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Comparative Study of Activity and Selectivity of Transition Metal Sulfides in Parallel Hydrodechlorination of Dichlorobenzene and Hydrodesulfurization of Methylthiophene

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Carbon-supported sulfides of V, Cr, Mn, Fe, Co, Ni, Mo, Ru, Rh, Pd, W, Ir, and Pt were compared in parallel hydrodechlorination (HDC) of *o*-dichlorobenzene and hydrodesulfurization (HDS) of 3-methylthiophene at 300°C and 1 MPa in a flow reactor. The reference catalyst was a commercial hydrotreating Ni–Mo/Al_2O_3 sulfide catalyst. The work was related to disposal of chlorinated organic wastes contaminated by sulfur and to HDC in organic technology. The kinetics were described by means of a parallel consecutive scheme of pseudo first-order reactions. Pt-group metal sulfides exhibited the highest HDS activity but their ranking did not fully correlate with literature results on HDS in the absence of HDC, the maximum activity being at Pd and Pt in the second and third rows, respectively. The Pd sulfide was by far the best HDC catalyst showing about two times higher activity than the reference Ni–Mo sample. The ranking of the sulfides in HDC corresponded with published reports on comparative studies on HDC over metals. The selectivity to intermediate chlorobenzene was the highest on Pd and the lowest on Ni–Mo, with maximum conversions to chlorobenzene during the reaction of 64 and 15%, respectively. HDC was faster than HDS over the conventional Ni–Mo system but the behavior of other sulfides was very heterogeneous. The Ni sample was very selective to HDC (HDC conversion of 90% at HDS conversion of 10%), the Pt and Ir sulfides were very selective to HDS (HDC conversion of 10% at HDS conversion of 90%), and the rates of HDC and HDS were about the same over the Mo sulfide. The features of the parallel HDC/HDS were discussed in the relation to performance of metal sulfides in other hydrotreating reactions: HDS in the absence of chlorine compounds, hydrodearomatization, and hydrodenitrogenation. © 1997 Academic Press

INTRODUCTION

Chlorinated hydrocarbons are hazardous pollutants which are contained in various waste oils and other waste organic liquids. The options of their disposal include incineration, catalytic incineration, pyrolysis, reaction with alkali metals or their compounds, catalytic hydrogenolysis, etc. The advantages and drawbacks of these alternatives have been discussed by previous authors (e.g., (1, 2)).

Catalytic hydrodechlorination (HDC) is simple, safe, and effective. The produced HCl is easily separated and the refined hydrocarbons can be recycled. There is no opportunity for the formation of more hazardous products such as chlorinated dibenzofurans or dioxins which can be formed in oxidative processes. HDC is easily catalyzed by metals of Group VIII of the Periodic Table under a mild temperature of 50–200°C (e.g., Pd/Al_2O_3, Rh/Al_2O_3 (3), Ni/SiO_2, Pd/Al_2O_3 (4), and Pt/zeolite (5)). However, metallic catalysts are very sensitive to sulfur and other poisons often contained in the processed waste. For instance, a typical feedstock considered for processing of used oils in a refinery contains 0.3% Cl and 0.2% S (6). The presence of poisons requires application of resistant sulfide catalysts at the higher temperatures of about 300–350°C.

The HDC process over sulfide catalysts represents the adoption of conventional hydrorefining technology of hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodearomatization (HDA) of oil fractions to disposal of chlorinated wastes. The commercial HDC processes reported in the literature are the UOP Decontamination process and the UOP Direct Contact Hydrogenation process (7–9) or the KTI Chloroff process (10, 11). The available information on catalysts used is very limited but the conventional Ni(Co)–Mo/alumina sulfide catalysts are presumably applied. Recently, the full-scale HDC of polychlorinated biphenyls in used oils under usual hydrotreating conditions over unspecified Ni(Co)–Mo/alumina catalyst was reported (12).

The choice of catalysts in previous basic studies on HDC over sulfides relating to disposal of wastes was limited to Co–Mo (e.g., (2, 13)), Ni–Mo (e.g., (2, 14–18)), and Ni, Mo, and Ni–Mo (19, 20) sulfides. These papers mostly dealt with the reaction network and kinetics of the HDC of mono-, di-, tri-, or hexachlorobenzene. HDC catalysts based on other transition metal sulfides have hardly been studied previously.

HDC over sulfides was also studied in relation to organic technology. During production of mono- and dichlorobenzenes by chlorination of benzene, the unwanted polychlorinated benzenes are formed. The selective dechlorination of these unwanted by-products to mono- and

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dichlorobenzenes was achieved by the selective HDC over sulfided Pt/Al_2O_3 and Pd/Al_2O_3 catalysts; the reaction over metals was nonselective producing benzene and cyclohexane (21).

The purpose of the present work was the comparison of parallel HDC and HDS over various transition metal sulfides. The relatively inert support active carbon was selected in order to avoid possible interactions of some metal ions with more reactive alumina which is the conventional support of industrial sulfide catalysts. The model reaction was parallel HDC of *o*-dichlorobenzene and HDS of 3-methylthiophene in the gas phase. The parameters evaluated were HDS and HDC activities, selectivity to intermediate chlorobenzene, and selectivity to HDC versus HDS. The reference sample was a commercial hydrotreating catalyst Ni–Mo/Al_2O_3.

EXPERIMENTAL

Catalysts

The support was the active carbon GA-1 (Slovenské lučobné závody, Hnúšt'a). The extrudates were crushed to the fraction 0.16–0.32 mm. It was refluxed several times with distilled water (total volume 20 dm^3 of water per 100 g of the support) to remove alkali and dried in a rotary vacuum evaporator (90–100°C, 4–6 kPa, 3 h). The BET surface area, pore volume, and micropore volume of the support were 1100 $m^2\ g^{-1}$, 0.75 $cm^3\ g^{-1}$, and 0.49 $cm^3\ g^{-1}$, respectively.

Industrial Ni–Mo/alumina hydrotreating catalysts typically contain 3–4% NiO (2.4–3.1% Ni), 12–18% MoO_3 (8–12% Mo), and their molar loading of Mo is about 0.98–1.60 mmol Mo per 1 g of the support. The metal (Me) loading of the present Me/C catalysts was 0.95 mmol Me per 1 g of active carbon. The catalysts, their Me weight loading, and the salts used in their preparation are summarized in Table 1.

The volume of the impregnation solution was 20% higher than the packing volume of the support. The slurry was left standing 1 h at 80°C under a reflux condenser and was dried in a rotary vacuum evaporator (90–100°C, 4–6 kPa, 2 h). The catalysts were not calcined because active carbon impregnated with transition metal salts is susceptible to oxidation. The supported salts were transformed to the active sulfide phase by *in situ* presulfidation in the catalytic reactor.

The reference catalyst was the industrial catalyst Ni–Mo/Al_2O_3 Shell 324. Its composition is shown in Table 1. The extrudates were crushed to 0.16–0.32 mm particle size fraction.

Apparatus and Procedure

A tabular flow reactor with a fixed catalyst bed and a gas phase reaction mixture was used. The liquid feed contained 3 mol% of *o*-dichlorobenzene (DCB) and 3 mol% of 3-methylthiophene (MTH) in *n*-decane (D). The solution was fed into the evaporator part of the reactor by a piston pump. The liquid products were collected in a condenser at 0°C and were drained off at 15-min intervals. They were analyzed by GLC (Apiezon L) using decane as the internal standard. The products of the DCB reaction were chlorobenzene (CB) and benzene (B) and the products of the reaction of MTH were C_5 hydrocarbons. Other carbon-containing products were negligible.

TABLE 1

Me/C Sulfide Catalysts Studied

Metal Me	Metal loading[a] (wt%)	Impregnation salt
Catalysts with molar loading 0.95 mmol Me per 1 g support		
V	4.60	NH_4VO_3
Cr	4.70	$Cr(NO_3)_3$
Mn	4.96	$MnCl_2$
Fe	5.03	$Fe(NO_3)_3$
Co	5.29	$Co(NO_3)_2$
Ni	5.27	$Ni(NO_3)_2$
Mo	8.35	$(NH_4)_6Mo_7O_{24}$
Ru	8.76	$RuCl_3$
Rh	8.89	$RhCl_3$
Pd	9.18	$PdCl_2$
W	14.86	$(NH_4)_2WO_4$
Ir	15.40	$(NH_4)_2IrCl_6$
Pt	15.60	H_2PtCl_6
Catalysts with other loading[b]		
Ni(0.41)	2.35	$Ni(NO_3)_2$
Ni(0.086)	0.50	$Ni(NO_3)_2$
Reference catalyst[b]		
Ni–Mo/Al_2O_3(0.54 + 1.44)	2.70 + 11.80	—

[a] Per weight of catalyst.

[b] Loading in parentheses is in mmol Me per 1 g support.

MTH was chosen as a model compound instead of the more usual thiophene for experimental reasons. The higher boiling point of MTH than that of thiophene is convenient for quantitative condensation of the reaction mixture at the reactor outlet. The GLC separation of thiophene and benzene (the product of the DHC reaction) is rather difficult, while the separation of all components when MTH is used is easy.

The catalyst charge (W) was in the range of 0.01 to 1.5 g and charges smaller than 0.03 g were diluted with inert low surface area corundum. It was presulfided *in situ* by an H_2S/H_2 mixture (molar ratio 1 : 10) at atmospheric pressure; the temperature was increased for 45 min to 400°C and kept at 400°C for 2 h. The reaction temperature was 300°C, the pressure was 1.0 MPa, and the molar composition of the feed was 0.33% DCB, 0.33% MTH, 10.73% D, and 88.61% H_2.

The composition of the reaction mixture was expressed in molar fractions, a_i: $a_{\mathrm{DCB}} = n_{\mathrm{DCB}}/n^{\circ}_{\mathrm{DCB}}$, $a_{\mathrm{CB}} = n_{\mathrm{CB}}/n^{\circ}_{\mathrm{DCB}}$, $a_{\mathrm{B}} = n_{\mathrm{B}}/n^{\circ}_{\mathrm{DCB}}$, and $a_{\mathrm{MTH}} = n_{\mathrm{MTH}}/n^{\circ}_{\mathrm{MTH}}$, where n°_i and n_i are the initial and final number of moles, respectively, and

$n^{\circ}_{\mathrm{DCB}} = n_{\mathrm{DCB}} + n_{\mathrm{CB}} + n_{\mathrm{B}}$. The molar fractions are related to the conversions: $a_{\mathrm{DCB}} = 1 - x_{\mathrm{DCB}}$, $a_{\mathrm{CB}} = x_{\mathrm{CB}}$, $a_{\mathrm{B}} = x_{\mathrm{B}}$, and $a_{\mathrm{MTH}} = 1 - x_{\mathrm{MTH}}$, where x_{DCB} is the overall conversion of DCB, x_{CB} is the conversion to CB, x_{B} is the conversion to B, and x_{HDS} is the HDS conversion.

The feed rate (F) was defined as the moles of one reactant: $F = F_{\mathrm{DCB}} = F_{\mathrm{MTH}}$. The integral curve of the composition (conversion) versus *W/F* for each catalyst was measured using three to five different charges of the catalyst, each charge being tested at two different F values. Steady-state conversions were achieved with the fresh catalyst charge after about 90–150 min on stream. Typically, a decrease of activity was observed in this initial time period; the maximum decrease among the catalysts was about 25% of the initial activity. However, the activity of Pd and Ir was essentially stable and the activity of Ru increased during initial time period. Activity changes during the next 6 h were negligible for all catalysts. It was checked experimentally using the Ni–Mo/Al_2O_3 catalyst that the conversions were not influenced by external or internal diffusion. In the steady state, the material balance of the reactor evaluated by chromatography (n°_{DCB} versus $n_{\mathrm{DCB}} + n_{\mathrm{CB}} + n_{\mathrm{B}}$ and n°_{MTH} versus $n_{\mathrm{C_5}}$) was always better than 100 ± 5%.

RESULTS AND DISCUSSION

Hydrogenation of Aromatic Ring

HDC of chlorobenzenes over metallic catalysts (in the absence of sulfur) is usually accompanied by hydrogenation of aromatic ring (HDA) even at low hydrogen pressure (3, 5, 22, 23). However, HDA is practically completely suppressed in HDC over sulfided Ni(Co)–Mo/Al_2O_3 (13–20) and Pt/Al_2O_3 and Pd/Al_2O_3 (21) catalysts. The results of the present work show that this conclusion can be generalized to all transition metal sulfides. The formation of cyclohexane was not observed over any Me/C sulfide catalyst studied. This high selectivity of sulfides to HDC versus HDA is important because it minimizes the consumption of expensive hydrogen in the processing of chlorinated wastes, which contain aromatics.

Analysis of the selectivity in hydrorefining HDS, HDN, and HDA reactions revealed that the activation energies of hydrogenolytic steps (substitution) are systematically higher than those of hydrogenation (addition) steps (24, 25). The rather scarce literature data support the generalization of this rule also to HDC: the activation energy of HDC of chlorobenzene to benzene over metallic Rh/Al_2O_3 catalyst was higher than of consecutive hydrogenation of benzene to cyclohexane (22). Typical HDC temperatures over metals and sulfides are 50–200 and 300–350°C, respectively. It can be concluded that the different selectivity HDC/HDA of metals and sulfides seems at least to a certain extent to be connected with their different working temperature.

Formal Kinetics

Each catalyst was characterized by the integral curve $a_i = f(W/F)$ at the same fixed pressure, temperature, and feed(index) composition. Hydrogen was present in large excess and the change of its partial pressure in the course of the reaction was neglected. Examples of the integral curves measured are presented in Fig. 1: the Rh/C catalyst exhibited about the same activity to HDC and HDS, the Co/C sample was selective to HDC and the Ir/C catalyst was selective to HDS.

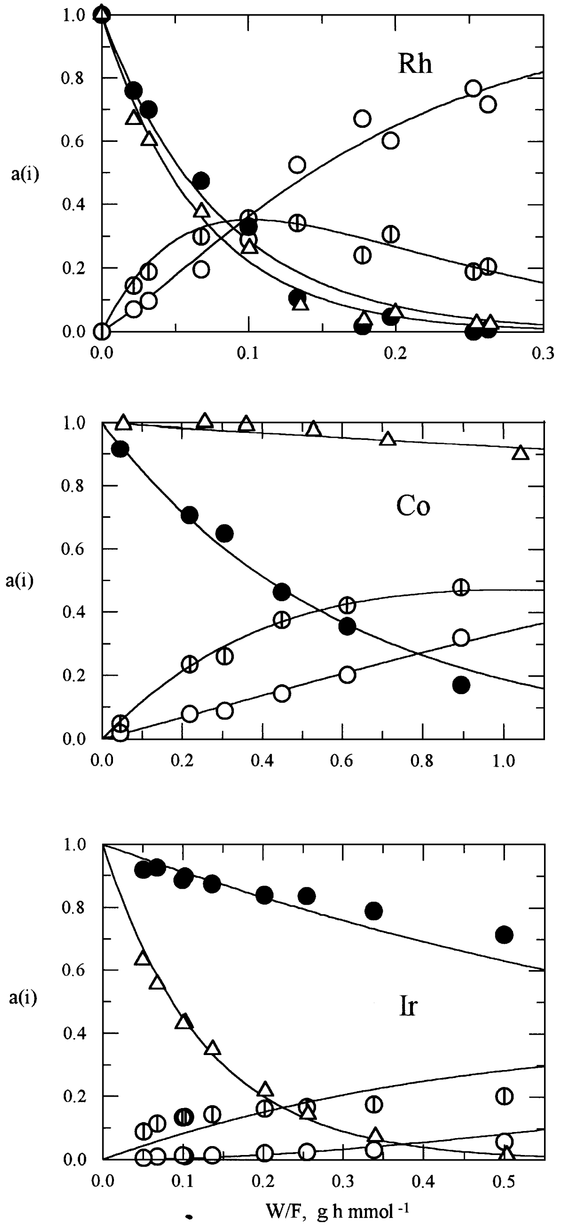
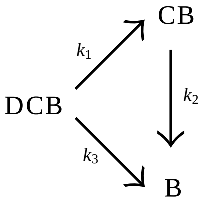


FIG. 1. Composition of the reaction mixture versus space time in parallel hydrodechlorination of dichlorobenzene (DCB) and hydrodesulfurization of methylthiophene (MTH). ●, DCB; ⦶, chlorobenzene; ○, benzene, △, MTH.

The range of conversions measured for Ni, Mo, Ru, Pd, and Pt catalysts was similar to those shown for Rh, Co, and Ir samples in Fig. 1 where the highest conversion of the more reactive reactant was in the range 0.85–1.00. The activity of W, V, Cr, Mn, and Fe catalysts was lower and the conversions at the highest achievable space time were in the range 0.1–0.3. The highest achievable space time was limited by the volume of the reactor and by the lowest flow rate acceptable from the point of view of external mass transfer. This space time was about 1.5 g h mmol^{-1}. However, the reliable evaluation of activity and HDC/HDS selectivity of these less active catalysts was always achieved; on the other hand, the precise evaluation of the selectivity to intermediate chlorobenzene was difficult from low conversion data (see below).

It would be expected that in a broad range of initial partial pressures of reactants the description of the parallel HDC and HDS would require the use of relatively complicated Langmuir–Hinshelwood type equations containing several rate and adsorption constants. However, the present data were obtained at one fixed initial composition and good correlation was obtained using a set of simple pseudo first-order rate equations. In this respect, the present kinetic analysis was similar to the approach used by previous authors (17) studying HDC of trichlorobenzene over a Ni–Mo/alumina catalyst in a batch reactor in the absence of parallel HDS (only with the addition of CS_2 to keep the catalyst in the sulfided form). The same kinetics were also used in our previous papers on HDC over sulfided Ni, Mo, and Ni–Mo catalysts supported on alumina (19) and active carbon (20).

The correlation of the HDC data by the scheme of two consecutive pseudo first-order reactions with the intermediate CB was unsatisfactory. However, a good fit was obtained using the consecutive-parallel scheme of three pseudo first-order reactions:



[1]

where k_1, k_2, and k_3 are the pseudo first-order rate constants.

Integration of the corresponding rate equations provides the dependence of the composition on space time:

$$a_{\mathrm{DCB}} = \exp[-(k_1 + k_3)W/F] \qquad [2]$$

$$a_{\mathrm{CB}} = \{k_1/(k_2 - k_1 - k_3)\} \times \{\exp[-(k_1 + k_3)W/F] - \exp[-k_2 W/F]\} \qquad [3]$$

$$a_{\mathrm{B}} = 1 - a_{\mathrm{DCB}} - a_{\mathrm{CB}}. \qquad [4]$$

The constants were calculated by a nonlinear regression and are summarized in Table 2. The quality of the fit over all catalysts was as good as those shown for Rh/C and Co/C samples in Fig. 1. The only exception from this rule was Ir/C catalyst where the curve for the intermediate was not well fitted (Fig. 1). However, to keep the kinetic evaluation of all catalysts uniform, no other kinetics were tried for the Ir/C sample.

TABLE 2

Kinetic Constants (mmol g^{-1} h^{-1}) of Parallel-Consecutive Scheme [1] of the Hydrodechlorination of Dichlorobenzene

Metal Me	k_1	k_2	k_3
First row			
V	0.136	0.0010	0.0289
Cr	0.172	0.0010	0.0284
Mn	0.230	0.0010	0.0230
Fe	0.0942	0.20	0.0001
Co	1.33	0.518	0.330
Ni	11.5	3.66	9.78
Second row			
(Nb)	—	—	—
Mo	0.330	0.0010	1.87
(Tc)	—	—	—
Ru	1.98	1.32	0.381
Rh	9.45	7.46	3.06
Pd	88.0	9.66	19.9
Third row			
(Ta)	—	—	—
W	0.130	0.0010	0.0790
(Re)	—	—	—
(Os)	—	—	—
Ir	0.918	1.00	0.0001
Pt	0.430	0.268	0.0658
Reference catalyst			
Ni–Mo/Al_2O_3	8.00	20.9	11.3

Exact definition of single-parameter HDC activity is difficult in Scheme [1]. None of the constants k_1, k_2, and k_3 alone characterizes the HDC activity and it is not possible to combine them into single parameter. However, two alternative approaches can be used to evaluate the HDC activity.

(i) As seen from Scheme [1] the disappearance of DCB followed the pseudo first-order rate equation with compounded rate constant ($k_1 + k_3$). This constant is a good measure of the HDC activity provided that the compared catalysts produce similar amount of the intermediate CB. However, this was not the case in the present work (see selectivity to CB below) and the use of this compounded constant would misrepresent the HDC activity.

(ii) The conversion x_{HCl} of organic chlorine to hydrogen chloride can be used for evaluation of HDC activity. This conversion is defined as

$$x_{\mathrm{HCl}} = n_{\mathrm{HCl}}/2n^{\circ}_{\mathrm{DCB}}, \qquad [5]$$

TABLE 3

Activity (mmol g^{-1} h^{-1}) of Me/C Sulfide Catalysts in Parrallel Hydrodechlorination and Hydrodesulfurization

Metal Me	k_{HCl}	k_{HDS}
First row		
V	0.132	0.088
Cr	0.157	0.149
Mn	0.013	0.004
Fe	0.043	0.012
Co	0.896	0.079
Ni	7.60	0.363
Second row		
(Nb)	—	—
Mo	1.82	1.26
(Tc)	—	—
Ru	1.37	2.60
Rh	7.41	15.0
Pd	38.2	26.3
Third row		
(Ta)	—	—
W	0.192	0.331
(Re)	—	—
(Os)	—	—
Ir	0.441	7.99
Pt	0.279	52.2
Reference catalyst		
Ni–Mo/Al_2O_3	15.2	8.80

where n_{HCl} is the final number of moles of hydrogen chloride. It is related to other conversions by the stoichiometric relationship

$$x_{HCl} = x_{DCB} - 0.5x_{CB} = x_B + 0.5x_{CB}. \qquad [6]$$

It was found that the experimental conversions x_{HCl} followed approximately the pseudo first-order kinetics:

$$x_{HCl} = 1 - \exp[-k_{HCl}W/F], \qquad [7]$$

where k_{HCl} is the rate constant characterizing HDC activity. The constants k_{HCl} were calculated by the nonlinear regression and are summarized in Table 3, the quality of fit being illustrated in Fig. 2. It is seen that the scope of the activity was broad and that the accuracy of the fit was quite sufficient to discriminate between the catalysts. A crossing of the curves $x_{HCl} = f(W/F)$ for various catalysts was not observed.

The same approach to evaluate HDC activity was also used by other authors in the HDC of trichlorobenzene in the absence of parallel HDS over sulfided Ni–Mo/Al_2O_3 catalyst in the liquid phase in a batch reactor (16, 17).

It should be mentioned that Scheme [1] and Eqs. [2]–[4] on the one hand and Eq. [7] on the other hand cannot hold simultaneously. This is seen by the substitution for x_{DCB} and x_{CB} from Eqs. [2] and [3], respectively, into Eq. [6]: a first-order equation is not obtained. The set of Eqs. [2]–[4] and Eq. [7] are two alternative and independent kinetic approximations.

The HDS data were well fitted by the pseudo first-order rate equation

$$a_{MTH} = 1 - x_{MTH} = 1 - x_{HDS} = \exp[-k_{HDS}W/F], \qquad [8]$$

where k_{HDS} is the rate constant. The calculated constants are summarized in Table 3 and the quality of the fit is illustrated in Fig. 1.

It should be stressed that the above kinetic correlation of the HDS and HDC data is only formal and the equations used have no chemical implications. For instance, it is clear that MTH is not transformed to pentane and hydrogen sulphide in one step (as would follow from chemical interpretation of Eq. [8]), and the simultaneous removal of two chlorine atoms from the benzene ring is not probable (as would follow from a chemical interpretation of step 3 in Scheme [1]). Chemical interpretation of Eqs. [2]–[4] and [8] would also mean that there is no interaction between HDC and HDS, which also seems improbable from a chemical point of view. The aim of the present kinetic measurement and correlation was evaluation of activity and selectivity of transition metal sulfides across the Periodic Table. The key experimental variable was the type of catalyst and the only kinetic variable was space time; other variables were fixed. The purpose of the above kinetic correlation using formal kinetic equations was to obtain space time-independent (conversion-independent) indexes of activity and selectivity. The kinetic study of chemical mechanism would require a quite different design of kinetic experiments: the catalyst type should be fixed (measurement with only one catalyst) and the data should be obtained in a broad range of HDS and HDC reactant pressures, broad range of hydrogen pressure, broad range of space time, and different temperatures. It was not the aim of the present work to study the chemical mechanism.

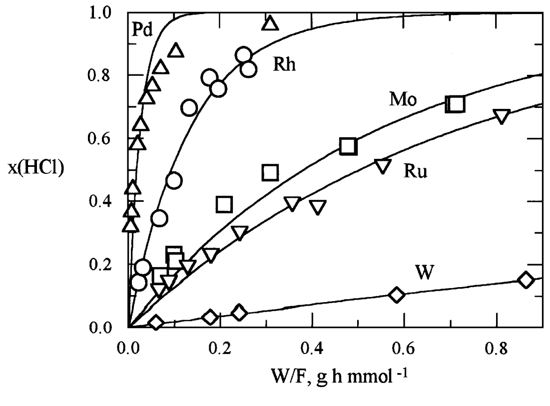


FIG. 2. Conversion of organic chlorine to HCl versus space time in parallel hydrodechlorination of dichlorobenzene and hydrodesulfurization of methylthiophene.

Trends in HDS Activity

Several previous comparative studies of HDS activity of transition metal sulfides have been published (26–30) and reviewed (31–33). However, no previous data on HDS activity in the presence of parallel HDC are available.

The literature data on the ranking of transition metal sulfides according to thier HDS activity (in the absence of parallel HDC) are summarized in Table 4. In spite of different model compounds, reaction conditions and form of catalysts (support, activation, normalization of activity), the following two general rules emerge. The universality of these rules is further corroborated by the literature data on HDN which are also presented in Table 4.

(i) Pt-group metal sulfides possess the highest activity. The activity of the best of them is comparable or even higher than the activity of the bimetallic synergistic system Ni(Co)–Mo.

(ii) The maximum activity among Pt-group metal sulfides in the second and third rows is mostly observed at Rh and Ir, respectively, or at Ru and Os, respectively. The only exception to this rule is the position of Pd and Pt in Refs. (29) and (30), respectively (see Table 4). However, the maxima at Pd and Pt are not particularly pronounced in these cases (relative activities were Pd/Rh = 1.2 and Pt/Ir = 1.9 in Refs. (29) and (30), respectively).

The HDS activities in the presence of parallel HDC observed in the present work are in full agreement with the above rule (i) (Tables 3 and 4). It is concluded that any possible specific effect of chlorine compounds on HDS activity is not strong enough to change the outstanding position of Pt-group metal sulfides among sulfide catalysts (including the bimetallic synergistic Co(Ni)–Mo system).

However, the HDS activities in the presence of parallel HDC do not obey the above rule (ii). A very pronounced maximum in the second and the third row at Pd and Pt is seen in Table 3 (relative reactivities are Pd/Rh = 1.8 and Pt/Ir = 6.5). Deeper insight into this observation requires further study of mutual interaction between HDS and HDC which was outside the scope of the present work.

Trends in HDC Activity

No previous data on comparison of the HDC activity of transition metal sulfides have been published. The HDC data of Table 3 will be discussed in connection with hydrogenolysis over metals (in the absence of sulfur) and with the overall activity of sulfide catalysts in hydrogenation reactions.

TABLE 4

Ranking of Sulfide Catalysts According to Their Hydrodesulfurization (HDS) and Hydrodenitrogenation (HDN) Activity[a]

Reference:	(26)	(27)	(28)	(29)	(30)	(34)	(35)	(36)	(35)	Present work
	HDS[b]	HDS[c]	HDS[c]	HDS[d]	HDS[e]	HDS[f]	HDS[g]	HDN[h]	HDN[i]	HDS
	Ru	Ir	Rh	Pd	Pt	Ru	Rh	Ir	Ir	Pt
	Os	Rh	Ir	Rh	Ir	Rh	Ru	Os	Pt	Pd
	Ir	Ru	Os	Ir	Rh	Cr	Ir	Pt	Rh	Rh
	Rh	Cr	Ru	Pt	Mo	Co	Pt	Re	Ru	Ir
	Re	Os	Re	Re	W	V	Pd	Rh	Pd	Ru
	Pt	Re	Pd	Ru	Cr	Mo		Ru		Mo
	Pd	Pt	Mo	Mo	Fe	Fe		Pd		Ni
	Mo	Co	Pt	Co	Ni	Nb		Mo		W
	Cr	Pd	Co	V	Co	Ni		W		Cr
	W	Fe	Cr	Ni	Mn	Pd		Ni		V
	Nb	Mo	V	Cr		Mn		Co		Co
	Ni	Ni	W	Fe				Cr		Fe
	Co	W	Ni	Nb				Fe		Mn
	Zr	Mn	Nb	W				Mn		
	V		Fe	Mn						
	Fe		Ta							
	Mn									

[a] Activity decreases from top down; the catalyst with the lowest activity among Pt group metal sulfides measured is underlined.

[b] Dibenzothiophene, unsupported MeS_x.

[c] Thiophene, MeS_x/C.

[d] Benzothiophene, MeS_x/C.

[e] Thiophene, MeS_x/Al_2O_3.

[f] Thiophene, unsupported MeS_x.

[g] Thiophene (parallel HDN), MeS_x/C.

[h] Quinoline, MeS_x/C.

[i] Pyridine, MeS_x/C.

It is well known that Pd is by far the most active metal in HDC in the absence of sulfur (3, 37). The same is seen for HDC over sulfides in Table 3. The Pd/C sulfide catalyst was even more active than the bimetallic synergetic system Ni–Mo. The activity of metallic catalysts Me/polyamide in HDC of chlorobenzene decreased in the order Pd > Rh > Pt (23) and the same is seen for sulfides in Table 3. All this suggests that the ranking in the Pt group metal sulfides is similar to that of metals.

The HDC activity of sulfides in Table 3 systematically increases with increasing atomic number in the first and second rows of Group VIII of the Periodic Table. However, this regularity is not preserved in the third row where Ir and Pt exhibited very low activity. The remarkable phenomenon is very different ranking of Pt in HDC and HDS activities: it is the best in HDS but the worst in HDC among Pt-group metal sulfides. The consequence of this activity behavior is the extremely low HDC/HDS selectivity of the Pt/C sample discussed below.

Selectivity to Intermediate Chlorobenzene

The intermediates with gradually decreasing number of chlorine atoms have been observed in all previous papers on HDC of di-, tri-, and hexachlorobenzenes in the absence of parallel HDS over Ni(Co)–Mo sulfide catalysts (2, 14–20). In agreement with this the intermediate CB was observed over all transition metal sulfides in the present work.

The amount of CB observed in the gas phase depends on the balance of rates of several processes: surface formation and dechlorination of adsorbed CB and adsorption and desorption of CB. The data of the present work do not allow a detailed kinetic analysis. However, they show that the balance between these steps is rather sensitive to the nature of the transition metal sulfide.

Examples of selectivity graphs $x_{\mathrm{CB}} = f(x_{\mathrm{DCB}})$ illustrating the differences between the catalysts are shown in Fig. 3. The curves in Fig. 3 were calculated using Eqs. [2] and [3] and the constants k_1, k_2, and k_3 from Table 2. It is seen in Fig. 3 that the constants k_1, k_2, and k_3, which were obtained by fitting the activity curves $x_i = f(W/F)$, do not describe the selectivity curves accurately for some catalysts. A nonlinear regression of the $x_{\mathrm{CB}} - x_{\mathrm{DCB}}$ selectivity data independent of the fitting of the activity data $x_i - W/F$ would certainly provide a better fit of the selectivity curves. However, to keep the kinetic description simple and uniform such an additional regression of the selectivity data was not performed. This approximate approach to selectivity evaluation was justified by the large differences between the catalysts.

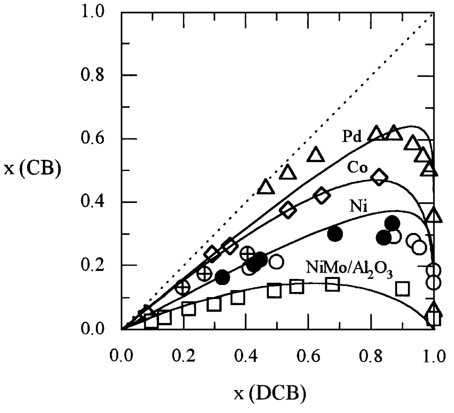


FIG. 3. Selectivity to intermediate chlorobenzene (CB) in parallel hydrodechlorination of dichlorobenzene (DCB) and hydrodesulfurization of methylthiophene (MTH). ○, Ni(0.95); ●, Ni(0.41); ⊕, Ni(0.086).

For the scheme of two consecutive first-order reactions, the selectivity curve of the conversion to intermediate versus conversion of starting compound is fully and simply described by a single parameter, the ratio of rate constants. The situation in the present case of the parallel-consecutive scheme of three first-order reactions is not so simple; the selectivity curve depends in a rather complicated way on the three constants k_1, k_2, and k_3 which cannot be combined into a single selectivity parameter. However, the selectivity can be discussed in terms of the maximum conversion to CB during the reaction, $x_{\mathrm{CB}_{\mathrm{MAX}}}$. The overall conversion x_{DCB} at which $x_{\mathrm{CB}_{\mathrm{MAX}}}$ occurs is named in the present work $x_{\mathrm{DCB}_{\mathrm{MCB}}}$ (the index MCB is for “maximum of chlorobenzene”). The values of these two conversions were calculated using Eqs. [2]–[4] and the constants k_1, k_2, and k_3 in Table 2 and are presented in Table 5.

It is seen that $x_{\mathrm{CB}_{\mathrm{MAX}}}$ was always located at relatively high $x_{\mathrm{DCB}_{\mathrm{MCB}}}$ above 0.5. With the Co, Ni, Mo, Ru, Rh, Pd, Ir, Pt, and Ni–Mo catalysts the determination of $x_{\mathrm{CB}_{\mathrm{MAX}}}$ was reliable because the experimental conversions covered the region of the maximum; the calculation represented interpolation among experimental points. On the other hand, with the less active catalysts, V, Cr, Mn, Fe, and W, the determination of $x_{\mathrm{CB}_{\mathrm{MAX}}}$ was rather uncertain because all conversions x_{DCB} and x_{CB} measured were considerably lower than the calculated $x_{\mathrm{DCB}_{\mathrm{MCB}}}$ and $x_{\mathrm{CB}_{\mathrm{MAX}}}$; the calculation represented extrapolation far beyond the region of experimental points. That is the reason why the values for the less active catalysts are presented in parentheses in Table 5 and will not be discussed.

It is seen in Table 5 that the lowest amount of CB was formed over the conventional Ni–Mo/Al$_2$O$_3$ catalyst. The $x_{\mathrm{CB}_{\mathrm{MAX}}}$ of the majority of the Me/C samples was between 0.35 and 0.47 (Co, Ni, Ru, Rh, Ir, Pt). However, Mo/C was much less selective to CB and Pd/C was much more selective than that, with values of $x_{\mathrm{CB}_{\mathrm{MAX}}}$ of 0.15 and 0.64, respectively.

The high selectivity to CB observed for Pd in the present work corresponds well with the patent (21) which recommended the sulfided Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts for selective production of CB and DCB by hydrogenation of polychlorobenzenes (with minimized formation of

TABLE 5

Selectivity of Me/C Sulfide Catalysts to Intermediate Chlorobenzene and to HDC versus HDS

	Selectivity to intermediate CB		
Metal Me	$x_{CB_{MAX}}$	$x_{DCB_{MCB}}$	$S_{HDC/HDS}$
First row			
V	(0.80)	(0.99)	1.48
Cr	(0.84)	(0.99)	1.07
Mn	(0.46)	(0.98)	2.50
Fe	(0.24)	(0.48)	3.33
Co	0.47	0.82	11.40
Ni	0.38	0.88	20.90
Second row			
(Nb)	—	—	—
Mo	0.15	0.99	1.44
(Tc)	—	—	—
Ru	0.40	0.73	0.53
Rh	0.35	0.72	0.49
Pd	0.64	0.93	1.45
Third row			
(Ta)	—	—	—
W	(0.61)	(0.99)	0.57
(Re)	—	—	—
(Os)	—	—	—
Ir	0.35	0.62	0.06
Pt	0.42	0.74	0.01
Reference catalyst			
Ni–Mo/Al_2O_3	0.15	0.62	1.73

benzene). The Pd catalyst was preferred over the Pt catalyst as for activity and selectivity in that patent.

Selectivity to HDC Versus HDS

A well-arranged and clear evaluation of the selectivity HDC/HDS is obtained by plotting x_{HCl} versus x_{HDS} at the same space time. The examples shown in Fig. 4 illustrate that the selectivity varied in a broad range over the set of the catalysts studied. The Ni catalyst was very selective to HDC on the one hand, while Ir was very selective to HDS on the other hand. The important feature of the data was that the experimental curves $x_{HCl} = f(x_{HDS})$ did not cross mutually.

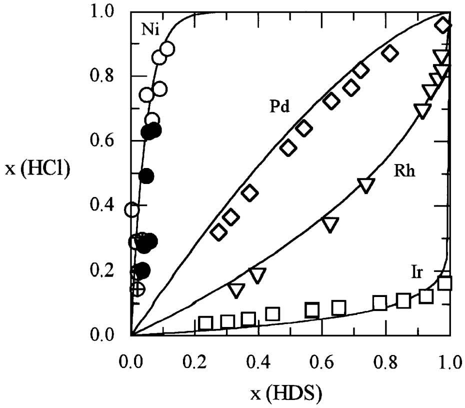


FIG. 4. Selectivity to hydrodechlorination versus hydrodesulfurization in parallel reaction of dichlorobenzene and methylthiophene: ○, Ni(0.95); ●, Ni(0.41); ⊕, Ni(0.086).

The selectivity, that is the position of the curve in Fig. 4, can be described by the single conversion-independent parameter $S_{HDC/HDS}$. Elimination of *W/F* from Eqs. [7] and [8] and rearrangement of the resulting equation gives

$$x_{HCl} = 1 - (1 - x_{HDS})^{S_{HDC/HDS}}, \qquad [9]$$

where $S_{HDC/HDS} = k_{HCl}/k_{HDS}$. HDC is faster than HDS over the catalysts with $S_{HDC/HDS} > 1$ and the opposite holds for the catalysts with $S_{HDC/HDS} < 1$. The values of $S_{HDC/HDS}$ were calculated using k_{HCl} and k_{HDS} from Table 3 and are summarized in Table 5.

It is seen in Fig. 4 that for Pd the fitting of the curve $x_{HCl} = f(x_{HDS})$ by Eq. [9] would provide slightly lower value of $S_{HDC/HDS}$ than that obtained from the ratio k_{HCl}/k_{HDS}. However, to keep the kinetic description uniform (the curves $x_{HCl} = f(x_{HDS})$, $x_{HCl} = f(W/F)$ and $x_{HDS} = f(W/F)$ are described by the same values of k_{HCl} and k_{HDS}), such fitting was not performed. Similarly as above for the selectivity to intermediate CB, such an approach was justified by the large differences in selectivity between the catalysts measured.

The Ni–Mo catalyst in Table 5 was selective to HDC ($S_{HDC/HDS} > 1$) which corresponds well with the scarce data previously published by other authors. Hydrogenation of 2,3-dichlorobenzothiophene over sulfided Co–Mo/Al_2O_3 catalysts proceeded via fast hydrogenolysis of chlorine substituents followed by slower consecutive desulfurization (38). Hydrotreating of a feed containing 0.11% Cl and 0.21% S over a Ni–Mo/Al_2O_3 catalyst produced an oil containing 0.005% Cl and 0.12% S; the conversion of organic Cl and S was 95 and 45%, respectively (6). However, the important new result seen in Table 5 is that the selectivity behavior of the conventional synergetic system Ni(Co)–Mo cannot be generalized to other transition metal sulfides. The HDS was much faster than HDC over some of them.

The dominant feature in Table 5 seems to be the difference between the rows. The sulfides of the metals of the first row are selective to HDC and this selectivity strongly increases with atomic number. The selectivity in the second row is medium. It is not strongly shifted to any side; two metal sulfides are rather selective to HDC and two others to HDS. The sulfides of the metals in the third row are selective to HDS and this selectivity strongly increases with atomic number.

Independence of Selectivities on Loading

Selectivity is an intensive parameter which is assumed to be much less dependent on metal sulfide loading than activity. This assumption was tested for the Ni/C catalyst which was prepared with the loading 0.95, 0.41, and 0.086 mmol Ni per 1 g of the support. The results are shown in Figs. 3 and 4. Both the selectivity to intermediate CB and the selectivity HDC/HDS were essentially independent of loading. It can be concluded that the selectivities reported in the present paper represent an intrinsic feature of the metal sulfides which is only little dependent on physical factors such as the active phase dispersion. The relatively small size of the test molecules seems to be important in this respect. For the large molecule of dibenzothiophene, a pronounced dependence of the selectivity to HDS versus hydrogenation on the morphology of MoS_2 catalyst was found (39).

General Comments on Catalytic Properties

In the present work the catalysts tested were presulfided and the feed contained sulfur compound. According to the literature on hydrotreating, the catalysts are in sulfide rather than in metal form under such conditions (see, for instance, Refs. (26, 27)). However, transformation of sulfides to chlorides should be considered in the presence of HCl during HDC. The literature on HDC over sulfided catalysts is practically limited only to Co(Ni)–Mo catalysts and gives no experimental information in this respect.

Stability of sulfides under hydrodechlorination conditions can be discussed using thermodynamic data summarized in Table 6. These data allow only very approximate evaluation of the situation because the thermodynamic data for well-defined bulk compounds are not fully representative for highly dispersed supported species. Nevertheless, it is seen that transformation of sulfides to chlorides is mostly very unfavorable. However, at least partial chlorination should be considered for Cr, Mn, and Fe. It would probably be more correct to use the term "presulfided transition metal catalysts" instead of "sulfide catalysts" for these latter metals.

TABLE 6

Gibbs Free Energy ΔG° of the Reaction of Metal Sulfide with Hydrogen Chloride at 327°C[a]

Metal	Reaction	ΔG° (kJ/mol of metal)
Cr	$Cr_2S_3 + 6HCl = 2CrCl_3 + 3H_2S$	−18
Mn	$MnS + 2HCl = MnCl_2 + H_2S$	−26
Fe	$FeS + 2HCl = FeCl_2 + H_2S$	−7
Co	$Co_9S_8 + 18HCl = 9CoCl_2 + 8H_2S + H_2$	+19
Ni	$Ni_3S_2 + 6HCl = 3NiCl_2 + 2H_2S + H_2$	+21
Mo	$MoS_2 + 4HCl = MoCl_4 + 2H_2S$	+231
Ru	$2RuS_2 + 6HCl + H_2 = 2RuCl_3 + 4H_2S$	+298
Pd	$PdS + 2HCl = PdCl_2 + H_2S$	+108
W	$WS_2 + 4HCl = WCl_4 + 2H_2S$	+265
Ir	$Ir_2S_3 + 6HCl = 2IrCl_2 + 3H_2S$	+225
Pt	$PtS + 2HCl = PtCl_2 + H_2S$	+142

[a] Calculated from data: Mo, Ref. (40); other metals, Ref. (41).

Several interesting attempts to rationalize the trends in activity of transition metal sulfides across the Periodic Table can be found in the literature (e.g. (26, 30, 42–44)). However, the principles which govern these trends are far from being understood. Among others, the fundamental obstacle which complicates generalization is that experimentally measured activity is composed of intensive and extensive factors (these can, for instance, be specified as quality and quantity of active sites, respectively). The reliable separation of these two factors is very difficult.

The most important (and mostly new) result of the present work seems to be that the catalytic features of transition metal sulfides in parallel HDC and HDS are very heterogeneous and often quite different from that of the conventional Ni–Mo/Al_2O_3 catalyst. A mechanistic explanation of the observed trends is not suggested in this discussion. However, the following concluding remarks illustrate the interest and importance of the present data.

The different efficiency of transition metal sulfides to activate hydrogen under hydrotreating conditions can be held as one of the most important factors determining their ranking according to activity. In previous comparative studies on HDS, HDN, and HDA the platinum group metal sulfides were with few exceptions distinctly more active than other metal sulfides and this might be explained by their outstanding properties in hydrogen activation. However, the data of the present work suggest that low degree of efficiency of reactant activation and/or unfavorable specific interaction with a reaction product (H_2S, HCl) might outweigh the effect of hydrogen activation over some catalysts. Platinum was by far the most active HDS catalyst in Table 3. It might be concluded that it is very effective in hydrogen activation in the presence of H_2S and HCl and that this should result in a reasonably fast HDC as well. However, the HDC activity of Pt in Table 3 was poor, even much lower than that of some metals outside the platinum group, Ni, Co, Mo. Better understanding of this behavior of Pt requires more detailed study of interaction between HDC and HDS which was outside the scope of the present work.

The mechanisms of HDS over sulfides and HDC over metals suggested in the literature exhibit certain resemblances. HDS was often interpreted as the formation/filling of sulfur vacancies (e.g., 32, 45). The HDC over metals was considered as the cycle chlorination/dechlorination of the surface (3, 46). Rather different ranking of metal sulfides in HDC and HDS seems to indicate that no simple parallelism exists between the rates of surface sulfidation/desulfidation and chlorination/dechlorination reactions.

The selectivity to intermediate CB is controlled by the ability of the catalyst to discriminate between CB and DCB. It is interesting that the two most active HDC catalysts represent two opposite extremes in the respect (Fig. 3 and Table 5).

The usual opinion in the literature is that among hydrotreating reactions over sulfide catalysts, HDN of aromatic heterocycles is more difficult, and HDC of chlorine bound to a benzene ring is easier than HDS of aromatic heterocycles. This view is based on the experience with Co–Mo and Ni–Mo catalysts and there seems to be the tendency in the literature to take it as a general phenomenon caused by the electronic structure of the reactants. However, it was recently shown that the relative HDN/HDS reactivity strongly depends on the catalyst and that HDN can be much faster than HDS (47). The present data proved that the same holds for the relative HDC/HDS reactivity. The behavior of some catalysts was quite different from the Ni–Mo sample. The HDC was much faster than HDS over Ni catalyst, while the completely opposite reactivity was found over the Pt sulfide.

The interaction between HDN, HDS, and HDA reactions is mostly strong and this is the important phenomenon in hydrotreating catalysis over sulfides (HDS inhibits HDA, HDN inhibits HDS and HDA, the effect of HDS on HDN is variable and not too strong; for a review see Ref. (48)). It is expected that this also holds for HDC/HDS and work in this direction over some selected sulfides is in progress in our laboratory.

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