; vapor pressure at 330 °C \approx 2.30 bar
Reactants	1,2,3-trichlorobenzene, 98%, Aldrich Co.; the initial concn. in hexadecane ranged between 3.03 and 3.48 wt%; Hydrogen GC grade (99.999%), from SIO ALPHAGAZ; the total pressure ranged between 35 and 90 bar
Catalyst	HDS-9A, American Cyanamid; NiO = 3.1%, MoO ₃ = 18.3%, WO ₃ = 0.04% and Na ₂ O = 0.05% (weight percent) supported on alumina. Specific surface 149 m ² /g; porosity = 0.51 cm ³ /g. Ground and sieved 150–200 mesh. The slurry concentration ranged between 0.5 and 0.69 wt%
CS ₂	For sulphided catalyst only; 13 ml of a 4 wt% solution in hexadecane

Table 2
Experimental conditions for the runs ($T = 330^\circ\text{C}$)

Run no.	p (bar)	W_R (g)	W_C (g)	W_L (g)	W_S (g)	Run time (min)
1	35	5.01	0.822	165.2	—	600
2	50	5.04	1.121	161.8	—	450
3	70	5.01	0.889	153.8	—	450
4	90	5.06	1.056	154.2	—	450
5	100	5.00	0.937	154.6	—	450
6	35	5.07	0.910	147.3	0.42	270
7	50	4.97	0.827	145.8	0.44	270
8	70	5.13	0.912	147.6	0.42	270
9	100	5.03	0.900	163.6	0.42	100

a mixture of $\text{H}_2\text{S}/\text{H}_2$ (90% H_2S , 10% H_2) gas being passed over it, the flow rate of the gas being approximately 100 ml/min. The sulphidation lasted five hours: one hour to heat the oven up to the required temperature of 400°C and four hours at this temperature. After these five hours the oven was turned off and the catalyst allowed to cool, still in the $\text{H}_2\text{S}/\text{H}_2$ environment. The flow of the gas was kept on until the temperature of the catalyst was close to the room temperature. To protect the sulphidation of the catalyst during the reaction runs, a quantity (see Table 2) of CS_2 was loaded in the autoclave together with the reactant and the catalyst. The CS_2 acts as an H_2S precursor [8]. Thus maintaining the catalyst in the sulphided form.

The modification induced on the surface of the catalyst by sulphidation are thoroughly discussed by Massoth [9] and Topsøe and Clausen [10].

2.1. Chemical analysis of samples

The analysis of the reaction samples taken during the course of the reaction was done by gas chromatography: GC-FID equipped with a capillary column (crosslinked methyl silicone; 50 m long). The species identified in the samples, listed in order of increasing elution time are: benzene (b), chlorobenzene (cb), 1,3-dichlorobenzene (1,3-dcb), 1,2-dichlorobenzene (1,2-dcb), 1,2,3-trichlorobenzene (tcb). In the rest of the paper the names in brackets will be used. The quantitative analysis of samples was done by the method of the internal standard using propylbenzene as the standard.

For convenience, the concentrations c_i are expressed in units of mol per g of reacting mixture at room temperature and 1 bar as directly obtained by the analytical procedure. Concentrations in units of mol per unit volume of the mixture at the temperature and pressures of the reactor (to be used in rate equations) are related to c_i (mol/g) by a constant factor. In fact, as shown below (Eq. (5)) the density of the reacting mixture is practically constant in the range of pressures adopted in the experiments.

3. Results and discussion

Fig. 1 reports as an example the concentration of all identified species vs. time for the run on unsulphided catalyst at the intermediate pressure of 50 bar. Similarly, Fig. 2 refers to the sulphided catalyst. All other results at the other pressures investigated are given in detail in a thesis [7]. The curves in Figs. 1–2 are model predictions to be discussed below.

3.1. Reaction mechanism and network identification

The quantity $\sum c_i$ reported in Figs. 1–2 is the concentration of the benzene ring at any time during the reaction. Inspection of Fig. 1 shows that on unsulphided catalyst $\sum c_i$ does not change during the course of the reaction. Thus indicating that the organic compounds identified are the only ones produced by the reaction and that the final result of the HDC process is the formation of benzene (ring preservation).

With the sulphided catalyst (Fig. 2) there is a significant decrease of $\sum c_i$. This is an indication that other compounds besides those identified may be produced. The

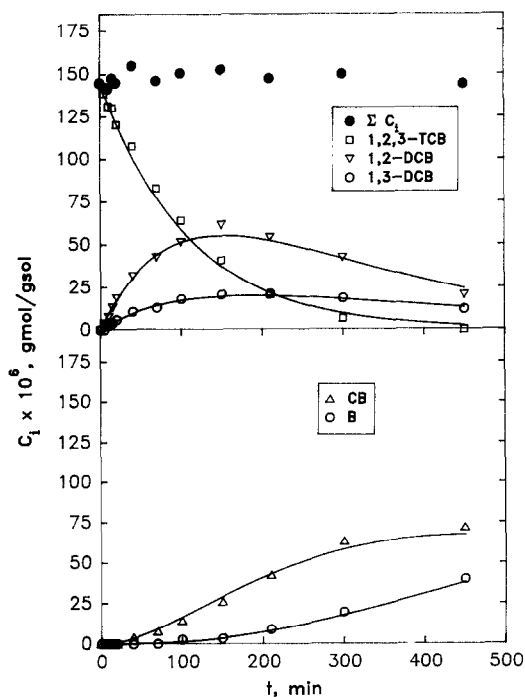


Fig. 1. Concentration of reactant, intermediates and product vs. time for unsulphided catalyst. Operating conditions: $p_{H_2} = 50$ bar; $T = 330^\circ\text{C}$. Filled symbols for checking material balance, they represent $\sum c_i$ ($i = 1, 2, \dots, 5$) vs. time.

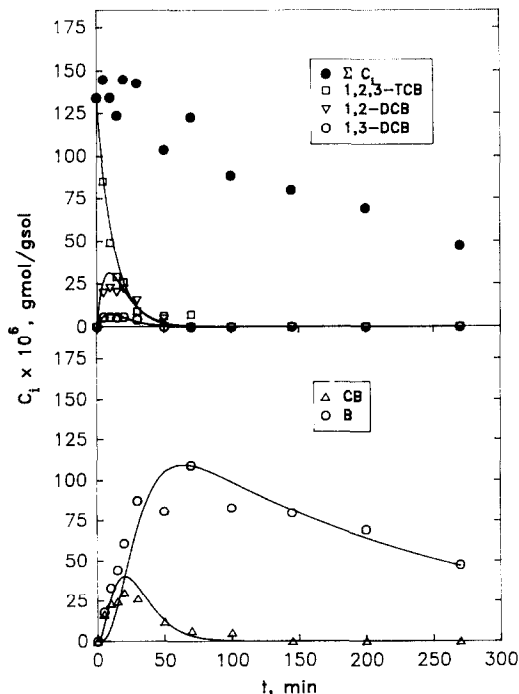


Fig. 2. Concentration of reactant, intermediates and product vs. time for sulphided catalyst. Operating conditions: $p_{H_2} = 50$ bar; $T = 330^\circ\text{C}$. Filled symbols for checking material balance, they represent $\sum c_i$ ($i = 1, 2, \dots, 5$) vs. time.

chromatographic analysis led us to exclude the presence of significant amounts of benzene hydrogenation products: i.e., cyclohexane, cyclohexene, cyclohexadiene.

The chromatograms of samples at large reaction times showed the presence of a number of very small peaks around that of benzene, and they were assumed to be hydrocracking reaction products of benzene. The fact that benzene hydrogenation products were not detected may be explained considering that they crack more rapidly than they are formed. This assumption is also supported by the statistical analysis of data (to be discussed below) which indicates the decomposition of benzene towards light hydrocarbons as the most probable. We have neither identified nor analyzed quantitatively these light hydrocarbons. It is not of interest to identify all these compounds and follow their evolution with time.

Since we are dealing with heterogeneous catalytic reactions, it is natural to assume that the reactions which form the network have a Langmuir–Hinshelwood (LH)-type kinetic equations. Furthermore, it has been shown [11, 12] that hydrogenation reactions follow LH theory with the surface reactions as the rate limiting step and that two different active sites exist on the catalyst. Namely the reaction takes place between an adsorbed molecule of compound i on one type of active site and adsorbed hydrogen molecules on another type of site. There is no competition for adsorption sites between hydrogen and all other compounds.

With these assumptions we may write (at constant hydrogen pressure) Eq. 1 where r_{ij} and k_{ij} refer to any reaction $i \rightarrow j$ of the network and K_i 's are adsorption equilibrium constants.

$$r_{ij} = \frac{k_{ij}c_i}{1 + \sum K_i c_i} \quad (1)$$

The correlative features of the c_i vs. t data (at each H_2 pressure) and a preliminary application of the regression technique proposed by Himmelblau et al. [13] (HJB) made apparent after a few attempts that the adsorption of organic compounds was not relevant for both unsulphided and sulphided catalyst. Thus Eq. (2) reduces to

$$r_{ij} = k_{ij}c_i \quad (2)$$

A first order dependence on c_i is confirmed by other authors [4] when low concentrations of reactants are used as in this case ($c_i < 0.1$ M for tcb and $c_i \ll 0.1$ M for all the other compounds).

The identification of a reaction network is necessarily a trial and error procedure. Although considerations on the chemistry of the compounds involved excluded some possibilities, several alternatives remained possible. Each alternative was compared with the data by using the regression technique (HJB) which applies to first order reactions. For each attempted network, the regression technique gives the best value of the reaction constants. Some of the networks could be readily excluded as they gave rise to a negative value of one or more of these constants. The identified network is reported in Fig. 3.

For both unsulphided and sulphided catalyst the analysis allowed us to exclude multiple dechlorination pathways (see also [6]).

In conclusion the calculation procedure for the k_{ij} is as follows: the HJB method was applied to each set of c_i vs. t data with the network of Fig. 3 allowing us to evaluate the set of pseudo-first-order kinetic constants k_{ij}'' [min^{-1}] for each run. Back integrating the set of differential equations which describes the network, the

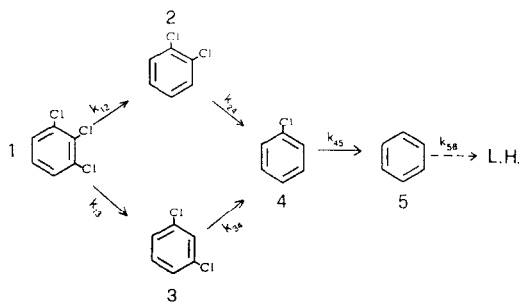


Fig. 3. Reaction network for 1,2,3-trichlorobenzene. L.H. stands for "lighter hydrocarbons". Arrows line type: solid = for both sulphided and unsulphided catalyst; dashed = for sulphided catalyst.

continuous curves of Figs. 1–2 were obtained. Inspection of these figures shows the good agreement between the data and the model predictions.

The k_{ij}'' were then reduced to the weight of catalyst by the relationship:

$$k_{ij} = (W_L/W_C)k_{ij}'' \quad (3)$$

The resulting values of the pseudo rate constants k_{ij} are reported vs. p_{H_2} in Figs. 4 and 5 for un sulphided and sulphided catalyst respectively. The continuous curves are based on Eq. 7.

The activation energies of the $i \rightarrow j$ reactions (at $p_{H_2} = 100$ bar) are reported by Gioia et al. [5] for un sulphided catalyst and by Murena et al. [6] for the catalyst in sulphided form.

3.2. Hydrogen pressure dependence of k_{ij}

Eq. (2), though adequate for describing the kinetics at constant hydrogen pressure, does not represent the complete rate equation insofar as k_{ij} might depend on p_{H_2} (see Figs. 4–5). Therefore we must further develop the description of the kinetics by

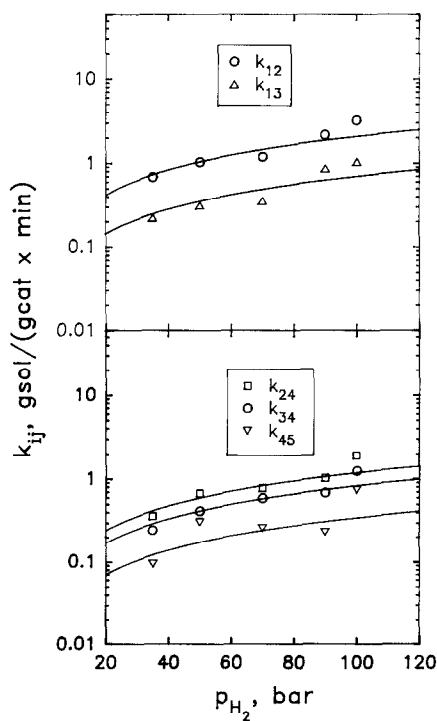


Fig. 4. Pseudo kinetic constants k_{ij} vs. hydrogen partial pressure for the un sulphided catalyst. Curves from Eq. (7) with parameters as reported in Table 3.

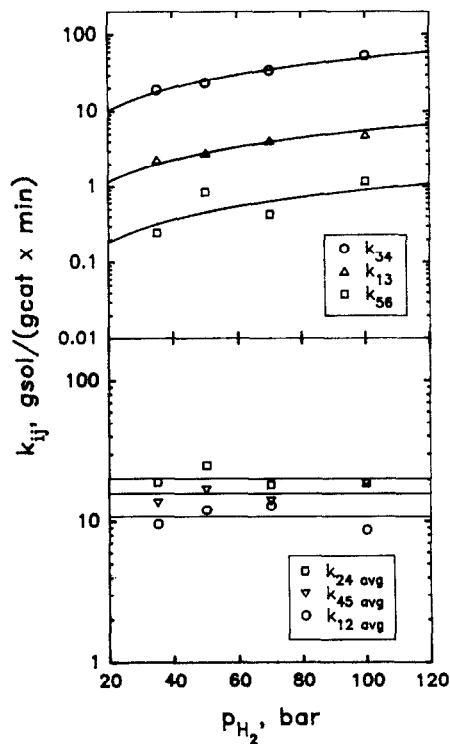


Fig. 5. Pseudo kinetic constants k_{ij} vs. hydrogen partial pressure for sulphided catalyst. Curves from Eq. (7) with parameters as reported in Table 3. Horizontal line through the data give $k_{ij(\text{avg})}$.

interpreting the role played by p_{H_2} on the various k_{ij} . Before progressing any further into the discussion, we must consider that it is the hydrogen concentration c_{H_2} (mol/ml), rather than the gas phase hydrogen pressure p_{H_2} , that influences reaction rates since the reactions are mainly taking place in the liquid phase.

The experiments were performed in such a way as to ensure that the hydrogen liquid phase concentration is in equilibrium with the hydrogen in the gas phase during the run. The relationship between hydrogen partial pressure and hydrogen solubility c_{H_2} in hexadecane was calculated, at the operating temperature (330 °C) and in the range of hydrogen pressure from 0 to 120 bar. The main steps of the calculating procedure are as follows: The Henry's constant at low pressure for H_2 in hexadecane is reported by Cukor and Prausnitz [14] up to 202 °C. The constant was extrapolated to 330 °C by using the method suggested by King et al. [15] with the Lee–Kesler equation for estimating the solvent molar volume [16, pp. 51, 64]. Extrapolation to higher pressures was made using the Krichevsky–Kasarnovsky equation [16, p. 335; 17]. Thus x_{H_2} vs. p_{H_2} was obtained. Then the molar volume of the liquid mixture at 330 °C vs. p_{H_2} was calculated using again the Lee–Kesler equation with appropriate mixing rules [16, p. 82]. Finally the molar fraction x_{H_2} was converted

to c_{H_2} (mol/ml). The following relationships were obtained at $T = 330^\circ\text{C}$ and $0 < p_{\text{H}_2} < 120$ bar:

$$c_{\text{H}_2} = 5.87 \times 10^{-6} p_{\text{H}_2}, \quad (4)$$

correspondingly, for the reaction mixture density we obtained:

$$\rho_m = 0.587 - 4.91 \times 10^{-4} p_{\text{H}_2} + 2.28 \times 10^{-6} p_{\text{H}_2}^2. \quad (5)$$

Eq. (4) shows that at the operating conditions adopted, c_{H_2} is proportional to p_{H_2} . Therefore, we are allowed to base the kinetic equations on p_{H_2} rather than on c_{H_2} ; the proportionality constant of Eq. (4) will be included in the kinetic constants and in the adsorption constant. The advantage in expressing rate equations in terms of p_{H_2} is that this variable is directly measured. c_{H_2} , on the contrary, must be predicted at conditions of pressures and temperatures where experimental data are not available. Thermodynamic equations are, therefore extrapolated leading to uncertainty in results. To predict linearity between p_{H_2} and c_{H_2} is far more reliable than to establish an accurate value of the proportionality constant.

Unsulphided catalyst: Inspection of Fig. 4 shows that all k_{ij} depend on hydrogen pressure. Many reaction mechanisms, all based on the LH rate theory, were attempted in order to regress the k_{ij} vs. p_{H_2} . Many of them led to physically inconsistent parameters. After many attempts the only two mechanisms which gave physically sound and statistically significant results are those described below under headings (i) and (ii). Both mechanisms are based on the assumptions that the organic compounds and hydrogen are adsorbed on different sites, and that the surface reaction is the limiting step; adsorption being at equilibrium.

(i) hydrogen adsorbs and dissociates. Adsorbed compound i reacts sequentially with one adsorbed hydrogen atom at time, passing through intermediates which, of course, are not detected in the reacting mixture. In this hypothesis the dependence of k_{ij} on p_{H_2} is:

$$k_{ij} = \frac{k'_{ij} \sqrt{p_{\text{H}_2}}}{1 + \sqrt{K_{\text{H}} p_{\text{H}_2}}}. \quad (6)$$

(ii) hydrogen adsorbs and dissociates. Adsorbed compound i reacts simultaneously with two adjacent adsorbed hydrogen atoms. In this case it is:

$$k_{ij} = \frac{k'_{ij} p_{\text{H}_2}}{(1 + \sqrt{K_{\text{H}} p_{\text{H}_2}})^2}. \quad (7)$$

The finding that hydrogen is adsorbed according to a Langmuir-type of dissociative adsorption and that the rate determining step is the surface reaction is in agreement with the results of Coq et al. [18] who studied the gas phase hydrogenation of chlorobenzene over a Pd–Rh catalyst.

In Eqs. (6) and (7) k'_{ij} is a “true” kinetic constant (independent of pressure) and K_{H} is the hydrogen adsorption constant. Therefore, regressing (vs. p_{H_2}) each set of the k_{ij} (a set contains a specific k_{ij} at the various H_2 pressures) pertaining to the runs with

unsulphided catalyst, would produce the k'_{ij} 's and K_H . The latter must be the same for the whole set of these constants.

The individual regression of each set of k_{ij} data using either Eq. (6) or Eq. (7), gave in both cases a reasonable fitting of data with K_H having similar values for all constants k_{ij} . However, a closer analysis of the correlation parameters suggests that the reaction mechanism represented by Eq. (7) is statistically more significant. On this assumption, the regression of k_{ij} was somewhat refined as follows.

Eq. (7) was rewritten as

$$\left(\frac{p_{H_2}}{k_{ij}}\right)^{1/2} = \frac{1 + K_H^{1/2} p_{H_2}^{1/2}}{k'_{ij}{}^{1/2}}. \quad (8)$$

Then the least-square method was applied to the whole set of these equations (using as dependent variable $Y = (p_{H_2}/k_{ij})^{1/2}$ while the independent variable is $X = p_{H_2}^{1/2}$ to determine the set of k'_{ij} as well as the single value of K_H . The results are reported in Table 3.

The fitting curves of the k_{ij} 's (see Fig. 4) are based on Eq. (7) with the results of Table 3.

Sulphided catalyst: Comparison of Figs. 4 and 5 highlights the following two features of hydrotreating of 1,2,3-trichlorobenzene on sulphided catalyst: (i) all the hydrodechlorination reactions are characterized by k_{ij} 's much larger than those on unsulphided catalyst. (ii) For a few k_{ij} 's the dependence on H_2 pressure is slighter on sulphided catalyst.

In order to analyze the effect of hydrogen pressure on k_{ij} 's in the light of LH rate theory, it is convenient to divide the reactions into two groups: (i) reactions having k_{ij} 's which are approximately constant with p_{H_2} (this is the case for reactions $1 \rightarrow 2$, $2 \rightarrow 4$, $4 \rightarrow 5$ (see Fig. 5) which are among those having the largest rate constants); (ii) reactions which show a pressure dependence in the range of p_{H_2} explored (reactions $1 \rightarrow 3$, $3 \rightarrow 4$, $5 \rightarrow 6$; see Fig. 5).

For the reactions belonging to heading (i) the k_{ij} 's are simply averaged. Results in Table 3. In the light of Langmuir–Hinshelwood theory, the constancy of these k_{ij} 's

Table 3
Results of the least square fitting procedure (units in nomenclature)

	Unsulphided catalyst	Sulphided catalyst	
	$K_H = 2.4 \times 10^{-7}$	$K_H = 7.3 \times 10^{-8}$	
	k'_{ij}	k'_{ij}	$k_{ij(av)}$
k_{12}	2.1×10^{-2}	—	10.79
k_{13}	7.1×10^{-3}	5.7×10^{-2}	—
k_{24}	1.2×10^{-2}	—	20.29
k_{34}	8.4×10^{-3}	5.1×10^{-1}	—
k_{45}	3.5×10^{-3}	—	15.85
k_{56}	—	9.1×10^{-3}	—

with p_{H_2} might indicate that the limiting step of reaction on the surface is either bond rupture or rearrangement of the structure of compound i , rather than hydrogenation. This would explain why the rate does not *increase* with increasing p_{H_2} . On the other hand, the rate does not *decrease* either, thus proving the assumption made before that there is no competition for adsorption sites between hydrogen and compound i .

For reactions of heading (ii) the k_{ij} 's have been regressed according to Eq. 7 adopting the same procedure as for the case of unsulphided catalyst. The results of the regression are reported in Table 3.

According to the LH rate theory [19], the constant K_{H} , which represents the overall equilibrium constant of adsorption and dissociation of H_2 on active sites l is related to K_{H_2} and K_{d} by the relationship

$$K_{\text{H}} = K_{\text{H}_2} K_{\text{d}} \quad (9)$$

where K_{H_2} is the equilibrium constant of the adsorption of molecular hydrogen on active sites l_2 , Eq. (10)



and K_{d} is the equilibrium constant of the dissociation step Eq. (11)



In a previous work [11] it was evaluated on the same catalyst in sulphided form $K_{\text{H}_2} = 1.9 \times 10^{-2} \text{ bar}^{-1}$. Therefore it may be estimated from Eq. (9) (on the sulphided form of our Ni–Mo/ γ - Al_2O_3 catalyst) $K_{\text{d}} = 7.3 \times 10^{-8} / 1.9 \times 10^{-2} = 3.8 \times 10^{-6}$.

It is useful to inspect how the detoxification proceeds with the hydrogenation of the reaction mixture. If we assume that the major source of toxicity of 1,2,3-tcb is the presence of chlorine atoms bonded to the benzene ring, then the degree of detoxification can be defined as:

$$\varphi = 1 - (c_{\text{tcb}} + c_{12\text{dcb}} + c_{13\text{dcb}} + c_{\text{cb}}) / c_{\text{tcb}}^0. \quad (12)$$

By computer-simulating the network of Fig. 3 with the kinetic parameters of Table 3, φ has been calculated vs. $(W_{\text{C}}/W_{\text{L}})t$, at the two pressures of 35 and 90 bar, for both unsulphided and sulphided catalyst. The results are reported in Fig. 6 which highlights clearly the following two features: (i) the sulphided catalyst is extremely more effective for detoxifying the 1,2,3-trichlorobenzene; (ii) the H_2 pressure plays a minor role on the detoxifying process when the sulphided catalyst is used. It must be pointed out that not all reactions of the network are equally enhanced by the sulphiding of the catalyst. In fact, inspection of Figs. 4 and 5 shows that the rates of the reactions $2 \rightarrow 4$, $3 \rightarrow 4$ and $4 \rightarrow 5$ are enhanced much more than those of reactions $1 \rightarrow 3$ and $1 \rightarrow 2$. In particular reaction $4 \rightarrow 5$, which is the slow step with unsulphided catalyst, does no longer play this role with the sulphided catalyst. Consequently the overall detoxifying process becomes very quick.

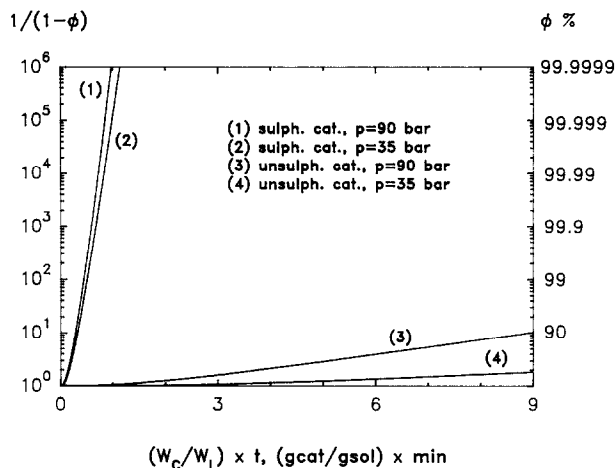


Fig. 6. Degree of detoxification vs. $(W_c/W_L)t$, for both unsulphided and sulphided catalyst, at the two hydrogen pressures of 35 and 90 bar; $T = 330^\circ\text{C}$.

4. Conclusions

The catalytic hydrodechlorination of 1,2,3-trichlorobenzene takes place through a reaction network where the benzene ring loses one Cl atom at a time. The reactions forming the network follow the Langmuir–Hinshelwood rate theory with hydrogen adsorbing and dissociating on sites which seem to be different from those for organic compounds. Furthermore, the adsorption of the organic compounds is in the linear part of the Langmuir isotherm so that the hydrogen equilibrium adsorption coefficient is the major term causing nonlinearity in the kinetic equation.

We have shown that effective dechlorination of the benzene ring can occur with an unsulphided form of Ni–Mo/ γ - Al_2O_3 catalyst and extreme dechlorination, with fracturing of the benzene ring, with a sulphided form of the same catalyst under the same conditions. But more importantly, from an engineering point of view, the major dechlorination path of the reaction network is pressure independent with sulphided catalyst. Therefore, to achieve a reasonable rate of reaction with sulphided catalyst it is not needed to work at high hydrogen pressures.

The choice of trichlorobenzene as model compound is based on the consideration that the C–Cl bond, where the carbon atom belongs to a benzene ring, is more stable than any other C–Cl bond. Hence the design of a reactor for HDC based on our results is in the upper bound of difficulty and can be regarded as quite conservative.

There are organic chlorinated compounds which are so toxic (e.g. polychlorinated dibenzodioxins), that trying to determine how to detoxify them, is itself hazardous. The results of the present work show potential of detoxifying quite safely these extremely dangerous chemicals.

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Nomenclature

c_i	molar concentration of compound i in liquid solution (key as in Fig. 3); mol/g of solution.
c^0	initial concentration; mol/g of solution
K_d	equilibrium constant of reaction 11.
K_H	equilibrium constant of adsorption and dissociation of H_2 ; bar^{-1}
K_{H_2}	adsorption constant of molecular hydrogen; bar^{-1}
k''_{ij}	pseudofirst order kinetic constant of the reaction leading from organic compound i to product j in the reaction network of Fig. 3; min^{-1}
k'_{ij}	true kinetic constant (see Eq. (7); i and j as above); g of solution/g of catalyst \cdot min \cdot bar)
k_{ij}	pseudo kinetic constant (see Eq. (3); i and j as above); g of solution/g of catalyst \cdot min)
p_{H_2}	hydrogen partial pressure; bar
r_{ij}	rate of reaction (i and j as above), mol/g of catalyst \cdot min)
T	temperature, K
W_C	catalyst loaded in the reactor; g
W_L	weight of liquid solution in the reactor; g
W_R	weight of 1,2,3-tcb loaded in the reactor; g
W_S	CS_2 loaded in the reactor; g
x_{H_2}	liquid phase concentration of hydrogen, mol fraction
φ	degree of detoxification; see Eq. (12)
ρ_m	density of the reacting liquid mixture at $T = 330^\circ\text{C}$ and p_{H_2} ; g/ml

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