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Catalytic hydrotreatment of water contaminated by chlorinated aromatics

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Abstract

The catalytic hydrotreatment at low temperature of water contaminated by chlorobenzene and *o*-chlorobiphenyl has been studied experimentally using a Pd/C catalyst. Reaction runs have been carried out in a stirred reactor at constant temperature ($T = 30\,^{\circ}\mathrm{C}$) and pressure ($P \cong 1\,\mathrm{bar}$). Liquid phase concentration of chlororganic reactant and hydrogenated products, chloride ions concentration and pH have been measured during reaction time. Experimental results have been modelled assuming gas–liquid and liquid–solid equilibrium and the kinetic constants of the HDCl surface reactions have been evaluated.

Keywords: Hydrotreatment; Chlorobenzene; *o*-chlorobiphenyl; Contaminated water

1. Introduction

Catalytic hydrogenation (HDCl) is a promising process for the treatment of several class of organic pollutants [1]. Many toxic compounds are organic chlorinated compounds (e.g., polychlorobiphenyls (PCBs), chlorobenzenes, polychlorodibenzodioxins (PCDDs). Their detoxification could be performed by catalytic hydrodechlorination. By an HDCl process the chlorine atoms present on the host organic molecule are substituted by hydrogen atoms producing the corresponding hydrocarbon and hydrochloric acid. Experimental results of organic liquid phase HDCl of different class of chloroaromatics are reported in literature [2–6]. In these studies similar formulations of Ni–Mo catalysts, developed for the hydrotreatment of petroleum distillation products, have been generally adopted. Noble metal catalysts have also been tested for the same process [7]. The results on pilot-plant scale confirm the validity of the process [8]. Organic liquid phase HDCl can be, therefore, proposed as an alternative to incineration in the case of treatment of significant class of industrial organic liquid wastes like chlorinated spent solvents, pesticides and dielectric oils (PCBs).

Another environmental application of catalytic hydrogenation is the treatment of industrial and natural contaminated waters. The decontamination of natural water polluted by chlororganic compounds resulting from land storage of toxic wastes, industrial spills and use of agricultural products is an environmental emergency. Noble metal catalysts have been tested for the treatment in water phase of several chlororganics [9,10]. The process is carried out at ambient temperature ($20 < T < 50\,^{\circ}\mathrm{C}$) and pressure ($P = 1\,\mathrm{bar}$). Palladium shows a higher activity in HDCl reaction with respect to other noble metals [9]. Reductive dehalogenation by metals has also been studied [11–13]. In this case, however, longer reaction time is necessary to reach significant dehalogenation levels.

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Nomenclature

c	concentration (mg/g cat.)
C	concentration (mg/kg$_w$)
C^o_{CBP}	*o*-chlorobiphenyl loaded in terms of concentration (mg/kg$_w$)
k	pseudo-first-order kinetic constant (min^{-1})
K	adsorption constant (kg$_w$/mg)
m	mass (g)
p^o	vapour pressure (bar)
PM	molecular weight (g/g mol)
q	catalyst saturation concentration (mg/g cat.)
r	reaction rate (mg/(g$_{cat.}$ min))
R	gas constant (0.082 atm l g mol^{-1} K^{-1})
t	time (min)
T	temperature (K)
V	volume of the gas phase (l)

Greek letter

γ_{iw}	activity coefficient of compound i in water

Subscripts

B	benzene
CB	chlorobenzene
CBP	*o*-chlorobiphenyl
i, j	any reactant or product of HDCl reactions
l	liquid phase (water)
s	solid phase (catalyst)
t	total (solid + liquid + vapour)
v	vapour phase
w	water

In the present study a kinetic analysis of the water phase HDCl process of chlorobenzene and *o*-chlorobiphenyl promoted by a Pd/C catalyst is reported.

2. Experimental

The experimental runs have been carried out in a 1.5 l stirred glass reactor. The reactor was set in a thermostatic bath and equipped with a manometer to measure the operating pressure and with a gas flowmeter to measure gas flow rate. Purge gas (nitrogen) or reacting gas (hydrogen) were fed to the reactor through a sparger at the bottom of the reactor. During reaction run liquid samples were withdrawn through a sampling line.

Chlorobenzene (CB) and *o*-chlorobiphenyl (CBP) have been adopted as reactants. A Pd/C catalyst (ESCAT-11 Engelhard) has been used. Catalyst particles, characterised by SEM analysis, are irregularly shaped with average dimension $\cong$10 μm.

Preliminary HDCl runs of chlorobenzene were performed with a constant hydrogen flow. They showed that some evaporation of chlorobenzene and benzene (B) took place. Therefore, successive HDCl runs of chlorobenzene were carried out at constant hydrogen pressure. Before each run the following operations were accomplished: (i) loading of bidistilled water into the reactor; (ii) purging of head space with nitrogen; (iii) loading of the chlorinated organic reactant followed by its dissolution in water; (iv) loading of the catalyst followed by the adsorption of the reactant on the surface of the solid phase; (v) loading of the hydrogen (time $t = 0$ for the reaction).

The HDCl runs of *o*-chlorobiphenyl were carried out at a constant hydrogen flow. The experimental procedure was the same adopted for chlorobenzene with the difference that in this case the reactant (*o*-chlorobiphenyl) due to its low solubility ($\cong$5 ppm) was previously diluted in methanol and then added to bidistilled water.

During each run several parameters have been measured to follow the reaction process: (i) chloride ion concentration (Orion Ionplus selective electrode, or colorimetric method in the case of *o*-chlorobiphenyl); (ii) H^+ concentration (Orion pH-meter model 420A); (iii) organic compounds concentration by sampling the liquid phase at fixed reaction time and using SPME (solid phase micro extraction) technique followed by GC-FID analysis; (iv) organic compounds adsorbed on the catalyst at the end of each run by extraction and GC-FID analysis.

However, the pH measurements have only a qualitative value. In fact, it was observed that catalyst itself influence the pH value. Therefore, in the next section only results from SPME and Cl^- ions analyses will be discussed.

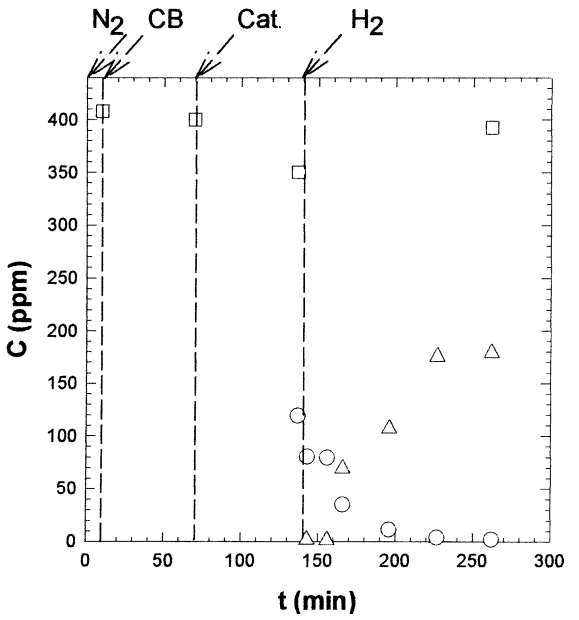

Fig. 1. Concentration in liquid phase during chlorobenzene HDCl. Symbols are: (□) total mass balance (liquid solid and gas phase as chlorobenzene); (○) chlorobenzene concentration in liquid phase; (△) benzene concentration in liquid phase. Short notations on upper axis indicate: nitrogen injection (N_2); chlorobenzene loading (CB); catalyst loading (Cat.) and hydrogen injection (H_2).

3. Results and discussion

3.1. Chlorobenzene HDCl

In Fig. 1 the pattern of chlorobenzene and benzene concentration in liquid phase are reported during a batch run carried out at $P_{H_2} = 810$ Torr. The experimental results in Fig. 1 show that when catalyst is loaded in the reactor, chlorobenzene is massively adsorbed on the catalyst. At this stage no reaction is observed. In fact, reaction products and chloride ions are not detected in the liquid phase. When hydrogen is fed to the reactor the reaction starts rapidly and the concentration of the dechlorinated organic product (benzene) in the liquid phase grows up (the occurrence of a dechlorination reaction is confirmed by chloride ions and pH analyses). In less than 2 h hydrodechlorination takes place on a quite complete extent. The complete dechlorination is confirmed also by the extraction of organic compounds from the catalyst collected at the end of each run. In fact, no chlorobenzene was detected in the extracted phase.

Preliminary adsorption tests were performed to study the liquid–solid equilibrium of both chlorobenzene and benzene separately on the catalyst. The adsorption isotherms follow a Langmuir equation:

$$c_{is} = \frac{q_i K_i C_{il}}{1 + K_i C_{il}} \tag{1}$$

The units in Eq. (1) are c_{is} (mg/g cat.) and C_{il} (mg/kg_w). The values of coefficients are $q_{CB} = 200.6$ (mg/g cat.), $K_{CB} = 0.18$ (kg_w/mg), $q_B = 100.8$ (mg/g cat.) and $K_B = 1.2 \times 10^{-2}$ (kg_w/mg).

Vapour–liquid equilibrium of chlorobenzene was also studied experimentally and the activity coefficient of chlorobenzene in water at $T = 30\,^{\circ}C$ is $\gamma_{CBw} = 1.1 \times 10^3$. The activity coefficient of benzene ($\gamma_{Bw} = 2.4 \times 10^3$) is reported in the literature [14].

In modelling the reaction process, liquid–solid and liquid–vapour equilibria have been assumed at any reaction time. The equilibrium equations have been written for both chlorobenzene and benzene in term of mass:

$$m_{iv} = \frac{V}{RT} p_i^{o} \gamma_{iw} \frac{m_{il}}{m_w} PM_w \tag{2}$$

$$m_{is} = \frac{qK_i C_{il}}{1 + K_i C_{il} + K_j C_{jl}} m_{cat.} \times 10^{-3} \tag{3}$$

Eqs. (2) and (3) coupled with the experimental values of liquid phase concentration, obtained from SPME analyses, give the concentration in vapour and solid phase at any sampling time *t*.

The analyses of chloride ions give at any sampling time the amount of chlorobenzene reacted and, consequently, of benzene produced. The concentration of both chlorobenzene and benzene can be evaluated in all phases adding to the system of Eqs. (2) and (3) the mass balance which is at any time *t*

$$m_{is} + m_{il} + m_{iv} = m_{it} \tag{4}$$

The system of Eqs. (2) and (3) (for SPME data) and 2–4 (for Cl^- data) have been solved using MATHCAD software to evaluate the unknown parameters at any sampling time *t*. Therefore, at any time *t* mass and concentration of both chlorobenzene and benzene are known in the three phases. The values of chlorobenzene total concentration vs. reaction time obtained

from both SPME and Cl^- measurements, have been averaged and fitted with a time decreasing exponential function. The HDCl rate was then evaluated at any time t as the derivative $-dc_{CBt}/dt$ of the fitting function. The following kinetic equation was then assumed [9]:

$$r_{CB} = -\frac{dc_{CBt}}{dt} = k_{CB}c_{CBs} \quad (5)$$

where r_{CB} is the rate of consumption of chlorobenzene, c_{CBt} the total (vapour + liquid + solid) concentration of chlorobenzene per unit mass of catalyst and k_{CB} is a pseudo-first-order kinetic constant in which the effect of hydrogen pressure can be included because all experimental runs were carried out at constant hydrogen pressure.

If Eq. (5) holds true a plot of reaction rate vs. c_{CBs} would be linear. This is confirmed observing Fig. 2. The slope of Fig. 2 is the pseudo-first-order kinetic constant ($k_{CB} = 4.2 \times 10^{-2}\,min^{-1}$) of Eq. (5). During the HDCl process, pH changed from neutrality to about 2.5. The effect of pH on HDCl rate, however, is not relevant [15].

GC-FID analyses showed that benzene undergoes successive hydrogenation, and both cyclohexene and cyclohexane are formed but on a limited extent.

3.2. *o*-Chlorobiphenyl HDCl

Preliminary adsorption tests have been carried out to evaluate the parameters of Langmuir isotherms of *o*-chlorobiphenyl (Eq. (1)). Values are $q_{CBP} = 3.6 \times 10^{-2}$ (mg/g cat.) and $K_{CBP} = 173.1$ (kg_w/mg). Analyses carried out by GC-FID have showed that biphenyl undergoes successive hydrogenation of the aromatic rings with formation of both bicyclohexyl and cyclohexylbenzene. Assuming for all dechlorinated products the same adsorption constant of CBP and considering that the fraction of all compounds in the gas phase is negligible, the Langmuir adsorption isotherm is

$$c_{CBPs} = \frac{qK_{CBP}C_{CBPl}}{1 + K_{CBP}C^{o}_{CBPl}} \quad (6)$$

To model the HDCl reaction of CBP the same procedure of chlorobenzene HDCl has been adopted. Due to the low solubility in water of CBP the change of pH, during the HDCl process, is limited. The average value of the kinetic constant of HDCl reaction of CBP (see Eq. (5)) at $T = 30\,^{\circ}C$ is $k_{CBP} = 0.317\,min^{-1}$ (Fig. 3).

The dechlorination efficiency is defined as

$$DE = \frac{m^{o}_{i} - m_{it}}{m^{o}_{i}} \quad (7)$$

It is for chlorobenzene HDCl DE = 98% and for *o*-chlorobiphenyl 91.2% (run 2) and 80.1% (run 3). These DE values correspond to about 2 h of treatment in correspondence of the experimental conditions reported in Table 1. Note that in HDCl runs of CBP a lower amount of catalyst was loaded.

In Figs. 2 and 3 the range of concentration in solid phase is quite broad and reaches the maximum value of

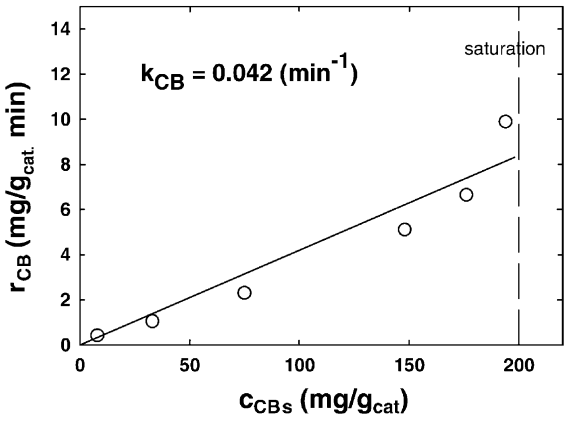

Fig. 2. Chlorobenzene HDCl rate vs. concentration of chlorobenzene adsorbed on the catalyst.

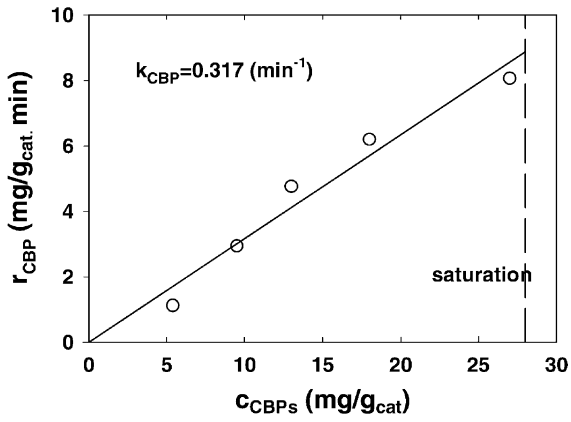

Fig. 3. *o*-Chlorobiphenyl HDCl rate vs. concentration of *o*-chlorobiphenyl adsorbed on the catalyst.

Table 1
Operating conditions. All runs were carried out at $T = 30\,^{\circ}C$

Run	Reactant	Reacting system	P_{H_2} (Torr)	Q_{H_2} (cm^3/min)	Stirrer speed (rpm)	Catalyst	W_w (kg)	$W_{cat.}$ (g)	W_i (mg)
1	CB	Batch	810	–	240	Pd/C	1	1.00	450
2	CBP	Semi-batch	760	10	240	Pd/C	1	0.025	4.8
3	CBP	Semi-batch	760	10	240	Pd/C	1	0.25	4.8

solid phase concentration of both chlorobenzene and *o*-chlorobiphenyl (saturation). Therefore, the quality of the fitting of the experimental data may be considered acceptable and the kinetic model proposed (Eq. (5)) may be considered adequate.

4. Conclusions

The water phase dechlorination process promoted by ESCAT-11 Pd/C catalyst is effective in the dechlorination of chlorobenzene and *o*-chlorobiphenyl. Pseudo-first-order kinetic constants have been evaluated for both chlorobenzene and *o*-chlorobiphenyl at $T = 30\,^{\circ}C$. A significant hydrogenation of the aromatic ring was observed in the case of biphenyl. This experimental evidence is relevant because aromatic hydrocarbons are generally more toxic and more recalcitrant to biological decomposition processes than corresponding aliphatic hydrocarbons. In chlorobenzene HDCl the hydrogenation of the aromatic ring of benzene took place on a limited extent and benzene is still toxic compound. In this case, however, the product (benzene) is somewhat more volatile than chlorobenzene and could be effectively removed by a stripping operation.

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