

Catalytic hydroprocessing of chlorobenzene: the effect of thiophene

F. Murena*

Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli "Federico II", Piazzale Tecchio, 80125 Naples, Italy

Received 15 October 1999; received in revised form 27 December 1999; accepted 30 December 1999

Abstract

The catalytic hydrotreatment of chlorobenzene–thiophene mixtures has been studied using a Ni–Mo/ γ -Al₂O₃ sulphided catalyst. Experimental runs were carried out in a batch reactor at constant temperature ($T = 300$ – 320 – 340°C) and hydrogen pressure ($P = 40$ bar). The reaction medium was hexadecane.

The experimental results show that chlorobenzene hydrodechlorination and thiophene hydrodesulphurization are not inhibited when chlorobenzene and thiophene are hydrotreated in admixture. The results that were obtained are of importance for the development of the hydrodechlorination (HDCI) process of chlorinated liquid wastes contaminated by other organic compounds. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic hydroprocessing; Chlorobenzene; Thiophene

1. Introduction

Recently many papers on hydrodechlorination (HDCI) as a safe disposal method of chlorinated organic liquid wastes have been published [1–5]. All these papers deal with model mixtures of chlorinated compounds in a heavy hydrocarbon reaction medium. Results show that high destruction and removal efficiency levels are reached. Hydroprocessing of real wastes, also on pilot-plant scale, [6–8] confirm the results obtained on model systems.

Very little information is available to predict the behaviour of the catalyst toward HDCI when chlorinated wastes are contaminated by organic compounds containing

* Tel.: +39-81-768-2272; fax: +39-81-239-1800.

E-mail address: murena@unina.it (F. Murena).

other heteroatoms. This is a topic of interest in different cases, i.e., mixed wastes treatment, refining of pyrolytic processing products from wastes of mixed plastics.

The hydrotreatment of chlorobenzene in model mixtures containing quinoline and benzothiophene [9] has been studied. The results showed that the HDCl process was strongly inhibited by the presence of the N-containing compounds but did not give clear information on the effect of the S-containing compounds. The inhibiting effect of N-compounds has been confirmed by treating mixtures of chlorobenzene and pyridine [10].

The main aim of this paper is to ascertain if sulphur containing organic compounds have any inhibiting effect on HDCl process, moreover the effect of chlorine containing organic compounds on HDS process has been studied as well.

Chlorobenzene and thiophene have been selected due to their relatively simple hydroprocessing networks characterised by a limited number of intermediates.

2. Experimental procedure

The hydroprocessing runs have been carried out in a 300-ml autoclave (Brignole, Italy) with magnetic stirrer at 800 rpm. Pure hexadecane has been adopted as the reacting medium. The experimental procedure is described in previous papers [3,10].

The materials adopted are listed in Table 1. The experimental conditions and the range of operating variables of the reaction runs are summarised in Table 2.

Before loading the catalyst in the reactor, it was sulphided to enhance its activity. The sulphidation treatment was carried out at 400°C (4 h) with a 100-cc/min flow of a gas mixture of H₂S (10%) and H₂.

The analyses of the liquid samples, withdrawn from the reactor during the experimental runs, were accomplished by a gas chromatograph PE-8500 (column: 5% phenyl methyl silicone, *l* = 50 m; *d* = 0.2 mm; film thickness = 0.5 μm) equipped with a flame ionization detector. Propylbenzene was adopted as internal standard for the quantitative analyses. Identification of S-compounds were confirmed using an FPD detector.

3. Results and discussion

3.1. Influence of thiophene on HDCL process

Operating conditions were selected in the range suitable for HDCl process, in fact our interest was focused on HDCl process. Therefore experimental runs were carried out at

Table 1
Materials

Reaction medium	Hexadecane 99%, Aldrich
Reactants	Chlorobenzene 99% Aldrich, Thiophene > 98% FlukaHydrogen SON (99.99%)
Catalyst	M8-24P BASF; NiO = 4%, MoO ₃ = 19.5%, (wt.%) supported on alumina. Specific surface 160 m ² /g, porosity = 0.47 cm ³ /g. Ground and sieved 150–200 mesh

Table 2
Experimental conditions

Run	Reactants	T [°C]	P [atm]	W_{THP} [g]	W_{CB} [g]	W_{cat} [g]	W_{sol} [g]	$W_{\text{cat}} / W_{\text{sol}}$ [g/g]
1	THP	300	40	2.23	0	0.73	149.5	4.88×10^{-3}
2	THP	320	40	2.33	0	0.88	149.8	5.88×10^{-3}
3	THP	340	40	2.23	0	0.84	149.7	5.63×10^{-3}
4	CB-THP	300	40	1.15	1.53	0.81	149.6	5.42×10^{-3}
5	CB-THP	320	40	1.13	1.50	0.85	149.4	5.71×10^{-3}
6	CB-THP	340	40	1.12	1.50	0.89	150.9	5.96×10^{-3}

temperature levels of 300°C, 320°C and 340°C and at the pressure of 40 atm (Table 2). When treated in admixture chlorobenzene and thiophene were loaded in equimolar amount.

Fig. 1 reports the experimental data of chlorobenzene concentration vs. reaction time during HDCI process carried out in the presence of thiophene. Experimental data have been fitted by assuming a pseudo first order kinetic expression for chlorobenzene HDCI:

$$r_{\text{CB}} = k'_{\text{CB}} C_{\text{CB}} \quad (1)$$

where k'_{CB} [min^{-1}] is a pseudo first order kinetic constant in which the effect of hydrogen pressure is included. Fitting curves are shown as dashed lines in Fig. 1.

Then the values of the kinetic constants in terms of catalyst concentration:

$$k_{\text{CB}} = k'_{\text{CB}} (W_{\text{L}} / W_{\text{c}}) \quad (2)$$

were calculated.

In Fig. 1 the theoretical curves for chlorobenzene HDCI in the absence of thiophene, evaluated using Arrhenius parameters from Ref. [5], are shown as solid lines. From this figure it can be observed that, at all the temperatures, chlorobenzene HDCI rate is not significantly modified by the presence of thiophene. In fact the dashed curves and solid curves have very similar patterns, a very slight depressive effect of thiophene on chlorobenzene HDCI can be observed at higher temperature ($T = 340^\circ\text{C}$). This effect is, anyway, not significant. Therefore, it can be stated that thiophene has no appreciable effect on the HDCI process of chlorobenzene.

First order kinetic constants of chlorobenzene HDCI in the presence of thiophene (Eq. 2) are reported in Table 3 (k_{CB} in column two). For comparison, kinetic constants of chlorobenzene HDCI, when thiophene is not present [5], are reported in the same table (k_{CB}° in column three). It can be observed that, apart from experimental uncertainties, the values are very similar.

3.2. Influence of chlorobenzene on HDS process

The HDS of thiophene has been largely studied due to its significance in petroleum refining processes. In these processes the effect of aromatic chlorinated compounds on HDS cannot be observed, since chlorine concentration in crude oil is very low. Moreover in HDS studies the temperature and pressure levels are generally lower than

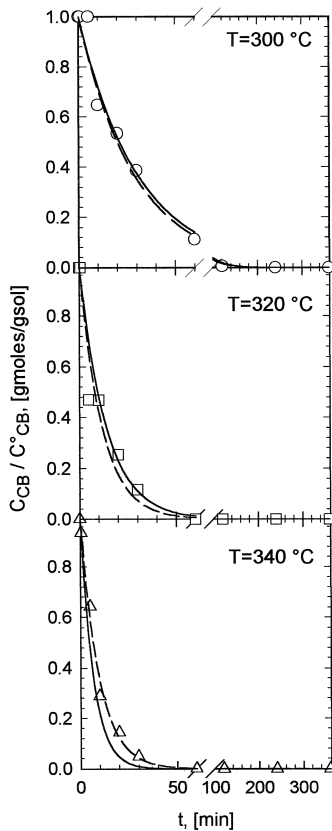


Fig. 1. Pattern of chlorobenzene concentration in HDCI in the presence of thiophene at $T = 300^{\circ}\text{C}$, 320°C and 340°C (runs 4–6). Solid lines are fit curves (kinetic constants in Table 3 column 2). Dashed lines represents chlorobenzene HDCI in the absence of thiophene, evaluated from Ref. [5] (kinetic constants in Table 3 column 3).

those studied in this case. In order to investigate the effect of chlorobenzene on HDS process, the HDS runs of thiophene (runs 1–3) have been carried out at the same operating conditions of HDCI–HDS runs of chlorobenzene thiophene mixtures (runs

Table 3
Kinetic constants of chlorobenzene HDCI

T [$^{\circ}\text{C}$]	k_{CB}^{a} [$\text{g}_{\text{sol}}/\text{g}_{\text{cat}} \text{ min}$]	$k_{\text{CB}}^{\text{ob}}$ [$\text{g}_{\text{sol}}/\text{g}_{\text{cat}} \text{ min}$]
300	6.4	6.0
320	15.1	12.8
340	17.7	25.8

^a Kinetic constants of chlorobenzene HDCI in the presence of thiophene (runs 4–6).

^b Kinetic constants of chlorobenzene HDCI from Ref. [5].

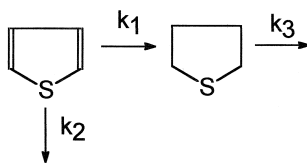


Fig. 2. Reaction network for thiophene HDS.

4–6). All the experimental runs have been carried out with constant molar concentration of the reactants (i.e.; thiophene in runs 1–3 and chlorobenzene + thiophene in runs 4–6) at time $t = 0$ (see Table 1).

Thiophene HDS using Ni–Mo catalysts occurs through a series of reactions which lead to the formation of tetrahydrothiophene and butanthiol as intermediates and of n butane, butene and H_2S as final products. However, in the literature different reaction networks of thiophene HDS are reported. Since the aim of this paper is mainly to study the effect of thiophene on chlorobenzene HDCl, the HDS process was simply modeled by the partial network of Fig. 2. Butanthiol was detected in a very limited amount in the liquid samples collected during experimental runs, for this reason it is not reported in the network of Fig. 2.

First order kinetic has been assumed for each reaction of the thiophene HDS network. The hypothesis of Langmuir kinetics was, also, tested but it was found that adsorption phenomena were negligible. The regression of the experimental data by the system of differential equations, corresponding to the reaction network of thiophene HDS in Fig. 2, has been solved by using a commercial software EASY-FIT [11]. Pseudo first order kinetic constants have been evaluated and then expressed in terms of catalyst concentration.

To show more clearly the effect of the presence of chlorobenzene on the HDS process the kinetic constants of the total HDS reactions of both thiophene and organic sulphur (S_{org}) are reported.

Kinetic constants of total reaction rate of thiophene are simply evaluated by summing $k_1 + k_2$ (see network in Fig. 2). The values obtained are reported in Table 4 both in the presence ($k_1 + k_2$) that in the absence of chlorobenzene ($k_1^\circ + k_2^\circ$).

Table 4
Kinetic constants of thiophene HDS

T [°C]	$k_1 + k_2^a$ [g _{sol} /g _{cat} min]	$k_1^\circ + k_2^{ob}$ [g _{sol} /g _{cat} min]	$k_{S_{org}}^a$ [g _{sol} /g _{cat} min]	$k_{S_{org}}^{ob}$ [g _{sol} /g _{cat} min]
300	10.6	5.2	9.8	4.9
320	18.4	6.3	17.0	5.8
340	25.4	24.3	16.8	24.9

^aFrom runs 4–6 carried out in the presence of chlorobenzene.

^bFrom runs 1–3 carried out in the absence of chlorobenzene.

HDS process may be simply described as the transformation of organic sulphur in H_2S :



where the organic sulphur concentration corresponds, at any time t , to the sum of the concentration of thiophene and tetrahydrothiophene. In Fig. 3 experimental data of the organic sulphur concentration are reported at $T = 300^\circ C$ and $T = 340^\circ C$ both in the presence and in the absence of chlorobenzene. Fitting curves in Fig. 3 were obtained assuming a first order kinetic for global HDS process in Eq. (3). The values of the obtained constants ($k_{S_{org}}$ and $k_{S_{org}}^{\circ}$) are reported in Table 4 at $T = 300^\circ C$, $320^\circ C$ and $340^\circ C$.

From the observation of the values of the kinetic constants reported in Table 4 for the HDS processes of both thiophene ($k_1 + k_2$) and of organic sulphur ($k_{S_{org}}$) it turns out that at lower temperatures ($T = 300^\circ C$ and $T = 320^\circ C$) the HDS rate is enhanced, even though slightly, by the presence of chlorobenzene. At higher temperature ($T = 340^\circ C$) the rate of the HDS process is not influenced by the presence of chlorobenzene as result from the evaluation of thiophene HDS (see Table 4), while from the study of organic sulphur HDS a negative effect of chlorobenzene at the same temperature has been shown.

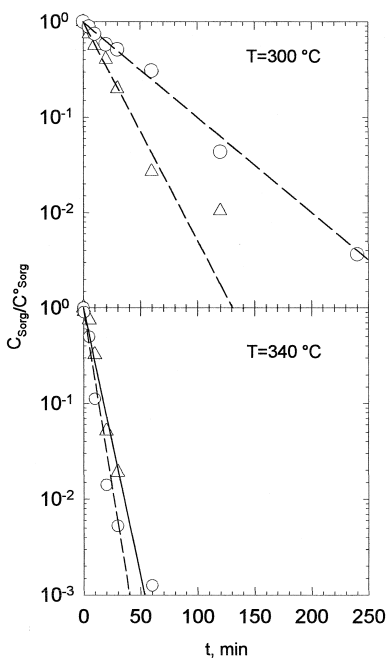


Fig. 3. Pattern of total organic sulphur (thiophene + tetrahydrothiophene) concentration at $T = 300$ and $340^\circ C$: in the absence of chlorobenzene (circles), in the presence of chlorobenzene (triangles). Lines are fitting curves assuming first order kinetic for reaction (3), kinetic constants are reported in Table 4.

This effect of chlorobenzene on the HDS process evaluated from HDS of thiophene or from HDS of organic sulphur at $T = 340^{\circ}\text{C}$ is not significant and may probably be attributed to a imperfect fitting of experimental data.

4. Conclusions

Catalytic hydrotreatment of chlorobenzene–thiophene mixtures showed that the effect of thiophene on chlorobenzene HDCl is not significant. Similarly the presence of chlorobenzene does not inhibit the HDS process. On the contrary, when chlorobenzene was present in the reacting mixture, a small positive effect on HDS rate has been observed especially at lower temperatures ($T = 300^{\circ}\text{C}$ and 320°C).

In fact, thiophene is not a basic compound so it does not adsorb strongly on the surface of the acidic catalyst adopted. In consequence, it does not block active sites to any great extent to chlorobenzene molecules. Moreover the sharing of active sites, that in any case takes place, may be balanced by the production of H_2S . In fact the production of H_2S determines in the reactor an atmosphere on the catalyst similar to that adopted for its sulphidation, maintaining the sulphidation of the catalyst.

The results obtained with chlorobenzene–thiophene mixtures are different from those observed when the HDCl process is carried out in the presence of basic aromatic nitrogen compounds (e.g., chlorobenzene–pyridine mixtures) [9,10]. In this case the HDCl process was strongly depressed. When chlorinated aromatic compounds are reacted in the presence of basic nitrogen compounds organic salts may be produced due to high basicity of nitrogen compounds. These salts have a deactivation effect on the HDCl rate when Ni–Mo catalysts are adopted [9,10]. In the case of simultaneous HDCl and HDS treatment since thiophene, its HDS intermediates and products are not strong bases, they do not form organic salts with the HCl produced by HDCl.

On the basis of the above results it can be inferred that the efficiency of catalytic hydrotreatment of toxic wastes containing chlorinated compounds (e.g., PCB, chlorobenzenes, chlorophenols) is not influenced by the presence of organic sulphur compounds. Moreover, when carrying out the HDCl process, if organic sulphur compounds are present, the HDS process takes place as well, therefore the final product is a mixture of hydrocarbons without heteroatoms. Heteroatoms are present in the gas phase as HCl and H_2S that can be removed by using standard processes.

Nomenclature

CB	chlorobenzene
C°	concentration at reaction time $t = 0$
k	kinetic constant, $\text{g}_{\text{sol}} \text{g}_{\text{cat}}^{-1} \text{min}^{-1}$
k'	kinetic constant, min^{-1}
k°	kinetic constants of single reactant hydrotreating processes (e.g., HDCl of chlorobenzene or HDS of thiophene)

S_{org}	Organic sulphur = (thiophene + tetrahydrothiophene)
THP	thiophene
W_{cat}	mass of catalyst loaded in the reactor, g
W_{CB}	mass of chlorobenzene loaded in the reactor, g
W_{sol}	mass of solution loaded in the reactor, g
W_{THP}	mass of thiophene loaded in the reactor, g

Acknowledgements

I wish to thank Prof. Francesco Gioia for his scientific contribution. The intelligent cooperation of the student Gianluca Meloro is also gratefully acknowledged. This work was financed by research grants from “Ministero dell’Università e della Ricerca Scientifica e Tecnologica” and from “Consiglio Nazionale delle Ricerche”.

References

- [1] B.F. Hagh, D.T. Allen, Catalytic hydroprocessing of chlorobenzene and 1,2-dichlorobenzene, *AIChE J.* 36 (1990) 773–778.
- [2] B.F. Hagh, D.T. Allen, Catalytic hydroprocessing of chlorinated benzenes, *Chem. Eng. Sci.* 45 (1990) 2695–2701.
- [3] F. Gioia, V. Famiglietti, F. Murena, Catalytic hydrogenation of 1,2,3-trichlorobenzene, *J. Hazard. Mater.* 33 (1993) 63–73.
- [4] F. Murena, V. Famiglietti, F. Gioia, Detoxification of chlorinated organic compounds using hydrodechlorination on sulfided NiO–MoO₃/γ-Al₂O₃, *Environ. Prog.* 12 (3) (1993) 231–237.
- [5] F. Murena, Catalytic hydrodechlorination of monochlorobiphenyls using Ni–Mo/γAl₂O₃ sulphided catalyst, *Environ. Technol.* 18 (1997) 317–324.
- [6] P.F. van den Oosterkamp, L.J.M.J. Blomen, H.J. ten Doesschate, A.S. Laghate, R. Schaaf, “Dechlorination of PCB’s, dioxins and difuranes in organic liquids” UNIDO Workshop “Hazardous Materials/Waste Management” Vienna, Austria, June 1987.
- [7] T.N. Kalnes, R.B. James, Hydrogenation and recycle of organic waste streams, *Environ. Prog.* 8 (1988) 185–191.
- [8] D.W. Brinkman, J.R. Dickson, D. Wilkinson, Full-scale hydrotreatment of polychlorinated biphenyls in the presence of used lubricating oils, *Env. Sci. Technol.* 29 (1995) 87–91.
- [9] F. Gioia, F. Murena, Simultaneous catalytic hydroprocessing of chlorine-, nitrogen-, and sulphur-containing aromatic compounds, *J. Hazard. Mater.* 57 (1998) 177–192.
- [10] F. Murena, F. Gioia, Catalytic hydroprocessing of chlorobenzene–pyridine mixtures, *J. Hazard. Mater.* 60 (1998) 271–285.
- [11] K Schittkowski, EASY-FIT: A software system for data fitting in dynamic systems, Dept. of Mathematics, University of Bayreuth, Germany, 1998, Preprint.