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Catalytic hydroprocessing of chlorobenzene–pyridine mixtures

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Abstract

The catalytic hydrotreatment of chlorobenzene–pyridine mixtures has been studied using a commercial Ni–Mo/ γ -Al₂O₃ sulphided catalyst. Experimental runs were carried out in a batch reactor at constant temperature ($T = 300$ and 350°C) and hydrogen pressure ($P = 5$ and 50 bar). The reaction medium was hexadecane. The experimental results show that both the hydrodechlorination (HDCI) and the hydrodenitrogenation (HDN) processes were strongly inhibited when pyridine and chlorobenzene were hydrotreated in admixture. The formation of salts due to the reaction of nitrogen basic compounds (particularly piperidine which is a pyridine HDN intermediate) with hydrochloric acid (produced by HDCI of chlorobenzene) is hypothesised to be the reason for the reduction of the catalyst activity. Experimental results are modelled assuming a Langmuir–Hinselwood kinetic. The obtained results are of importance for the development of the HDCI process of chlorinated liquid wastes contaminated by nitrogen compounds. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic hydrotreatment; Hydrotechbrination; Hydrodenitrogenation

Abbreviations: C_i , molar concentration of species i in liquid solution; (mol g^{-1} of solution); C_i^0 , concentration of compound i at time $t = 0$ equal to concentration loaded = $W_i / \text{PM}_i W_{\text{sol}}$ (mol g^{-1} of solution); K , adsorption constant ($\text{g of solution mol}^{-1}$); k_i , pseudo-first order kinetic constant of compound i hydrotreated alone, (min^{-1}); PM_i , molecular weight of compound i ; t , reaction time, (min); T , temperature, ($^\circ\text{C}$); W_{cat} , catalyst loaded in the reactor, (g); W_i , weight of compound i loaded in the reactor, (g); W_{sol} , weight of liquid solution in the reactor, (g); θ , fraction of free active sites; B, benzene; CB, chlorobenzene; PPD, piperidine; PPD–Cl, organic salt of piperidine; PRD, pyridine; PRD–Cl, organic salt of pyridine

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1. Introduction

Recently many papers on hydrodechlorination (HDCI) as a safe disposal method of chlorinated organic liquid wastes have been published [1–6]. All these papers deal with model mixtures of chlorinated compounds in a heavy hydrocarbon reaction medium. Reaction networks and the corresponding kinetic constants, in some cases with Arrhenius parameters, are reported. Results show that high destruction and removal efficiency (DRE) levels are reached. Therefore HDCI can be considered as a promising process for the detoxification of liquid industrial wastes containing chlorinated compounds. Other papers reporting results obtained with real wastes also on pilot-plant scale [7–9] confirm these results. High DRE levels are also reached in these cases.

Very little information is available to predict the catalyst behaviour toward HDCI when chlorinated wastes are contaminated by organic compounds containing other etheroatoms. The realest possibility seems to be the contamination with N-, and S-containing organic compounds. Frimmel and Zdrzil [10] have studied the parallel HDS of 3-methylthiophene and HDCI of *o*-dichlorobenzene, thus simulating the disposal of chlorinated organic wastes contaminated by sulphur compounds. The investigation [10], however, is focused on comparing the magnitude of synergism in HDS and HDCI over alumina (or active carbon) supported Ni, Mo, and Ni–Mo catalysts. A synergistic effect was already known to exist for HDS and HDN. Frimmel and Zdrzil [10] have proved that even for HDCI the activity of composite Ni–Mo catalysts is higher than the sum of the activities of the single metal components Ni and Mo.

The hydrotreatment of a model mixture containing chlorobenzene, quinoline and benzothiophene employing a sulphided commercial Ni–Mo/ γ -Al₂O₃ catalyst has been studied by the authors [11]. The results showed that the HDCI and the HDS reactions were strongly inhibited by the presence of the N-containing compounds (i.e. quinoline and its reaction intermediates). The basic nature of the intermediates of the HDN of quinoline (particularly decahydroquinoline) determined their strong adsorption on the acidic sites of the catalyst thus reducing the number of active sites available for the HDCI and HDS reactions.

These results indicated that a more systematic study on the effect of N-compounds on HDCI process was necessary. This is, in fact, the aim of this paper. Pyridine and chlorobenzene 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. Runs 1–5 were carried out in the following way. Hexadecane was loaded in the reactor and heated to reaction temperature. When this temperature was reached, the reactant/s and the sulphided catalyst, in admixture with additional hexade-

Table 1
Materials

Reaction medium	Hexadecane 99%, Aldrich
Reactants	Chlorobenzene 99%, Pyridine 99 + % (Aldrich). Hydrogen GC grade (99.999%) from SIO ALPHAGAZ.
Catalyst	M8-24P BASF; NiO = 4%, MoO ₃ = 19.5%, (weight percent) supported on alumina. Specific surface 160 m ² g ⁻¹ , porosity = 0.47 cm ³ g ⁻¹ . Ground and sieved 150–200 mesh.

cane, were loaded in the reactor using a pressurised loader connected to the reactor by a globe valve. In this way the reaction takes place at a constant temperature from $t = 0$. Run 6 was carried out in a different way. HDCl of chlorobenzene was performed, with the same procedure described before, for 240 min, a time long enough for a complete conversion of chlorobenzene to benzene and hydrochloric acid. At this time pyridine was loaded in the reactor using the external loader and HDN of pyridine in the presence of benzene and HCl was carried out.

During all the runs the hydrogen pressure was adjusted to the set value when necessary. The reacting process has been controlled by withdrawing samples of the liquid phase at fixed reaction times, using a sampling line at the bottom of the reactor. A sintered steel filter, at the opening of the sampling line, inside the reactor, prevented loss of catalyst.

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 its loading in the reactor the catalyst was sulphided to enhance its activity. The sulphidation treatment was carried out at 400°C (4 h) with a 100 cc min⁻¹ 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 HP-9850 (column stationary phase = crosslinked methyl silicone; column length = 50 m; diameter = 0.2 mm; film thickness = 0.5 μm) equipped with a FID detector. Propylbenzene was added to liquid samples as internal standard for the quantitative analyses. Identification of N-compounds were confirmed by a PE-Autosystem GC equipped with a NPD detector.

Table 2
Experimental conditions

Run	T [°C]	P [atm]	W_{CB} [g]	W_{PRD} [g]	W_{PPD} [g]	W_{cat} [g]	W_{sol} [g]	W_{cat} / W_{sol}
1	350	50	—	1.51	—	0.46	149.0	6.5×10^{-3}
2	350	50	—	—	1.51	0.46	149.5	6.5×10^{-3}
3	300	50	1.52	1.50	—	0.39	150.0	6.2×10^{-3}
4	350	50	1.51	1.51	—	0.42	149.4	5.9×10^{-3}
5	350	5	1.56	1.53	—	0.41	149.3	6.3×10^{-3}
6	350	50	1.50	1.54	—	0.42	150.0	7.1×10^{-3}

3. Results and discussion

Before studying the catalytic hydrotreatment of chlorobenzene–pyridine mixtures it is necessary to know the reaction networks and the corresponding kinetic constants when the two reactants (chlorobenzene and pyridine) are hydrotreated separately.

The values of the kinetic constant for the HDCI of chlorobenzene in hexadecane in the temperature range 250–350°C had already been evaluated by the authors and results have been reported [5,6].

HDN of pyridine and piperidine has been deeply studied. Reaction networks and the corresponding kinetic constants are reported in a review [12]. But generally experimental results refer to vapour-phase reactions, and the HDN rates measured in the various experiments are expressed in different ways; moreover, the catalysts adopted are not exactly the same as that adopted in this paper. Therefore, in order to make comparisons based on data internally consistent (obtained at the same operating conditions, with the same catalyst), we have carried out runs of HDN of pyridine (run 1) and of piperidine (run 2) in the absence of chlorobenzene. Since our interest is focused on HDCI process we have performed these two runs at $T = 350^\circ\text{C}$ and $P = 50$ bar which are operating conditions more suitable for HDCI than for HDN. In fact optimum operating conditions for HDCI range between $300 \leq T \leq 350^\circ\text{C}$ and $5 \leq P \leq 50$ atm, while HDN requires higher value of both pressure and temperature.

3.1. HDN of pyridine and piperidine

The reaction network of pyridine HDN, as reported in the literature [12], is represented in Fig. 1. Pyridine HDN occurs through a series of reactions which lead to the formation of: piperidine, *n*-pentylamine, and of the final products *n*-pentane and ammonia. Actually, in the liquid samples withdrawn during run 1, we observed only the presence of pyridine (reactant) and *n*-pentane (final product). Both piperidine and *n*-pentylamine (reaction intermediates) were not detected by our analytical apparatus. In run 2, where piperidine was loaded as the reactant, *n*-pentylamine (reaction intermediate) was not observed again, and only piperidine and *n*-pentane were detected.

The experimental data of concentration vs. time for pyridine and piperidine HDN are reported in Fig. 2. In both runs a quite complete conversion of the reactant was reached in the observed reaction time (see Fig. 2). A high concentration (gmolsgol⁻¹) of *n*-pentane, more than 50% of the reactant loaded, was measured in the final samples withdrawn at the end of runs 1 and 2. This value did not fit the mass balance because the sampling efficiency of the experimental apparatus, toward volatile compounds like *n*-pentane is low. However, we can conclude that in runs 1–2 the HDN processes have

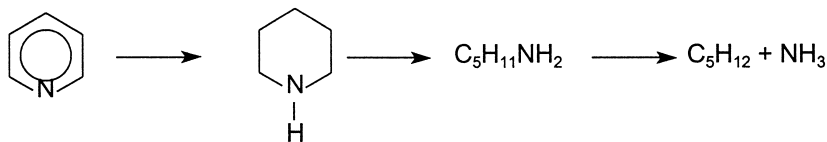


Fig. 1. Reaction network of pyridine from Ref. [12].

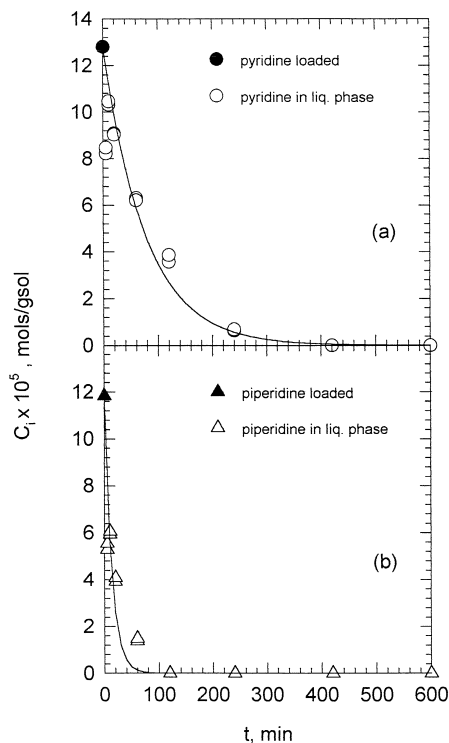


Fig. 2. Graph (a) Pyridine HDN in hexadecane (run 1: $T = 350^{\circ}\text{C}$; $p_{\text{H}_2} = 50$ bar). Fitting curve based on Eq. (1). Graph (b) HDN of piperidine in hexadecane (run 2: $T = 350^{\circ}\text{C}$; $p_{\text{H}_2} = 50$ bar). Fitting curve based on Eq. (2).

been completed with the conversion of the nitrogenated reactants to NH_3 and hydrocarbons.

Observing Fig. 2 it is clear that HDN of piperidine is faster than HDN of pyridine. In fact it was completed in less than 200 min, while HDN of pyridine needed about 500 min to approach zero concentration of pyridine. Since in both runs 1 and 2 we did not observe the presence of *n*-pentylamine we conclude that HDN rates are in the following order: *n*-pentylamine > piperidine > pyridine. This succession of HDN reaction rates is confirmed by other authors [12].

Experimental data reported in Fig. 2 were modelled assuming a Langmuir–Hinselwood kinetic. Best fitting for HDN of pyridine (PRD) and piperidine (PPD) were obtained respectively by the equations:

$$\frac{dC_{\text{PRD}}}{dt} = - \frac{k_{\text{PRD}} C_{\text{PRD}}}{1 + K_{\text{ad1}}(C_{\text{PRD}}^0 - C_{\text{PRD}})} \quad (1)$$

$$\frac{dC_{\text{PPD}}}{dt} = - \frac{k_{\text{PPD}} C_{\text{PPD}}}{1 + K_{\text{ad2}} C_{\text{PPD}}^0} \quad (2)$$

In Eq. (1) it is assumed that the reaction products of pyridine HDN (piperidine,

n-pentylamine and ammonia) adsorb more strongly than pyridine whose contribution is therefore neglected.

In Eq. (2) it is assumed that the reactant (piperidine) and the products (*n*-pentylamine and ammonia) adsorb with the same strength. Both these equations are in good agreement with those reported in literature [12] for modelling respectively the HDN of pyridine and piperidine.

Commercial software *Mathematica* was adopted to fit the experimental data of runs 1 and 2 with Eqs. (1) and (2) respectively. Fitting curves are reported in Fig. 2. The following values of the parameters were evaluated: $k_{\text{PRD}} = 0.013 \text{ min}^{-1}$, $K_{\text{ad1}} = 2 \times 10^2 \text{ gsol mol}^{-1}$, $k_{\text{PPD}} = 0.109 \text{ min}^{-1}$, and $K_{\text{ad2}} = 1.5 \times 10^4 \text{ gsol mol}^{-1}$.

Even though we did not measure the ammonia concentration it is possible to state that in Eq. (1) $K_{\text{ad1}}(C_{\text{PRD}}^0 - C_{\text{PRD}}) \cong K_{\text{NH}_3}C_{\text{NH}_3}$. In fact other reaction products in liquid phase (piperidine and *n*-pentylamine) were not detected. With this assumption, Eq. (1) would correspond exactly to kinetic equation of pyridine HDN reported by other authors [12].

In Eq. (2) $K_{\text{ad2}}C_{\text{PRD}}^0 \cong K_{\text{PPD}}C_{\text{PPD}} + K_{\text{NH}_3}C_{\text{NH}_3}$ because *n*-pentylamine was not detected in the liquid. In Ref. [12] it is inferred that adsorption constants for piperidine and ammonia have the same value, therefore the kinetic equation for piperidine HDN reported in Ref. [12] is the same as Eq. (2).

The adsorption of nitrogen compounds on the acidic catalyst is evidenced also when observing the concentrations of both pyridine and piperidine (Fig. 2) measured in the first samples (sampling time $\cong 0.5 \text{ min}$). At this time the concentration of the reactant, measured in the liquid phase samples (empty symbols), was significantly lower than the loaded or nominal concentration (full symbols in Fig. 2) and lower also of that measured in the second sampling (sampling time = 5 min). The proposed explanation is the following: the catalyst and the reactant (pyridine in run 1 and piperidine in run 2) were loaded with hexadecane in the external loader, they remained in contact a few minutes before the loading operation could be carried out. In this time adsorption of the N-reactant on the catalysts particles took place in the loader at room temperature. Therefore, when the loading operation was carried out, a mixture with a concentration in the liquid phase of N-reactant lower than the nominal was injected into the reactor. This is the reason for the low concentration level of the N-reactant in the first samples ($t \cong 0.5 \text{ min}$). In the first minutes after loading, due to the high temperature present in the reactor, partial desorption of the N-reactant adsorbed on the catalyst particles took place. Correspondingly the concentration in the liquid phase increased. After this initial phase the consumption of the N-reactant due to the HDN process prevailed and the concentration in the liquid phase decreased. In the case of piperidine HDN (run 2) the adsorption took place to a greater extent and the concentration in the first sample was about one half of the nominal value (Fig. 2b). In fact piperidine has a greater adsorption constant than pyridine: $K = 0.58 \text{ kPa}^{-1}$ for piperidine and $K = 0.43 \text{ kPa}^{-1}$ for pyridine (values at $T = 360^\circ\text{C}$ [13]).

3.2. HDN and HDCl of mixtures of pyridine and chlorobenzene in hexadecane

The effect of pyridine on chlorobenzene HDCl has been tested at different operating conditions. Runs 3–5 have been carried out at the temperature levels of 300 and 350°C

and at the pressures of 5 and 50 atm, with the aim of exploring the range of operating conditions more suitable for the HDCl process.

In Fig. 3 experimental data of chlorobenzene concentration vs. reaction time for runs 3–5 are reported in comparison with the theoretical curves (dashed curves in Fig. 3) corresponding to the HDCl of chlorobenzene in hexadecane carried out in the absence of pyridine. Dashed curves in Fig. 3a–c were evaluated at the same temperature for runs 3, 4 and 5, respectively, using Arrhenius parameters reported in Ref. [6]. Effect of pressure in HDCl of chlorobenzene is a minor one [14] and has not been considered in the dashed curves reported in Fig. 3.

It can be observed that, at all the operating conditions tested, the HDCl rate of chlorobenzene is strongly reduced when it is hydrotreated in the presence of pyridine. This is in agreement with the findings of the authors when mixtures of chlorobenzene–quinoline–benzothiophene have been hydroprocessed [11].

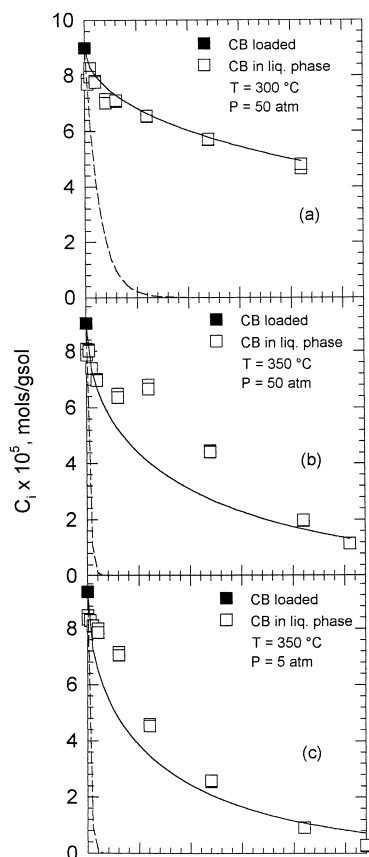


Fig. 3. Chlorobenzene (CB) HDCl in presence of pyridine [graph (a): run 3; graph (b): run 4; graph (c): run 5]. Solid curves are model predictions from Eq. (13). Dashed curves represent chlorobenzene HDCl in the absence of pyridine, evaluated from Ref. [6].

In Fig. 4 the patterns of pyridine concentration vs. reaction time in runs 3–5 are reported. By comparing the experimental pattern of pyridine concentration vs. the reaction time of run 4 (Fig. 4b) with that of run 1 (Fig. 2a), which was carried out at the same operating conditions as run 1 but in the absence of chlorobenzene, it can be observed that also HDN reaction rate of pyridine is significantly reduced by the presence of chlorobenzene. Moreover, in the liquid samples withdrawn during runs 3–5 (carried out in presence of chlorobenzene) the formation of the reaction products: piperidine, *n*-pentylamine and *n*-pentane, was not detected.

The results of runs 3–5 are in partial, but not complete, agreement with those observed by the authors in the case of chlorobenzene–quinoline mixtures [11]. In that case the effect of chlorobenzene on the HDN rate of quinoline was negligible. Both the

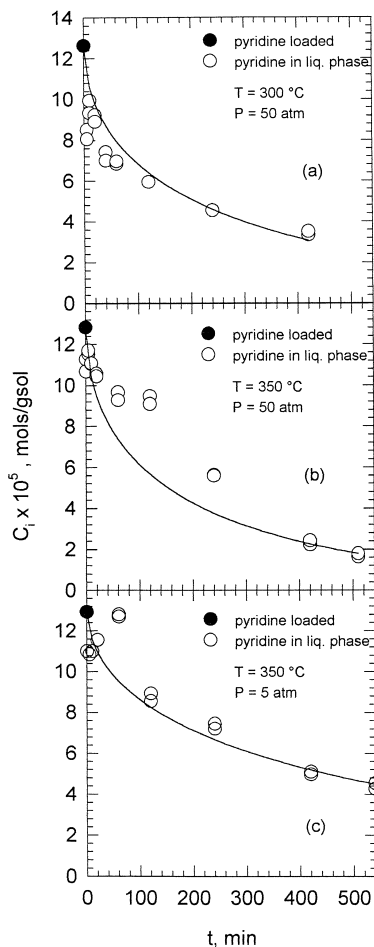


Fig. 4. Pyridine HDN in presence of chlorobenzene [graph (a): run 3; graph (b): run 4; graph (c): run 5]. Fitting curves are model prediction from Eq. (14).

reaction network of quinoline HDN and the corresponding kinetic constants were only slightly modified by the presence of chlorobenzene [11]. This was justified by assuming that the sharing of the active site was in favour of the basic N-compounds.

In the case of chlorobenzene–pyridine mixtures the situation seems to be different. In fact:

- Pyridine HDN rate is significantly depressed by the presence of chlorobenzene;
- Pyridine HDN reaction network is modified by the presence of chlorobenzene, indeed the reaction product *n*-pentane, which was in fact detected in run 1 was not detected in runs 3–5.

It must be observed that piperidine is a very basic nitrogen organic compound. As a matter of fact pK_a and proton affinity (PA) of piperidine are higher than those of pyridine, quinoline and its HDN intermediates like 1,2,3,4-tetrahydroquinoline. This indicates a higher basicity of piperidine. In fact values of pK_a measured at $T = 25^\circ\text{C}$ in aqueous solutions and of gas-phase proton affinity reported in literature [13] are: for piperidine $pK_a = 11.12$ and $\text{PA} = 229.7$ (kcal mol^{-1}); for pyridine $pK_a = 5.29$ and $\text{PA} = 222$ (kcal mol^{-1}); for quinoline $pK_a = 4.80$ and $\text{PA} = 227.6$ (kcal mol^{-1}), for 1,2,3,4-tetrahydroquinoline (intermediate of quinoline HDN) $\text{PA} = 225$ (kcal mol^{-1}).

The HDCl process produces hydrochloric acid, then HCl and piperidine can react to form salts which could clog catalyst pores and then reduce the rate of both the hydrogenation processes: HDN and HDCl. However, even though it is less basic, pyridine can form salt with HCl as well.

These hypotheses have been confirmed by three different experimental tests.

At ambient temperature a concentrated aqueous solution of HCl was reacted with pyridine and piperidine. In the second case the formation of a solid phase was observed in a few minutes.

At the end of each run the catalyst was collected and treated with a solution of a strong base (NaOH). After mixing a three-phase system was formed: catalyst, aqueous phase, and oily phase. The oily phase was analysed by GC. The results of these analyses are reported in Table 3. It can be observed that when pyridine was reacted without chlorobenzene as in run 1 the treatment with NaOH did not extract any compound from the catalyst. The same happened when piperidine was reacted without chlorobenzene (run 2). When pyridine was hydroprocessed with chlorobenzene (runs 3–6) the treatment with NaOH of the residual catalyst determined the extraction of piperidine (the

Table 3

Compounds extracted from catalyst residue after the treatment with NaOH solutions

Run	T [$^\circ\text{C}$]	P [atm]	Reactants	Compounds extracted after NaOH treatment
1	350	50	pyridine	–
2	350	50	piperidine	–
3	300	50	pyridine and chlorobenzene	piperidine
4	350	50	pyridine and chlorobenzene	piperidine
5	350	5	pyridine and chlorobenzene	pyridine
6	350	50	pyridine and chlorobenzene	piperidine

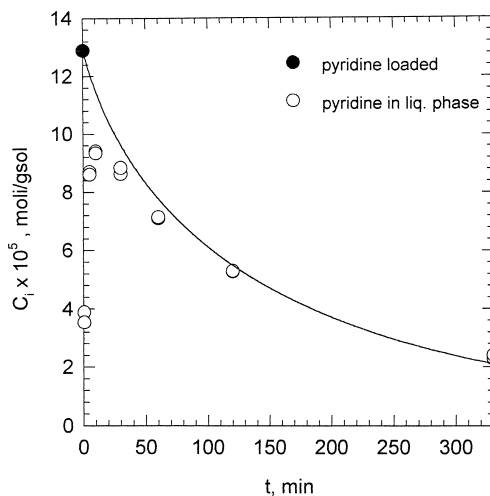


Fig. 5. Pyridine HDN in presence of HCl (run 6). Solid line is fitting curve from Eq. (14) with $k_{\text{PRD}} = 1.3 \times 10^{-2}$ and $K_{\text{S2}} = 2.0 \times 10^4$.

extraction of pyridine in run 5 will be explained later). A possible explanation is that the strongest base (NaOH) moved the piperidine from the organic salt letting piperidine dissolve in the oily phase. It was not possible to carry out a quantitative evaluation of the piperidine extracted, but its amount was relevant.

Last proof of salt formation is given indirectly by run 6. In this run HDN of pyridine was carried out not in the presence of chlorobenzene but in the presence of its reaction products: i.e. benzene and HCl. By comparing the data of run 1 (Fig. 2a), run 4 (Fig. 4b) and run 6 (Fig. 5), all at the same operating conditions, we observe that the concentration pattern corresponding to run 6 (Fig. 5) is very similar, apart from the first reaction minutes, to that obtained in run 4 (Fig. 4b) rather than that obtained in run 1 (Fig. 2a). The similarity of concentration pattern corresponding to runs 4 and 6 indicates that HCl, but not chlorobenzene itself, is responsible of HDN rate depression, thus confirming the hypothesis of salt formation.

The extraction of pyridine instead of piperidine from the catalyst collected at the end of run 5 can be explained considering that in this run a very low pressure ($P = 5$ atm) was adopted. Therefore HDN process took place to a limited extent and piperidine was formed only in a small amount. Then the salt formed in run 5 was that of pyridine.

4. Modelling the inhibition of HDCl and HDN due to salt formation

On the basis of the previous considerations, when chlorobenzene and pyridine are hydrotreated simultaneously the following reaction mechanism may be assumed:





where the abbreviations are: CB = chlorobenzene; B = benzene; PRD = pyridine; PPD = piperidine; PRD-Cl = organic salt formed by pyridine and HCl; PPD-Cl = organic salt formed by piperidine and HCl.

Information in the literature about the reactions between bases and strong acids in organic media is very limited. Therefore, we have written reactions (5) and (6) assuming that the formation of the salts in an organic medium has the same stoichiometry as holds true for aqueous media. In reaction (6) we assume that pyridine in salt PRD-Cl is substituted by piperidine which is a stronger base. This reaction is confirmed by results of catalyst treatment with NaOH solutions (see Table 3) which show that after treatment only piperidine is extracted in massive amount (the case of run 5 has been explained before).

Still considering a behaviour similar to that in water, we assume that: i) reactions (5) and (6) are instantaneous with respect to reactions (3) and (4); ii) reaction (5) is completely shifted to the right due to the high basicity of piperidine.

On the basis of the reaction mechanism (3)–(6) with the above hypotheses a mass balance on chlorine atoms gives at any time t :

$$C_{\text{PRD-Cl}} + C_{\text{PPD-Cl}} = C_{\text{CB}}^0 - C_{\text{CB}} \quad (7)$$

where C_{CB}^0 is the chlorobenzene concentration in the reactor at time $t = 0$. Since this concentration was not be exactly measurable (sampling time is never equal to zero), we assume C_{CB}^0 the value calculated on the basis of the mass of the compounds loaded in the reactor.

By a simple mass balance pyridine concentration at any time t can be written as:

$$C_{\text{PRD}} = C_{\text{PRD}}^0 - (C_{\text{PRD-Cl}} + C_{\text{PPD-Cl}}) \quad (8)$$

where, analogously to C_{CB}^0 , it assumed that C_{PRD}^0 is equal to the value calculated on the basis of the mass of the compounds loaded in the reactor.

By substituting Eq. (7) into Eq. (8) we obtain at any reaction time t :

$$C_{\text{PRD}} = C_{\text{PRD}}^0 - (C_{\text{CB}}^0 - C_{\text{CB}}) \quad (9)$$

If both salts have the same adsorption constant the free active sites fraction on the catalyst, assuming a Langmuir–Hinselwood mechanism, is given by:

$$\theta = 1 - \frac{K_s(C_{\text{PRD-Cl}} + C_{\text{PPD-Cl}})}{1 + K_s(C_{\text{PRD-Cl}} + C_{\text{PPD-Cl}})} \quad (10)$$

where K_s is the salt adsorption constant. Therefore the HDCl rate of chlorobenzene is:

$$\frac{dC_{\text{CB}}}{dt} = -k_{\text{CB}} C_{\text{CB}} \theta \quad (11)$$

where k_{BC} the kinetic constant of chlorobenzene HDCl in the absence of pyridine,

which can be calculated in Ref. [6] at any temperature. Analogously the kinetic equation for the HDN of pyridine is:

$$\frac{dC_{\text{PRD}}}{dt} = -k_{\text{PRD}}C_{\text{PRD}}\theta \quad (12)$$

where k_{PRD} is the kinetic constant of pyridine HDN in the absence of chlorobenzene.

Therefore the kinetic equations of chlorobenzene HDCl and pyridine HDN, when treated simultaneously are:

$$\frac{dC_{\text{CB}}}{dt} = -\frac{k_{\text{CB}}C_{\text{CB}}}{1 + K_{\text{S1}}(C_{\text{CB}}^0 - C_{\text{CB}})} \quad (13)$$

$$\frac{dC_{\text{PRD}}}{dt} = -\frac{k_{\text{PRD}}C_{\text{PRD}}}{1 + K_{\text{S2}}(C_{\text{PRD}}^0 - C_{\text{PRD}})} \quad (14)$$

In Eqs. (13) and (14) two different symbols (K_{S1} and K_{S2}) are adopted for the adsorption constants of the two salts. In fact HDCl of chlorobenzene is an hydrogenolysis reaction. On the contrary, in our case, the HDN of pyridine is limited to reaction (4) which is an hydrogenation reaction. If hydrogenolysis active sites are different from the hydrogenation ones, as often reported in the literature, different values of constants K_{S1} and K_{S2} could be expected.

Eqs. (13) and (14) have been integrated by *Mathematica*; then fitting the experimental data of run 4 the adsorption constants K_{S1} and K_{S2} have been evaluated. The value of the kinetic constants k_{CB} has been calculated in Ref. [6], while the value of k_{PRD} , obtained by fitting experimental data of run 1 with Eq. (1) has been reported in a previous paragraph. A similar procedure was adopted to fit the experimental data of runs 3 and 5. In these cases, however, the value of k_{PRD} was not available, because of the different temperature and/or pressure adopted. Therefore the value of k_{PRD} was calculated by a best fitting procedure together with K_{S1} and K_{S2} . All the parameters of Eqs. (13) and (14) are reported in Table 4.

The fitting curves obtained by Eqs. (13) and (14) with the parameters listed in Table 4, are drawn in Figs. 3 and 4 respectively together with the experimental data.

To have an experimental confirmation of the role played by HCl, the HDN of pyridine run 6 was carried out (see Section 2) in a reacting mixture in which HCl and benzene were present while chlorobenzene was not present.

Table 4
Parameters of Eqs. (13) and (14)

Run	T [°C]	P [atm]	k_{CB} [min^{-1}]	k_{PRD} [min^{-1}]	K_{S1} [gsol mols^{-1}]	K_{S2} [gsol mols^{-1}]
3	300	50	3.7×10^{-2}	1.3×10^{-2}	1.0×10^6	5.0×10^4
4	350	50	2.1×10^{-1}	1.3×10^{-2}	1.1×10^6	3.6×10^4
5	350	5	2.3×10^{-1}	9.3×10^{-3}	5.3×10^5	7.0×10^4

The experimental findings of run 6 are the following: i) pyridine concentration measured at time $t \cong 0$ is about a third of the nominal value. Then it increases during the first ten minutes. After that time pyridine concentration decreases continuously (see Fig. 5), ii) reaction products of pyridine HDN (piperidine, *n*-pentylamine and *n*-pentane) were not detected, iii) NaOH treatment of catalyst collected at the end of the run gave as result the extraction of piperidine.

Experimental findings ii) and iii) are identical to those observed in run 4 in which pyridine and chlorobenzene were reacted together at the same operating conditions.

Experimental data of run 6 have been fitted by Eq. (14) which is the model equation obtained for pyridine HDN carried out in the presence of chlorobenzene. The values of k_{CB} and k_{PRD} adopted to fit run 6 are the same as reported in Table 4 for run 4, which was carried out at the same temperature and pressure as run 6. Best fitting of run 6 was obtained assuming for the adsorption constant K_{S2} the value of 2.0×10^4 which is very similar to 3.6×10^4 obtained by fitting experimental data of run 4 (see Table 4). It can be observed from Fig. 5 that apart from the first 60 min the experimental data of run 6 are well fitted by Eq. (14). In other words, apart from the first minutes, the model developed for the HDN of pyridine in the presence of chlorobenzene is able to fit the experimental data of pyridine HDN in the presence of HCl.

We consider the results of run 6 a proof that in the hydrotreatment of chlorobenzene–pyridine mixtures the catalyst activity is reduced by salt formation due to the reaction of HCl with nitrogen basic products (pyridine and piperidine).

In discussing the dissimilar concentration patterns between runs 4 and 6 with respect to the first minutes it must be considered that the two reacting systems are significantly different. In run 4 HCl is formed on the catalyst surface due to chlorobenzene HDCl, where it reacts with pyridine or piperidine adsorbed on the same surface. These reactions lead to salts formation. In run 6 HCl is dispersed in the bulk of the liquid phase and not on the catalyst surface, which is acidic. When pyridine is loaded HDN reactions could take place on the catalyst surface in a similar way to run 4, but at the same time homogeneous acid–base reactions, between HCl and pyridine, could take place as well and the salts formed are then adsorbed on the catalyst surface. Therefore the patterns of salts formation in run 4 and 6 are different. This could be an explanation of the significant difference observed in the experimental data of pyridine concentration vs. reaction time between run 4 and 6 at the beginning of the process. When salts are formed and adsorbed on the catalyst surface, independently of how it happened, catalyst activity was reduced and HDN process to final products was stopped. This could be the reason for the very similar concentration patterns observed for $t > 60$ min between run 4 and 6.

Modelling the pyridine concentration pattern at the beginning of run 6 would require a better knowledge of the salt formation chemistry in organic phase.

5. Conclusions

The treatment of chlorinated liquid wastes by catalytic hydrodechlorination with Ni–Mo catalysts can be troublesome if basic nitrogen compounds are present.

In the most favourable situation [11] nitrogen compounds adsorb more strongly on the active sites of the catalyst thus reducing HDCl rate. In this case it would be sufficient to adopt higher temperature ($350 < T < 450^{\circ}\text{C}$) and pressure ($50 < P < 150$ bar) in order to let the HDN process reach a complete conversion. After that the HDCl process can take place rapidly. To enhance HDCl rate it would be necessary to maintain a low partial pressure of basic gaseous products of HDN (i.e. ammonia) in the reactor.

In the worst cases, as those studied in this paper, the very basic nitrogen compounds (like pyridine and piperidine) react with the hydrochloric acid, produced by HDCl, and form organic salts which adsorb strongly on the catalyst surface. As a consequence the HDN process is stopped and the activity of the catalyst toward HDCl is dramatically reduced. In these cases the use of higher temperature and pressure would not be useful and different process solutions must be found to realise the HDCl process economically.

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