

Simultaneous catalytic hydroprocessing of chlorine-, nitrogen-, and sulphur-containing aromatic compounds

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Received 10 April 1997; accepted 30 June 1997

Abstract

With the aim of assessing catalytic hydrogenation as a promising method for the disposal of hazardous organic waste liquids, an experimental investigation on the simultaneous hydroprocessing of chlorine-, sulphur- and nitrogen-containing chemicals over a Ni–Mo/ γ -Al₂O₃ sulphided catalyst is presented. The model compounds chlorobenzene (CB), quinoline (Q) and benzothio-
phene (BT) were hydroprocessed one at a time or in admixture using hexadecane as reaction medium. The behaviour of these chemicals, in the hydrogenation runs carried out, gives useful information regarding the problems which could arise when organic industrial waste liquids containing chlorine-, nitrogen-, and sulphur-compounds are hydrotreated. The model compounds have been hydrotreated separately at $T = 320^\circ\text{C}$ and in admixture at the temperatures 280, 300, 320, and 350°C . The hydrogen pressure was kept constant at 40 bar. The experimental results show that both hydrodechlorination (HDCI) and hydrodesulphurization (HDS) processes were strongly inhibited by the presence of quinoline. On the contrary hydrodenitrogenation (HDN) of quinoline was not significantly influenced by the presence of both chlorobenzene and benzothio-
phene. The reason for this behaviour resides in the fact that the nitrogen compounds are strongly basic and adsorb preferentially on the acidic catalyst surface. Therefore, the sharing of the active surface was strongly in favour of the nitrogen compounds. In particular, it was found that decahydroquinoline (DHQ), which is the intermediate with the highest adsorptivity, played the dominant role in subtracting, in a substantial way, active sites to the HDCI and HDS processes.
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Keywords: Catalytic hydrogenation; Hydrochlorination (HDCI); Hydrodenitrogenation (HDN)

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1. Introduction

As discussed by Gioia [1], catalytic hydrogenation is a possible alternative method for the disposal of hazardous waste liquids formed by organic chemicals. In fact, the toxic nature of most organic waste liquids is primarily due to the presence of chemical compounds containing heteroatoms (primarily Cl, N, O, S) in their chemical structure. Catalytic hydroprocessing would, therefore, be an appropriate method for detoxifying these wastes because the heteroatoms are eliminated by hydrogenolysis as HCl, NH₃, H₂O or H₂S, respectively (which are easily controlled inorganics) leaving the host compound non-toxic. The final product is, thus, a mixture of hydrocarbons that can be used in many different ways.

A great deal of research has been devoted to hydroprocessing. In particular the hydrodenitrogenation (HDN) and the hydrodesulphurization (HDS) processes have long been thoroughly investigated for the upgrading of petroleum fractions and coal-derived liquids. More recently, many papers on hydrodechlorination (HDCI) as a safe disposal of chlorinated organic waste liquids have been published [2–7]. In fact, many chlorinated hydrocarbons (particularly the aromatic ones) are known to pose a threat to the environment; e.g. the production of polychlorinated biphenyls was banned in the '80s.

In the present work, the hydroprocessing of liquid mixtures of chlorine-, nitrogen-, and sulphur-containing organic compounds was investigated. Thus simulating the hydroprocessing of real life toxic wastes. The hydrotreating of single organic compounds containing more than one heteroatom in their chemical structure is reported in the literature; (e.g.: halogeno-benzothiophenes over Co–Mo/Al₂O₃ [8]; chloropyridinols over Ni–Mo/ γ -Al₂O₃ [9]). Recently, 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] prove that even for HDCI the activity of composite Ni–Mo catalysts is higher than the sum of the activities of the single components Ni and Mo.

The aim of the present study is to investigate on the presence of synergistic or antagonistic effects when chlorine, nitrogen, and sulphur compounds are simultaneously hydroprocessed employing a presulphided commercial Ni–Mo/ γ -Al₂O₃ catalyst. In order to achieve this goal chlorobenzene, quinoline and benzothiophene have been catalytically hydroprocessed both simultaneously and one (or two) at a time. The combined hydroprocessing was compared with the hydroprocessing of the single compounds. The investigation showed that both the reaction networks and the kinetic constants of each single compound are indeed influenced to a greater or lesser extent by the presence of the other compounds. In particular, the HDCI and the HDS reactions were strongly inhibited by the presence of quinoline. The explanation is that the intermediates of the HDN of quinoline being basic, they were strongly adsorbed on the acidic catalyst thus reducing the number of active sites available for the HDCI and HDS reactions.

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. It was loaded in the reactor and heated to reaction temperature. When this temperature was reached, the reactant/s and the sulphided catalyst (Ni–Mo/ γ -Al₂O₃) 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 $t = 0$. During the run the hydrogen pressure was adjusted to the set value when necessary. The reacting process has been controlled by regular sampling of the liquid phase carried out, at fixed reaction times, using a sampling line at the bottom of the reactor. A sintered steel filter, at the beginning of the sample line, prevented loss of catalyst. The materials are listed in Table 1. The experimental conditions and the range of operating variables of the reaction runs are summarised in Table 2.

The catalyst sulphiding was carried out at 400°C (4 h) with a 100 cm³/min flow of a gas mixture of H₂S (10%) and H₂. To protect the sulphidation of the catalyst during the reaction runs, a quantity ($\cong 0.04$ g) of CS₂ was loaded in the autoclave together with the reactant and the catalyst. The CS₂ acts as an H₂S precursor, thus maintaining the catalyst in the sulphided form.

The analysis of the reaction samples withdrawn from the reactor during the course of the reaction was carried out by two gas-chromatographs: PE-8000 equipped with FPD (for sulphur compounds) and FID detectors, and PE-Autosystem with NPD (for nitrogen

Table 1
Materials

Reaction medium	Hexadecane 99% (Aldrich)
Reactants	Chlorobenzene 99%, Benzothiophene 99%, Quinoline 98% (Aldrich) Hydrogen GC grade (99,999%) from SIO ALPHAGAZ.
Catalyst	HDS-9A, American Cyanamide; NiO = 3.1%, MoO ₃ = 18.3%, (weight percent) supported on alumina. Specific surface 149 m ² /g, porosity = 0.51 cm ³ /g. Ground and sieved 150–200 mesh.
CS ₂	99+ % (Aldrich)

Table 2
Experimental conditions; $p_{H_2} = 40$ bar for all runs

Run	T [°C]	W_{CB} [g]	W_Q [g]	W_{BT} [g]	W_{cat} [g]	W_{cat}/W_{sol}
1	280	0.60	0.61	0.57	0.46	4.76×10^{-3}
2	300	0.54	0.53	0.54	0.46	4.71×10^{-3}
3	320	–	0.65	–	0.39	4.27×10^{-3}
4	320	–	–	0.53	0.42	4.33×10^{-3}
5	320	–	0.56	0.58	0.41	4.20×10^{-3}
6	320	0.51	0.53	0.54	0.42	4.37×10^{-3}
7	350	0.60	0.63	0.58	0.24	2.50×10^{-3}

compounds) and ECD (for chlorine compounds) detectors. Both instruments carried a capillary column (crosslinked methyl silicone; 50 m long).

3. Results and discussion

The general purpose of the present work is to observe how the hydroprocessing reaction networks of the single model compounds (chlorobenzene, quinoline, and benzothiophene) change when they are hydrotreated as a mixture. The basis for interpreting the modification of the reaction patterns, when the three components were hydrotreated in a mixture, are the networks of the single components. We have chosen to run experiments in the range 280–350°C which is suitable for HDCI and HDS but not for HDN. This choice is dictated by the desire of developing a reliable technique for detoxifying chlorinated wastes even when contaminated by N- and S-compounds. In order to make comparisons based on data internally consistent (obtained at the same operating conditions and in the same laboratory), besides the runs in which the three components are in admixture, we also carried out runs of HDN of quinoline alone (run 3) and HDS of benzothiophene alone (run 4) at $T = 320^\circ\text{C}$. Runs of HDCI of chlorobenzene alone in the temperature range 250–350°C had already been carried out in our laboratory and are discussed in Refs. [5–7].

3.1. HDN of quinoline

The hydrodenitrogenation network for quinoline over Ni–Mo/ $\gamma\text{-Al}_2\text{O}_3$ catalyst has been studied extensively for producing environmentally acceptable clean fuels. The results of the numerous investigations are reported in the literature: e.g. Refs. [11–13]. In order to reach high denitrogenation levels, temperatures greater than 350°C are necessary [13]. In practice, the HDN level passes from 6% to 42% by raising the temperature from 330 to 375 [11]. Therefore, results of the experimental investigations reported in the literature are in the temperature range between 350–400°C inasmuch as the HDN process is usually carried out in this temperature range. Therefore, in order to acquire data in the temperature range chosen for this work, we carried out a specific run of HDN of quinoline alone at $T = 320^\circ\text{C}$ (run 3). The compounds identified in the course of the reaction are the same as those reported in the literature [11–13]: quinoline (Q), 1,2,3,4-tetrahydroquinoline (1THQ), 5,6,7,8-tetrahydroquinoline (5THQ), decahydroquinoline (DHQ), orthopropylaniline (OPA), propylcyclohexene, *n*-propylcyclohexane and propylbenzene. However, unlike a previous investigation at 350°C by Gioia and Lee [12], at 320°C we observed that decahydroquinoline (DHQ) was present at very small concentration levels and only in the final samples (i.e. after 4–5 h from the beginning of run), and that the overall mass balance based on the identified compounds did not check.

The results of run 3 ($T = 320^\circ\text{C}$ quinoline only) were interpreted on the basis of the network reported in Fig. 1. This network is a simplified version of the complete network of HDN of quinoline reported by Gioia and Lee [12]. The simplifications introduced are consistent with the experimental findings at $T = 320^\circ\text{C}$ and appropriate for the aim of the present work. Namely, because at $T = 320^\circ\text{C}$ the formation of DHQ through 5THQ

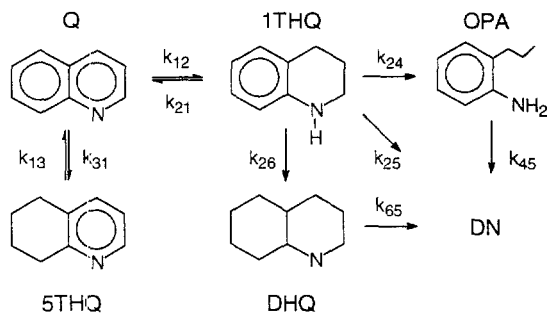


Fig. 1. Reaction network used for modelling quinoline hydrodenitrogenation at $T = 320^{\circ}\text{C}$ and $p_{\text{H}_2} = 40$ bar.

is not relevant [13] reaction $5\text{THQ} \rightarrow \text{DHQ}$ was not considered. Furthermore, the denitrogenated compounds (propylcyclohexene, *n*-propylcyclohexane and propylbenzene) were lumped together in a group named DN. The experimental concentration data points vs. time of: Q, 1THQ, 5THQ, OPA, and DN for run 3 are reported in Fig. 2. The DHQ which was detected only in the last few samples is not considered in Fig. 2, due to its very low concentration levels.

Since we are dealing with heterogeneous catalytic reactions, a sensible assumption would be to adopt Langmuir-type kinetic equations to model HDN of quinoline. However, for the purpose of this work (i.e. comparison of reaction patterns), it proved sufficient to adopt the simple pseudo-first order approximation. We remark that this is a strong assumption because N-compounds are basic and adsorb strongly on the acidic

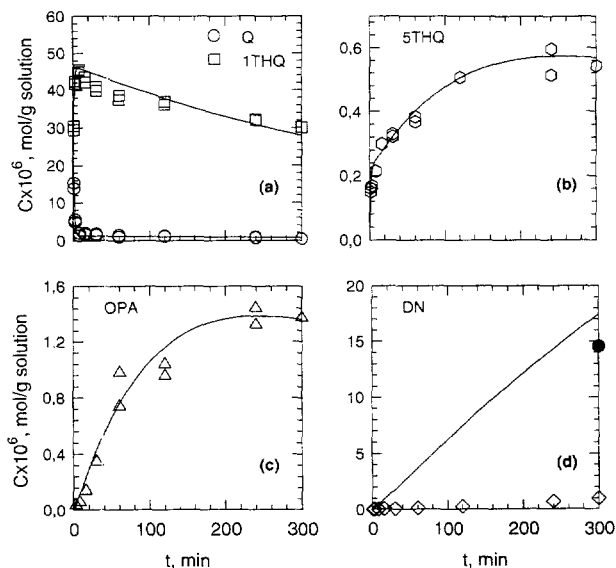


Fig. 2. Quinoline HDN in the absence of benzothiophene and chlorobenzene. Run 3 ($T = 320^{\circ}\text{C}$ and $p_{\text{H}_2} = 40$ bar). DN stands for denitrogenated compounds. Fitting curves based on the network of Fig. 1 and the kinetic constants of Table 3.

Table 3

Kinetic constants k'_{ij} [g solution/(g cat min)] for the HDN of quinoline

Run	T	Reactants	k'_{12}	k'_{21}	k'_{13}	k'_{31}	k'_{24}	$k'_{25} + k'_{26}$	k'_{45}
1	280	Cl–N–S	190.6	11.87	0	0	0	0.77	0
2	300	Cl–N–S	174.5	7.96	0.70	2.34	0.02	0.48	0.3
3	320	N	200.0	5.45	0.96	1.38	0.09	0.32	1.94
5	320	N–S	180.9	8.29	0.57	2.28	0.02	0.18	0.41
6	320	Cl–N–S	188.6	8.55	0	0	0.10	0.43	2.81
7	350	Cl–N–S	169.8	6.45	0.11	3.11	0	0.78	3.44

For ij , see Fig. 1.

catalyst. Thus, assuming first order kinetics, we regressed the concentration vs. time data points of the N-compounds only (i.e. Q, 1THQ, 5THQ, and OPA) by using the statistical method proposed by Himmelblau et al. [14], and determined the values of the pseudo-first order kinetic constants: k_{12} , k_{21} , k_{13} , k_{31} , k_{24} , $(k_{25} + k_{26})$, k_{45} [min^{-1}]. Then, using these kinetic constants, the set of differential equations describing the disappearance of N-compounds was integrated. The fitting curves obtained for run 3 are reported in Fig. 2. The kinetic constants were expressed in terms of the unit weight of catalyst by multiplying them by the ratio $W_{\text{sol}}/W_{\text{cat}}$ (see Table 2), and are reported in Table 3. Notice that the high values k'_{12} indicate that the reaction $Q \leftrightarrow 1\text{THQ}$ is an equilibrium reaction. It is indeed reported in the literature [13] that this reaction proceeds almost quantitatively up to the equilibrium concentration at temperatures even below 200°C.

Inspection of Fig. 2 shows that while the concentration data points of Q, 1THQ, 5THQ and OPA are well fitted, those of the DN group are not fitted at all and the mass balance does not check. The hypothesis to explain this mass balance discrepancy is that, due to the acidic nature of the catalyst and to the basicity of nitrogen compounds, some nitrogen intermediate remains strongly adsorbed on the catalyst. As a matter of fact the most basic intermediate is DHQ. Actually the $\text{p}K_{\text{a}}$ of DHQ is not available in the literature. However, it must be close to that of piperidine ($\text{p}K_{\text{a}} = 11.1$). Notice, for comparison, that quinoline has a $\text{p}K_{\text{a}} = 4.9$ and ammonia has a $\text{p}K_{\text{a}} = 9.3$; higher basicity is indicated by higher $\text{p}K_{\text{a}}$. Therefore, we may infer that DHQ is the intermediate which remains strongly adsorbed on the catalyst surface. The same conclusion may be reached if we consider the adsorption constants of nitrogen compounds on Ni–Mo/ $\gamma\text{-Al}_2\text{O}_3$ as calculated by La Vopa and Satterfield [15]. The data of these authors indicate that DHQ has indeed the largest adsorption constant with respect to other intermediates (e.g. $K_{\text{DHQ}}/K_{\text{Q}} = 2.0$; $K_{\text{DHQ}}/K_{\text{1THQ}} = 4.3$; $K_{\text{DHQ}}/K_{\text{NH}_3} = 42$). In order to prove experimentally that the mass balance discrepancy is due to nitrogen compounds which remain adsorbed, the catalyst at the end of the run was recovered from the reactor and contacted with a very strong base (NaOH solution). The organic compounds eventually released by the catalyst were extracted in hexadecane and analysed. The analysis showed that the compound released was essentially DHQ. The amount of DHQ recovered is reported, in terms of concentration of DHQ in the reacting mixture, as a filled circle in Fig. 2d. This data point shows that taking the DHQ adsorbed into account, noticeably improves the mass balance of the run.

In conclusion, the DHQ produced during the hydrotreating, due to its high basicity, remained strongly adsorbed on the acidic catalyst. Only at the end of the run, when the amount adsorbed became larger, some DHQ appeared in the liquid phase. It will be shown later that the strong adsorptivity of DHQ was responsible for a noticeable depression of HDCl and HDS processes in the presence of quinoline.

3.2. HDN of quinoline in admixture with benzothiophene and chlorobenzene

The HDN of quinoline, when this compound was reacted together with benzothiophene (run 5) and with benzothiophene + chlorobenzene (runs 1, 2, 6, 7) was interpreted by a procedure analogous to that described previously for run 3. The calculated kinetic constants are reported in Table 3. Inspection of this table shows that in all cases reaction $Q \leftrightarrow 1THQ$ is an equilibrium reaction and that production of 5THQ is negligible in the temperature range 280–350°C.

When quinoline was hydrotreated in admixture with benzothiophene only (run 5, $T = 320^\circ\text{C}$) a slight reduction of the kinetic constants k'_{24} , $(k'_{25} + k'_{26})$ and k'_{45} may be observed with respect to the case of HDN of quinoline only (run 3). These constants refer essentially to hydrogenolysis reactions. Therefore, the reduction of these kinetic constants can be attributed to the sharing of the hydrogenolysis active sites with the intermediates of benzothiophene HDS.

Even when quinoline was hydrotreated in admixture with chlorobenzene and benzothiophene (run 6, $T = 320^\circ\text{C}$) only minor changes in the kinetic constants were observed. The rate of reaction $Q \leftrightarrow 1THQ$ still remained practically unchanged, while the kinetic constants k'_{24} , $(k'_{25} + k'_{26})$ and k'_{45} were this time somewhat larger than those pertaining to run 3 (quinoline only, $T = 320^\circ\text{C}$) and thus even more larger than in run 5 (Q in admixture with BT, $T = 320^\circ\text{C}$). Therefore it seems that the presence of Cl-compounds has a positive, even though slight, effect on the hydrogenolysis reactions of HDN of quinoline. Maybe that the hydrochloric acid produced by HDCl reacted with the basic DHQ, thus reducing its inhibiting effect.

Observing the dependence on temperature (runs 1, 2, 6 and 7) we can state that, apart from the experimental uncertainties, the kinetic constants (besides k'_{45}) are not strongly influenced by the temperature in the investigated range. In fact, it is reported in the literature [13] that significant changes in the reaction rates of quinoline HDN occur at $T > 350^\circ\text{C}$.

By the above analysis the following preliminary conclusions may be drawn: (i) the HDN of quinoline is not substantially influenced by the presence of S- and Cl-compounds; (ii) the presence of benzothiophene has a weak depressive effect on HDN; (iii) the presence of chlorobenzene has a slight positive effect on HDN. These conclusions allow us to infer that the sharing of active sites is in favour of the strongly basic nitrogen compounds.

3.3. HDCl of chlorobenzene

The catalytic HDCl of chlorobenzene over Ni–Mo/ γ -Al₂O₃ sulphided catalysts is simply described by the single reaction



The rate of this reaction has been successfully described by a pseudo-first order kinetics [2–7]. The values of the kinetic constant of reaction (1) and of the parameters of the Arrhenius equations, as obtained in our laboratory in the temperature range 250°C–350°C and for hydrogen pressures varying from 30 to 100 bar, are reported in Refs. [5–7].

The $\ln(C/C^0)$ vs. the reaction time of chlorobenzene, when this compound is hydrotreated in the presence of quinoline and benzothiophene, is reported in Fig. 3 for

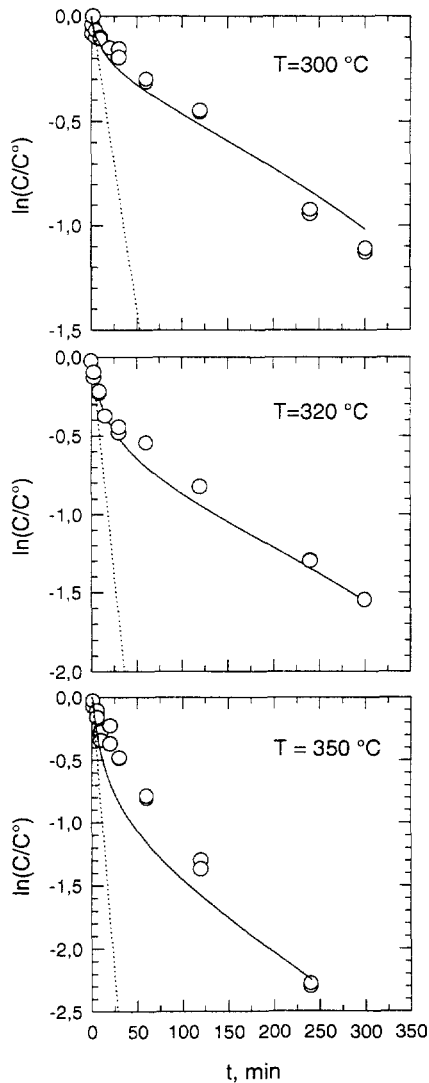


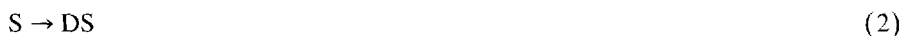
Fig. 3. Chlorobenzene HDCl in the presence of benzothiophene and quinoline (runs 2, 6 and 7). Solid lines are fitting curves based on Eq. (10). Dotted lines are theoretical curves for HDCl of chlorobenzene in the absence of quinoline and benzothiophene based on kinetic constants from Ref. [7] (see Table 4).

the runs of major interest: 2, 6 and 7. The dotted lines are the calculated values of $\ln(C/C^0)$ using the kinetic constant of reaction (1) at the temperature of the runs [7]. The solid lines are model predictions to be discussed later. By comparing the data points with the dotted lines, we observe that the rate of reaction (1) is dramatically reduced when chlorobenzene is in admixture with quinoline and benzothiophene.

3.4. HDS of benzothiophene

Run 4 was carried out hydrotreating only benzothiophene at $T = 320^\circ\text{C}$. The compounds identified during the reaction run were: benzothiophene (BT), 2,3-dihydrobenzothiophene (HBT), ethylbenzene (EB) and styrene (ST). The data are well correlated by the network of Fig. 4, identified by other authors [16,17] over a similar catalyst (Co–Mo). The values of the pseudo-first-order kinetic constants for run 4, obtained by means of the regression procedure proposed by Himmelblau et al. [14], are reported in the same figure in units of [g sol/g cat min]. The fitting of the concentration data points of the identified compounds of run 4 using the kinetic constants reported in Fig. 4 is represented in Fig. 5.

When BT was reacted with quinoline (run 5) the HDS network was strongly modified. In particular, we observed that styrene did not appear anymore among the reaction products, and that the path $\text{BT} \rightarrow \text{HBT} \rightarrow \text{EB}$ was no longer important. Moreover, the rate of all reactions was drastically reduced. As it is not our purpose in this work to determine quantitatively how the single HDS reactions are retarded by the presence of N- and Cl-compounds we will refer to the overall desulphurization as expressed by the single reaction:



where S represents all the S-compounds (BT and HBT), and DS stands for the desulphurated compounds (ST and EB). Experimental data of S-compound concentrations vs. t (expressed as $\ln(C/C^0)$) at $T = 320^\circ\text{C}$ (runs 4, 5 and 6) are reported in Fig. 6. By comparing the data of run 4 (BT only) with those of run 5 (BT + Q) we observe that quinoline has a strong depressive effect on HDS of benzothiophene. An important depressive effect of N-compounds on HDS of thiophene is reported by [15]. On the contrary, the data points of run 6 (CB + Q + BT) show that the further addition of chlorobenzene in the mixture has only a slight effect on HDS rate.

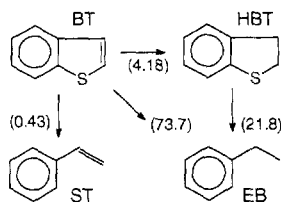


Fig. 4. Reaction network for HDS of benzothiophene in the absence of chlorobenzene and quinoline. Numbers in brackets are kinetic constants [g sol/g cat min] for run 5 ($T = 320^\circ\text{C}$, $p_{\text{H}_2} = 40$ bar).

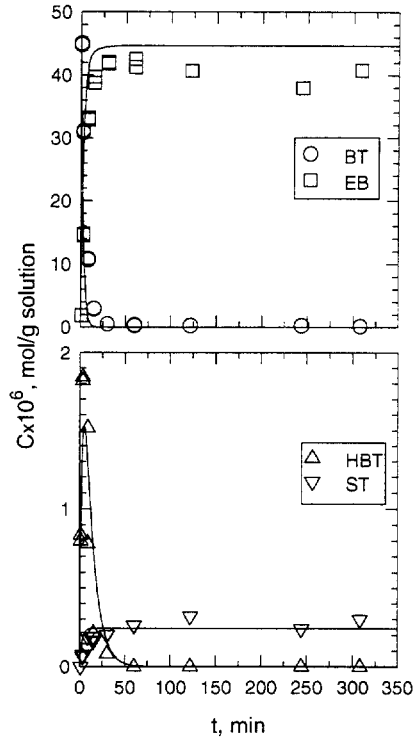


Fig. 5. Benzothiophene HDS in the absence of chlorobenzene and quinoline. Run 5 ($T = 320^\circ\text{C}$ and $p_{\text{H}_2} = 40$ bar). Fitting curves based on the network and the kinetic constants of Fig. 4.

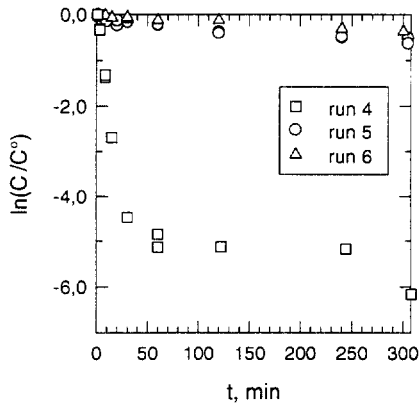


Fig. 6. Benzothiophene HDS. Variation of S-compounds (BT + HBT) concentration vs. time. Runs: 4 (BT); 5 (BT + Q); 6 (BT + Q + CB). $T = 320^\circ\text{C}$ and $p_{\text{H}_2} = 40$ bar. The data at the top of the diagram (runs 5, 6) are detailed in Fig. 7.

These evidences, together with that previously discussed that HDN of quinoline is not significantly influenced by both chlorobenzene and benzothiophene, allow us to state that N-compounds depress strongly both HDCl and HDS processes on Ni–Mo/ γ -Al₂O₃ catalysts. On the contrary, chlorobenzene and benzothiophene interfere only weakly on one another. Moreover, the data show that the depressive effect of quinoline is stronger on HDS than on HDCl. In fact after 60 min (at 320°C) the ratio C_S/C_{S^*} is about 100 while the ratio C_{CB}/C_{CB^*} is about 10.

4. Modelling the inhibition of HDCl and HDS due to N-compounds

The starting hypothesis on which the model is based is that the activity lost by the catalyst toward the HDCl and HDS reactions can be thought of as a surface coverage by an intermediate of HDN of quinoline. We assume that DHQ, which has the largest adsorptivity [15], is the intermediate responsible for the blocking of the active sites necessary for the course of HDCl and HDS reactions.

Referring to the symbols in Fig. 1, the rate of DHQ formation is:

$$\frac{dC_{DHQ}}{dt} = k_{26}C_{1THQ} - k_{65}C_{DHQ} \quad (3)$$

As reported in Ref. [13], and as it results also from the data of Table 3, at $T \leq 350^\circ\text{C}$ reaction $Q \leftrightarrow 1THQ$ is a fast equilibrium reaction shifted to the right, and the rate of reaction $1 \leftrightarrow 3$ is negligible. Therefore, we may write:

$$C_{1THQ} \approx C_Q^0 \exp[-(k_{2 \rightarrow})t] \quad (4)$$

where for brevity it has been set:

$$k_{2 \rightarrow} = (k_{24} + k_{25} + k_{26}) \quad (5)$$

which is the overall kinetic constant of the rate of disappearance of 1THQ. Substituting Eq. (4) into Eq. (3) and integrating we obtain:

$$C_{DHQ} = \frac{k_{26}C_Q^0}{k_{65} - k_{2 \rightarrow}} [\exp(-k_{2 \rightarrow}t) - \exp(-k_{65}t)] \quad (6)$$

DHQ adsorbs on the active sites of the catalyst according to a Langmuir mechanism. Assuming that the adsorption rate is much faster than the surface reaction, the adsorption step is at equilibrium. Therefore at any time t , the fraction of active sites not blocked by DHQ is given by:

$$\frac{C_{/\alpha}}{C_{/\alpha}^0} = 1 - \frac{K_{DHQ,\alpha}C_{DHQ}}{1 + K_{DHQ,\alpha}C_{DHQ}} \quad (7)$$

$C_{/\alpha}^0$ is the total concentration of active sites. Active sites involved in reactions (1) and (2) are not the same. Reaction (1) takes place on hydrogenolysis sites, while reaction (2) takes place on both hydrogenation and hydrogenolysis sites. For simplicity we assume that reactions (1) and (2) involve completely different sites. Therefore, the values of $C_{/\alpha}$, $C_{/\alpha}^0$, and $K_{DHQ,\alpha}$ depend on the reaction we consider. For brevity, we have introduced the subscript α which may be either CB or S. Namely, when we consider

reaction (1) then $C_{\ell\alpha}$ is $C_{\ell\text{CB}}$ and $K_{\text{DHQ},\alpha}$ is $K_{\text{DHQ},\text{CB}}$. When we consider reaction (2), $C_{\ell\alpha}$ is $C_{\ell\text{S}}$ and $K_{\text{DHQ},\alpha}$ is $K_{\text{DHQ},\text{S}}$. Substituting Eq. (6) into Eq. (7) we obtain:

$$\frac{C_{\ell\alpha}}{C_{\ell\alpha}^0} = \frac{1}{1 + \frac{K_{\text{DHQ},\alpha} k_{26}}{k_{65} - k_{2\rightarrow}} C_{\text{Q}}^0 [\exp(-k_{2\rightarrow} t) - \exp(-k_{65} t)]} \quad (8)$$

Consider runs 1, 2, 5, 6 and 7 in which CB and BT are hydrotreated in presence of Q. We can determine the rate of reaction (1) or reaction (2) by means of the following reasoning: it has been shown [2–7] that a first order rate equation is a good approximation for reaction (1) similar assumption holds true for reaction (2). Therefore, the rate of either reaction (1) or reaction (2) may be shortly written as:

$$\frac{dC_{\alpha}}{dt} = -k_{\alpha}^0 \frac{C_{\ell\alpha}}{C_{\ell\alpha}^0} C_{\alpha} \quad (9)$$

in which k_{α}^0 is the kinetic constant of reaction (1) or reaction (2) when either CB or BT are hydrotreated alone. Substituting Eq. (8) into Eq. (9) we obtain:

$$\frac{dC_{\alpha}}{dt} = -k_{\alpha}^0 \frac{C_{\alpha}}{1 + \frac{K_{\text{DHQ},\alpha} k_{26}}{k_{65} - k_{2\rightarrow}} C_{\text{Q}}^0 [\exp(-k_{2\rightarrow} t) - \exp(-k_{65} t)]} \quad (10)$$

In the case of chlorobenzene, k_{α}^0 is k_{CB}^0 . The values of this kinetic constant, in the temperature range 280–350°C, are obtained from Murena [7] and are reported in Table 4 in units of min^{-1} . In the case of benzothiophene, the constant k_{α}^0 is k_{S}^0 . The value of k_{S}^0 , reported in Table 4, has been evaluated by reworking the data of run 4 ($T = 320^{\circ}\text{C}$) according to the simple reaction (2). The value of $k_{2\rightarrow}$ is calculated from the data of Table 3.

The experimental data of runs 1, 2, 5, 6 and 7 have been regressed using Eq. (10). The product $K_{\text{DHQ},\alpha} k_{26}$ and the constant k_{65} have been determined as adjustable parameters and are reported in Table 4. The fitting curves, obtained from Eq. (10) with the parameters of Table 4, are drawn as continuous lines in Fig. 3 (runs 2, 6 and 7) for

Table 4

Parameters of Eq. (10) for modelling the HDCl of chlorobenzene and the HDS of benzothiophene in the presence of quinoline

Run	T [°C]	Reactants	Input parameters			Output parameters		
			k_{CB}^0 [min^{-1}]	k_{S}^0 [min^{-1}]	$k_{2\rightarrow}$ [min^{-1}]	$K_{\text{DHQ}} k_{26}$ [g sol/mol min]	k_{65} [min^{-1}]	
1	280	Cl–N–S	1.3×10^{-2}		3.7×10^{-3}	2.5×10^3	8.0×10^{-3}	
2	300	Cl–N–S	2.8×10^{-2}		2.4×10^{-3}	6.5×10^3	2.0×10^{-2}	
5	320	N–S		0.13	8.6×10^{-4}	4.8×10^4	1.3×10^{-2}	
6	320	Cl–N–S	5.6×10^{-2}		2.4×10^{-3}	6.0×10^3	1.0×10^{-2}	
7	350	Cl–N–S	9.0×10^{-2}	0.13	2.4×10^{-3}	7.0×10^4	1.0×10^{-2}	
					2.0×10^{-3}	4.5×10^3	1.0×10^{-2}	

HDCI reaction (1), and in Fig. 7 (runs 5 and 6) for HDS reaction (2). As can be observed the experimental data points are satisfactorily correlated. It must be noted that we obtained at 320°C the same value of the constant k_{65} (see Table 4) by separately regressing the HDCI and the HDS data of run 6 and a very similar value when regressing HDS data of run 5. In the paper by Gioia and Lee [12] it is reported, at 350°C, a value of k_{65} which is comparable with that of Table 4 at the same temperature.

Inspection of Table 4 shows, on the contrary, that the regression of the S data and the CB data of run 6 produce $K_{DHQ,S}$ which is larger than $K_{DHQ,CB}$ for a factor of about 10. Possible explanation is that in HDCI only hydrogenolysis sites are involved, while in HDS both hydrogenation and hydrogenolysis sites play a role. If we assume that DHQ adsorbs preferentially on hydrogenation sites more than on hydrogenolysis sites, the difference in the values of the two adsorption constants may be justified. In fact, Nagai et al. [18], studying the poisoning effect of nitrogen compounds on the HDS of dibenzothiophene on sulphided Ni–Mo/ γ -Al₂O₃ catalyst, report that N-compounds are effective poisons for dibenzothiophene hydrogenation but not for the desulphurization

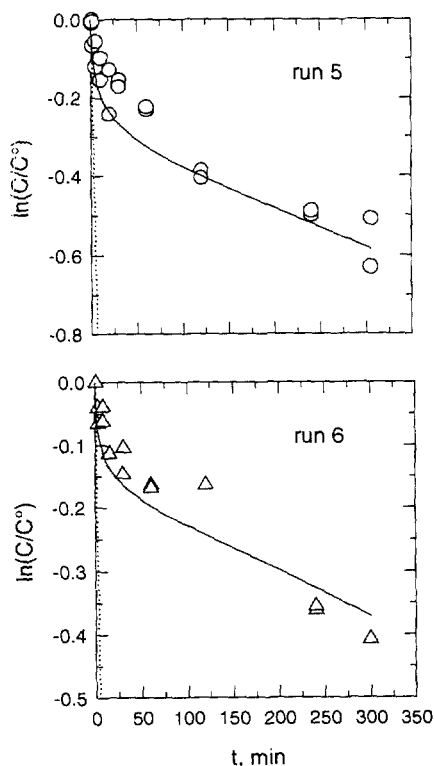


Fig. 7. Benzothiophene HDS in the presence of chlorobenzene and quinoline. Variation of S-compounds (BT+HBT) concentration vs. time. Runs: 5 (BT+Q); 6 (BT+Q+CB). $T = 320^{\circ}\text{C}$ and $p_{\text{H}_2} = 40$ bar. Solid lines are fitting curves based on Eq. (10) and constants of Table 4. Dotted lines are theoretical curves for HDS of benzothiophene alone based on reaction (2) and kinetic constant k_6° of Table 4.

reaction. They conclude that nitrogen compounds adsorb strongly on the hydrogenation sites. As a matter of fact we found that the path $BT \rightarrow HBT \rightarrow EB$ is no more important when BT is reacted with Q.

5. Conclusions

A particularly interesting means of detoxifying liquid wastes containing chlorine-, nitrogen-, and sulphur-organic compounds is catalytic hydroprocessing. The results obtained from this work indicate that when quinoline, benzothiophene and chlorobenzene are treated in admixture, the reaction networks and the reaction rates are modified. In particular, our results show that HDN is only slightly modified by the presence of sulphur- and chlorine- compounds. On the contrary, the rates of HDS and of HDCI are dramatically reduced by N-compounds. In particular HDS is depressed more than HDCI. The reason is that N-compounds may be strongly basic and adsorb preferentially on the active surface of the acidic Ni–Mo/ γ -Al₂O₃ catalyst. In particular decahydroquinoline, which is the intermediate of HDN of quinoline with the highest adsorptivity, plays the dominant role in poisoning the catalyst. This phenomenon leads the HDCI and HDS processes almost to a stop. Further investigation is needed to ascertain if higher temperatures and longer reaction times could be beneficial to the HDCI and HDS processes in the presence of N-compounds. At higher temperatures the adsorption constant of the inhibitor would be reduced and its rate of disappearance would be increased. Therefore its poisoning effect would be reduced. Longer reaction times would make the HDN process arrive at completion, thus destroying (NH₃ aside) the strongly basic intermediates and making active sites again available for the HDCI and HDS reactions.

6. Nomenclature

C°	Initial concentration (mol/g of solution)
C_i	Molar concentration of species i in liquid solution (mol/g of solution)
$C_{i^{\circ}}$	Molar concentration of species i in liquid solution when compound i is hydrotreated alone (mol/g of solution)
$C_{f\alpha}/C_{f\alpha}^{\circ}$	Fraction of free active sites.
k_{ij}	Pseudo-first order kinetic constant of the reaction leading from compound i to product j (min^{-1})
k'_{ij}	Pseudo-first order kinetic constant (i and j as above) (g of solution/min g of catalyst)
k_{α}°	Pseudo-first order kinetic constant of compound α hydrotreated alone (min^{-1}).
$k_{2 \rightarrow}$	See Eq. (5) (min^{-1})
K_i	Adsorption constant of compound i (g of solution mol^{-1})
p_{H_2}	Hydrogen partial pressure (bar).
t	Reaction time (min)

T	Temperature (°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)

Subscript

α	CB or S (see reactions (1) and (2))
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Mathematical operations

$\ln x$	The logarithm of x to the base e .
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Acknowledgements

This work was financed by research grants from ‘Ministero dell’Università e della Ricerca Scientifica e Tecnologica’ and from ‘Consiglio Nazionale delle Ricerche’. The intelligent contribution of Ingg. Vincenzo Scarpa and Enrico Ruocco in carrying out the experiments and in working out the experimental data is to be acknowledged.

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