Catalytic Hydrodeoxygenation

II. Interactions between Catalytic Hydrodeoxygenation of *m*-Cresol and Hydrodesulfurization of Benzothiophene and Dibenzothiophene

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Interactions during simultaneous catalytic hydrodesulfurization (HDS) and hydrodeoxygenation (HDO) are studied with (benzothiophene, dibenzothiophene)/(*m*-cresol) conversions over CoMo HDS catalysts. The mutual inhibition of cresol on HDS and of the benzothiophenes on HDO is shown. The reaction patterns observed are rationalized by competition between oxygenate and sulfur heterocycle for the catalyst sites. A Langmuir–Hinshelwood kinetic form provides a useful rate equation for simultaneous HDO/HDS operation. The relative reactivity in equimolar feed experiments is benzothiophene > dibenzothiophene > *m*-cresol. The modest reactivity of *m*-cresol, coupled with its inhibitory influence of HDS of benzothiophene and dibenzothiophene, has clear implications for HDS in coal liquids processing and HDN in shale oil conversions. In the mixed feeds of the present paper (II), as for the pure oxygenate feeds studied previously (I), no evidence is obtained that ring saturation of cresol is required prior to HDO.

INTRODUCTION

The interactions between hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions in relation to coal-liquefaction and hydroprocessing applications are only now appreciated (*1*). Since the catalytic studies of Satterfield *et al.* (*2*) on the interactions between HDS of thiophene and HDN of pyridine, increasing attention has been given to mixture studies involving both synthetic (model compounds) and real feedstocks (*1, 3, 4, 22*). While interactions during simultaneous HDO/HDS or HDN/HDO may also be important (*1*), their study has not yet enjoyed comparable attention (*21*).

The interactions between catalytic HDS and HDN are now fairly well understood. Satterfield *et al.* (*2*) investigated the coupling between HDS of thiophene and HDN of pyridine in a flow microreactor at 200–500°C and 4 to 11 atm pressure on

commercial catalysts consisting of CoMo/Al$_2$O$_3$, NiMo/Al$_2$O$_3$, NiW/Al$_2$O$_3$, and NiW/SiO$_2$–Al$_2$O$_3$. Inhibition of the HDS reaction by pyridine was observed. Thiophene showed a dual influence on HDN reaction, inhibiting the HDN reaction at low temperature, but enhancing it at higher temperatures. The pattern of inhibition was interpreted in terms of a two-site model analogous to that of Desikan and Amberg (*5*). Satterfield *et al.* (*2*) postulated the presence of two kinds of sites (type I and type II) on the sulfided catalyst capable of catalyzing the HDS reaction. In this picture, type-I sites are very active and are responsible for the majority of the HDS activity with pure thiophene feedstocks. However, these sites are very sensitive to basic nitrogen compounds and are easily poisoned by pyridine. The type-II sites are presumed to have less HDS activity but also to be less susceptible to poisoning. Thus they are held responsible for the residual HDS activity of the catalyst after all type-I sites are blocked.

Following this study many investigators

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reported on the HDS of heterocyclic sulfur compounds (*10–14*), the HDN of heterocyclic N compounds (*7–9*), and the interactions between HDS and HDN reactions (*1, 3–4*). Major findings from these studies include the following:

(a) In the presence of nitrogen-containing compounds, the HDS activities for all reactions are reduced.

(b) Denitrogenation is in general more difficult than desulfurization since it requires good hydrogenation and hydrocracking activities.

(c) There are two types of active sites on the sulfided catalysts, one of which is competitively available to reactant (e.g., thiophene) and one of the reaction products (e.g., H_2S).

(d) For heteropolyaromatic compounds, the first step in the reaction is an equilibrium step (*1, 6, 7*) and under certain reaction conditions this step is thermodynamically unfavorable, and hence limits the (eventual) subsequent hydrogenolysis step, e.g.,

hydrogenolysis step

None of these studies specifically addressed the influence of oxygen compounds on desulfurization and denitrogenation.

Two studies are of particular interest with regard to the present paper:

(a) Rollmann (*3*) reported on relative rates of *simultaneous* heteroatom removal from synthetic mixed feeds containing N, S, and O compounds. From data collected at 344°C and 48 atm over sulfided Co–Mo catalysts, he concluded that where *nitrogen* or *oxygen* was located in a heteroaromatic ring, saturation of that ring was necessary before C–N or C–O bond scission could occur and such saturation was rate determining. This was not found to be the case for *sulfur* species. Rollmann's data indicated the following decreasing order of reactivity (i.e., reactivity to HDS, HDN, and HDO) on Co–Mo and similar catalysts:

(b) Furimsky (*1*) examined the relative rates of simultaneous S, N, and O removal from a heavy gas oil. He operated a bench scale fixed-bed reactor at 400°C, 136 atm, and a liquid hourly space velocity of 2 hr^{-1} for his relative rates study. He observed that for related heterocyclic compounds the relative rates of S, N, and O removal from a heavy gas oil are in qualitative agreement with the C–S, C–N, and C–O bond strengths. Thus the rate of HDS is highest, followed by HDN and HDO for molecules of analogous structures.

These two reports (*1, 3*) are significant because they address kinetic factors which become important in mixed feed HDO operation.

In the present paper, we report our stud-

ies on the interactions between the HDO of *m*-cresol (CRE) and the HDS of benzothiophene (BT) and dibenzothiophene (DBT) in mixed feeds containing CRE–BT, and CRE–DBT, respectively. The experimental results of this work are obtained under essentially differential reactor conditions to avoid or minimize complicating effects due to mass transfer limitations, undesirable secondary reactions, or reactor concentration nonuniformities. A Langmuir–Hinshelwood kinetic model is developed to interpret the data and to provide insight into the mutual influence of *m*-cresol and benzothiophene on HDS and HDO, respectively.

EXPERIMENTAL METHODS

The experimental packed bed trickle reactor is a smooth-bore, thick-walled, ¼-in.-o.d. 316 stainless-steel tube. Two thermocouple probes are located in the reactive zone and on the outer wall of the reactor to monitor temperature. The rest of the apparatus has been fully described previously (*19, 20*).

The catalysts used for these series of experiments are those described as catalyst I in the previous paper (*20*). The catalyst activation procedure was the following:

(i) *Reduction* in hydrogen overnight at 150–200°C, then at 350°C for 22 hr and then at 400°C for 11 hr.

(ii) *Sulfiding* with H_2/H_2S mixture (11 vol% H_2S) at 400°C for 3¼ hr, followed by cooling to ambient in argon. This treatment restored the catalyst activity to ~87% of its activity at the start of the HDS/HDO experiments.

High-purity *m*-cresol (99+%), benzothiophene (97%), dibenzothiophene (95%), ethylbenzene, and *n*-hexadecane (99+%) (Aldrich Chemicals) were used as received without further purification. Biphenyl was obtained from Eastman. Ultra-high-purity hydrogen gas (99.9999%), H_2/H_2S, helium and air ultra zero were obtained from Matheson, and were dried before use.

To provide a basis for comparing the conversions of *m*-cresol in the mixed cresol-benzothiophene (CRE–BT) and mixed cresol–dibenzothiophene (CRE–DBT) feeds, a single reactant feed containing only *m*-cresol and *n*-heptyl mercaptan in hexadecane (Expt. A_1 in Table 1) was run first under the same reaction conditions as the mixed feeds. Following this a mixture of *m*-cresol and *p*-cresol (Expt. A_3 in Table 2) was run to test for first-order behavior in a mixed oxygenate (cresol) feed. For mixed S/O feeds, the concentration of benzothiophene (S) was progressively increased from 0.0075 *M* to 0.15 *M* while the absolute concentration of *m*-cresol (O) remained constant at 0.15 *M*. A similar pattern was followed for the cresol/dibenzothiophene runs (Expts. C_3, C_6). Some benzothiophene-only feed runs were done (Expt. B_6 and B_7 of Table 1) to allow comparison of the HDS results in the single and mixed feeds. Each liquid reactant feed contained 0.0075 *M*

TABLE 1

Operating Conditions and Reactant Feed Composition

Temperature	375°C. 400°C
Hydrogen pressure	69 atm
Hydrogen flow rate	~120 cm³/min (SCCM)
Liquid reactant flow rate	4.5–12.5 cm³/hr
Catalyst	0.085 g of CoO–MoO₃/γ-Al₂O₃ diluted with 1.301 g quartz chips. Catalyst was presulfided before use.

Expt. No.	No. of moles of components in feed mixture[a]				
	m-Cresol	BT	DBT	RSH	*n*-HXD
A_1	0.15	—	—	0.0075	3.356
B_1	0.15	0.0075	—	0.0075	3.354
B_2	0.15	0.025	—	0.0075	3.336
B_3	0.15	0.075	—	0.0075	3.296
B_4	0.15	0.025	—	0.0075	3.336
B_5	0.15	0.15	—	0.0075	3.236
B_6	—	0.15	—	0.0075	3.290
B_7	—	0.15	—	0.0075	3.290
C_3	0.15	—	0.025	0.0075	3.336
C_6	0.15	—	0.15	0.0075	3.236

Note. BT = Benzothiophene, DBT = dibenzothiophene, RSH = heptyl mercaptan, *n*-HXD = *n*-hexadecane.

[a] Concentration in moles per liter.

(~0.2 mole% of total feed) of *n*-heptyl mercaptan added to ensure that the catalyst would remain in a sulfided form throughout the runs. Complete conversion of the mercaptan was observed most of the time.

A standard operating procedure was employed for all the HDO and HDS runs. Deoxygenation (HDO) of *m*-cresol and desulfurization (HDS) of benzothiophene proceeded by passing the solution of the reactant feed over the sulfided catalyst at the standard conditions of 400°C (or 375°C), 69 atm of hydrogen pressure, 120 cm³/min (STP) hydrogen flow, and the desired liquid reactant flow rate. At the beginning of the runs immediately following catalyst sulfiding, a liquid reactant flow rate of 1 cm³/hr was maintained for about 2–3 days until conversion and product distribution reached a nearly steady state. Operating conditions were then changed and the run continued until a new "steady state" was reestablished (6–12 hr). The liquid samples were analyzed on a Perkin–Elmer Sigma 1 GC (*24*). For each reactant feed, the total liquid flow rate was varied to obtain conversion vs reciprocal space velocity data. Periodically, previous conditions were repeated to examine the magnitude of catalyst deactivation.

RESULTS AND DISCUSSION

HDO of m-Cresol

The deoxygenation reaction shows apparent first-order dependence on *m*-cresol concentration both in the *m*-cresol-only and the mixed (*m*-cresol–*p*-cresol) feed (Fig. 1). The experimentally determined pseudo-first-order rate constant of the mixed *m*- and *p*-cresol feed [3.4×10^{-3} liter · hr^{-1} · (g · cat)$^{-1}$] is within 13% of the expected value [3.9×10^{-3} liter · hr^{-1} · (g · cat)$^{-1}$], based on our knowledge (*20*) of the relative reactivity of *m*-cresol and *p*-cresol.

Cresol HDO shows apparent first-order dependence on cresol in the presence of benzothiophene. The HDO reaction rate decreased as the level of benzothiophene
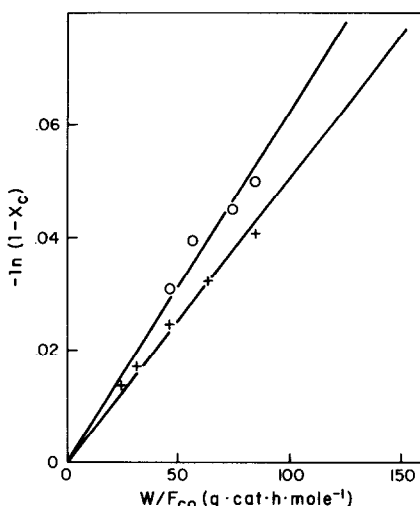
FIG. 1. Hydrodeoxygenation of cresol. Pseudo-first-order behavior of single-component (*m*-cresol, ○) and two-component (*m*-cresol *p*-cresol, +) feed.

(BT) in the feed was increased, and a maximum decrease of 67% was observed for the feed containing equimolar amounts (0.15 *M* each) of *m*-cresol and benzothiophene (Fig. 2). Figure 2 shows the linear plots of $- \ln(1 - X_c)$ versus $W/F_{c,o}$ (where X_c = cresol conversion and $W/F_{c,o}$ is space time in g · catalysts · hr · mole^{-1}) for different levels of benzothiophene (BT) in the reactant feed. The maximum cresol conversion was 8%. The apparent first-order HDO rate constants, k'_{HDO}, calculated as [slope (Fig. 2)/ (cresol concentration)] are given in column 3 of Table 2.

Similar pure component and mixed feed experiments with cresol + dibenzothiophene (DBT) also showed the presence of DBT inhibition (Table 3). Again the *m*-cresol HDO plots of $\ln(1 - X_c)$ vs W/F were linear in the presence of DBT (Fig. 3). Thus the inhibition pattern of the HDO reaction is similar for BT and DBT, but the strength of DBT inhibition of cresol conversion is less than that of BT, as indicated by comparison of Tables 2 and 3.

Toluene (TOL), methylcyclohexane, and methylcyclohexene are the main measurable products of *m*-cresol HDO in the pres-
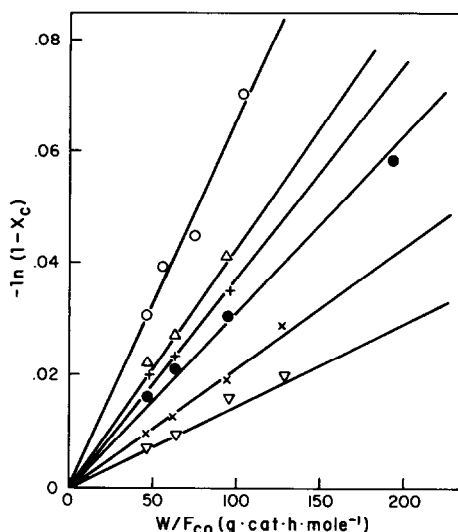
FIG. 2. Inhibition of m-cresol hydrodeoxygenation by benzothiophene. $T = 400°C$ (except ∇, 375°C). Feed composition: 0.15 M cresol + benzothiophene at 0.0 M (O), 0.0075 M ($\triangle$), 0.025 M (+), 0.075 M (●), 0.025 M (∇, 375°C), 0.15 M (×). (See Table 1.)

ence of BT and DBT. Defining the sum (cycloalkane + cycloalkene) $\equiv$ [MCH], at 400°C, the product ratio ([MCH]/[TOL]) remains approximately constant at 23% as the m-cresol conversion increases. This constant behavior at 400°C is as we found for the m-cresol-only feeds in our previous paper (20) on conversion of individual cresols. Further, the product ratio [MCH]/

TABLE 2

HDO–HDS of Cresol–Benzothiophene Feeds: Rate Constants and Rate Constant Ratios

Expt. No.	No. moles BT	HDO $10^3 k'_{HDO}$	HDS $10^3 k'_{HDS}{}^a$	k'_{HDO}/k'_{HDS}	
A_1	—	4.5	—	—	
A_3	—	3.5^c	—	—	
B_1	0.0075	2.7	26.3	0.10	
B_2	0.025	2.4	28.3	0.08	Mixed-feed experiments
B_3	0.075	2.1	27.1	0.08	
B_4	0.025^b	1.0^b	16.1^b	0.06^b	
B_5	0.15	1.5	19.0	0.08	
B_6	0.15	—	42.3	—	
B_7	0.15^b	—	24.1^b	—	

^{a} Liters hr^{-1} (g · cat)$^{-1}$.
^{b} Reaction at 375°C; all others at 400°C.
^{c} 0.15 M in *both* m-cresol and p-cresol.

TABLE 3

Rate Constants and Rate Constant Ratios for CRE and DBT

Expt. No.	Temp. (°C)	No. moles of DBT	$10^3 k'_{HDO}$ (liters · hr^{-1} (g cat)$^{-1}$)	$10^3 k'_{HDS}$ (liters · hr^{-1} (g cat)$^{-1}$)
C_1	375	—	0.73	—
C_2	400	—	1.15	—
C_3	400	0.025	0.96	2.01
C_4	375	—	0.59	—
C_5	400	—	1.02	—
C_6	400	0.150	0.68	1.80

Note. After Expts. C_1, C_2, and C_3 catalyst was resulfided with H_2/H_2S before Expts. C_4, C_5, and C_6 were done.

[TOL] does not vary as the level of benzothiophene in the mixed CRE–BT feeds increases. Thus although BT inhibits the cresol HDO reaction rate, it does not affect the selectivity to aromatic vs (cycloalkane and cycloalkene).
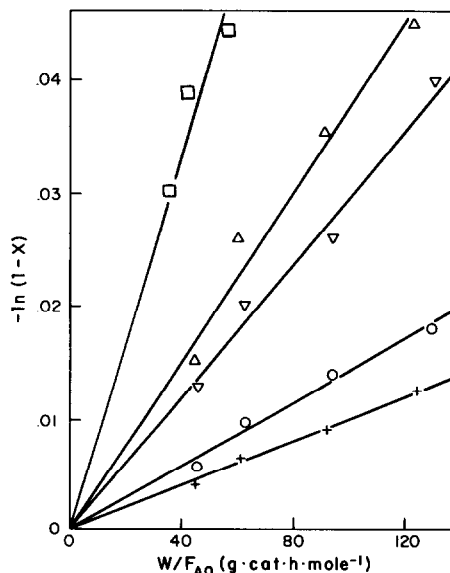

FIG. 3. Pseudo-first-order plots of simultaneous HDS/HDO of dibenzothiophene/m-cresol at 400°C (0.025 M DBT + 0.15 M CRE): Expt. C_3, HDS (∇), HDO (O); (0.15 M DBT + 0.15 M CRE): Expt. C_6, HDS (∇), HDO (+) (see Table 3 for inhibition influences). (□) Cresol only (Expt. A_1).
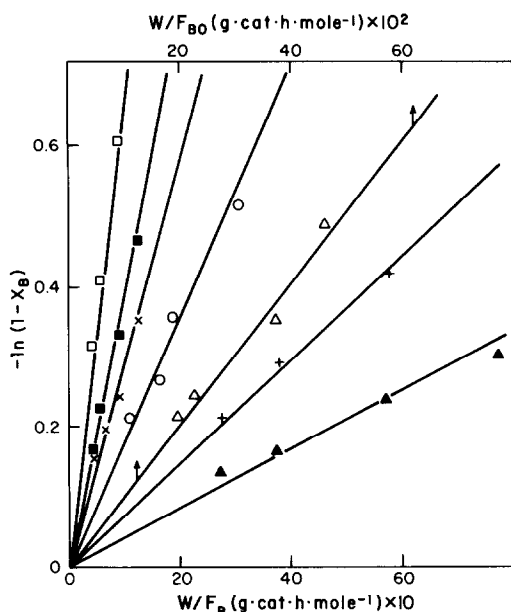
FIG. 4. Inhibition of benzothiophene hydrodesulfurization by m-cresol. $T = 400°C$; feed: $0.15\ M$ BT ($\square$); mixed feeds: $(0.15\ M$ CRE) + BT $(0.0075\ M$ ($\triangle$), $0.025\ M$ (+), $0.075\ M$ ($\bigcirc$), $0.15\ M$ ($\times$)). $T = 375°C$; feed: $0.15\ M$ BT ($\blacksquare$), $0.15\ M$ CRE + $0.025\ M$ BT ($\blacktriangle$). (See also Table 2.)

HDS of Benzothiophene (BT)

The HDS of benzothiophene (BT) gave ethylbenzene as the only major product, both for the benzothiophene-only feed and for the CRE–BT mixed feeds. Trace amounts of dihydrobenzothiophene and 2-phenylethanethiol were also formed, but these were less than 5% of total product. The conversion of BT was calculated as ethylbenzene formed divided by the original BT feed level; benzothiophene conversions ranged from 12 to 54%. Defining X_B as BT conversion, plots of $-\ln(1 - X_B)$ versus the reciprocal space velocity (W/F_{BO}) gave straight lines passing through the origin (Fig. 5). This linear behavior for integral conversions demonstrates that the HDS of BT appears to be first order in BT both for the BT-only as well as for the CRE–BT mixed feeds. The data in Fig. 4 clearly establish the dominant inhibition effect of m-cresol on the HDS reaction. The distribu-

tion of the BT HDS products is unaffected by the presence of m-cresol. The apparent first-order rate constants, k'_{HDS}, calculated for BT HDS from the slopes of Fig. 4 appear in column 4 of Table 2.

The Arrhenius plots for the m-cresol deoxygenation and benzothiophene desulfurization yield apparent activation energies of 20 and 19.5 kcal/mole for CRE and BT, respectively.

HDS of Dibenzothiophene (DBT)

In both the DBT-only and the mixed CRE–DBT feeds the HDS of DBT gave biphenyl as the only detectable product. Dihydrobenzothiophene (DHBT) and other partially hydrogenated derivatives of DBT were not observed. From the conversion data of DBT hydrodesulfurization, plots of $-\ln(1 - X_c)$ versus the reciprocal space velocity ($W/F_{DBT,0}$) are linear (Fig. 3).

Relative Reactivities

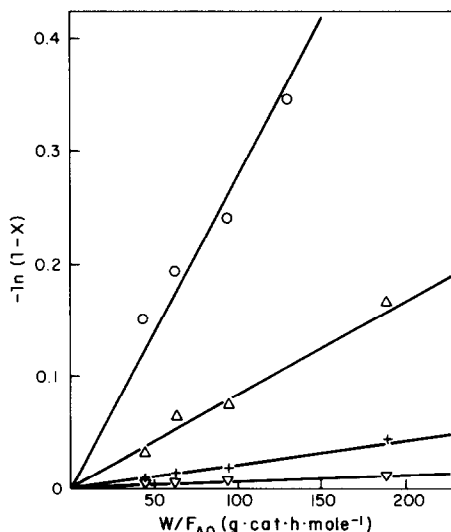To determine the relative reactivities of m-cresol, benzothiophene, and dibenzo-

FIG. 5. Relative reactivities in equimolar feed experiments at 400°C: $(0.15\ M$ DBT + $0.15\ M$ CRE): Expt. C_6, HDS ($\triangle$), HDO (∇); $(0.15\ M$ BT + $0.15\ M$ CRE): Expt. B_5, HDS ($\bigcirc$), HDO (+). (See also Tables 2 and 3.)

thiophene, feed mixtures containing equimolar (0.15 M each) amounts of cresol and benzothiophene (Expt. B_5 in Table 2), and equimolar (0.15 M each) amounts of cresol and dibenzothiophene (Expt. C_6 in Table 3) were passed over the sulfided catalysts under our standard reaction conditions (400°C, 69 atm H_2 pressure). Figure 5 summarizes the results, showing that benzothiophene is more reactive than dibenzothiophene, which in turn is more reactive than m-cresol. From the pseudo-first-order rate constants (Tables 2 and 3) we find that in the mixed feed, benzothiophene HDS is at least 10 times as rapid as m-cresol HDO. In a similar run for the cresol–dibenzothiophene feed, the HDS of DBT is about 2–3 times as fast as the m-cresol HDO reaction.

Catalyst Activity

A gradual loss of catalyst activity was observed as the experiments progressed. For the m-cresol-only feed runs, this loss of activity is largely recoverable by catalyst re-reduction and resulfiding using H_2/H_2S mixture at 400°C. A greater loss of activity was observed for the mixed cresol–benzothiophene feed runs, especially when the concentration of BT in the mixed feed reached 0.1075 M. The HDS of the BT-only feed runs (Expt. B_6) was accompanied by an irrecoverable catalyst poisoning. Following this run, re-reduction and resulfiding did not increase catalyst activity to any significant extent. Further loss of catalyst activity was observed during the CRE–DBT runs as the data of Tables 2 and 3 show. The trend in activity loss can be seen by comparing the apparent first-order rate constants for HDO experiments done at 400°C (A_1, C_1, and C_4) and 375°C (C_2 and C_5). We notice a continued loss of catalyst activity despite resulfiding operations (compare C_1 and C_4, and C_2 and C_5 in Table 3). Thus the catalyst appears to have been permanently poisoned by benzothiophene, its reaction products, or both.

Kinetic Analysis

The summary of the data in Tables 2 and 3 and Figs. 2–5 shows that the HDO of m-cresol and the HDS of benzothiophene in a mixed-reactant feed of m-cresol and benzothiophene conform to pseudo-first-order kinetics. Straight lines passing through the origin are obtained when $- \ln(1 - X)$, where X is the conversion, is plotted against the reciprocal space velocity ($W/F_{i,o}$).

However, since our data show inhibition of the HDO reaction by BT and DBT, and a similar inhibition of the HDS reaction by CRE, a more detailed kinetic analysis is required.

Several investigators have attempted thorough kinetic analysis of the HDS of single feedstocks of thiophene (16, 17), benzothiophene (18), and dibenzothiophene (13), using models obeying Langmuir–Hinshelwood kinetics. Although these studies were done at different reaction conditions, several general qualitative trends emerge from all of them:

(a) The desulfurization reaction is inhibited by product hydrogen sulfide, and in some cases by other reaction products.

(b) The surface reaction involving the hydrogenolysis of the C–S bond is the rate-determining step.

(c) Models advocating separate sites on the CoMo catalysts for adsorption of hydrogen vs other reactants and products appear most frequently.

Combining our HDO–HDS observations with these trends, we consider a Langmuir–Hinshelwood kinetic model involving two active sites. Here, m-cresol, benzothiophene, (or DBT) and product water and hydrogen sulfide competitively adsorb on one site, and hydrogen is noncompetitively adsorbed on the other type of active sites. Thus we have the following equations, taking the first-order dependence on P_H into account.[2]

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[2] Subscripts: S = mercaptan, W = water, c = cresol, B = benzothiophene.

(a) HDO of *m*-cresol in a cresol-only feed:

$$F_c \frac{dX_c}{dW} = \frac{k_{HDO}K_H K_c C_c P_H}{(1 + K_c C_c + K_W C_w + K_s C_s)}.$$

$$F_c \frac{dX_c}{dW} = \frac{k_{HDO}K_H K_c C_c P_H}{(1 + K_c C_c + K_W C_w + K_s C_s + K_B C_B + K_{H_2S}C_{H_2S})} \qquad (2)$$

(c) HDS of BT in a BT-only feed:

$$F_B \frac{dX_B}{dW} = \frac{k_{HDO}K_B K_H C_B P_H}{(1 + K_B C_B + K_s C_s + K_{H_2S}C_{H_2S})}. \qquad (3)$$

(d) HDS of BT in a mixed CRE–BT feed:

$$F_B \frac{dX_B}{dW} = \frac{k_{HDS}K_B K_H C_B P_H}{(1 + K_B C_B + K_c C_c + K_W C_w + K_s C_s + K_{H_2S}C_{H_2S})}. \qquad (4)$$

Corresponding equations apply equally well for the CRE–DBT feeds.

Equations (1)–(4) may be reduced in complexity with some assumptions:

(i) The term $(1 + K_{H_2S}C_{H_2S})$ in the denominator is a constant, and can be divided out, shifting other K values. Note that this convenience will not change the relative magnitudes of the binding constants (K), nor does it alter any rate constant (k).

(ii) From our results on the cresols (*24*), water inhibition was found not to be significant. Thus we neglect the term $K_W C_W$ (no other oxygenates were noted).

(iii) As the product $K_H P_H$ is constant throughout our study, we incorporate this product into the constants k_{HDO} and k_{HDS}.

(iv) For our typically differential conditions, the denominator varies considerably less rapidly than the numerator, and we take the former to be approximately constant, i.e., determined by feed conditions.

Applying these assumptions to Eqs. (1) through (4) results in the following integrated rate forms:

(b) HDO of *m*-cresol in a mixed CRE–BT feed:

(a) HDO of *m*-cresol in CRE-only feed:

$$W/F_{co} = - \left[\frac{1 + K_c C_{co}}{k_{HDO}K_c C_{co}} \right] \ln(1 - X_c) \qquad (5a)$$

$$= - \frac{1}{k'_{HDO}C_{co}} \ln(1 - X_c). \qquad (5b)$$

(b) HDO of *m*-cresol in mixed CRE–BT feed:

$$W/F_{co} =$$

$$- \left[\frac{1 + K_c C_{co} + K_B C_{Bo}}{k_{HDO}K_c C_{co}} \right] \ln(1 - X_c) \qquad (6a)$$

$$= \left[\frac{1}{k'_{HDO_m}C_{co}} \right] \ln(1 - X_c). \qquad (6b)$$

(c) HDS of benzothiophene in a BT-only feed:

$$W/F_{Bo} = - \left[\frac{1 + K_B C_{Bo}}{k_{HDS}K_B C_{Bo}} \right] \ln(1 - X_B) \qquad (7a)$$

$$= - \frac{1}{k'_{HDS}C_{Bo}} \ln(1 - X_B). \qquad (7b)$$

(d) HDS of benzothiophene in a mixed CRE–BT feed:

$$W/F_{Bo} = \left[\frac{1 + K_B C_{Bo} + K_c C_{co}}{k_{HDS} K_B C_{Bo}}\right] \ln(1 - X_B) \tag{8a}$$

$$= \left[\frac{1}{k'_{HDS_m} C_{Bo}}\right] \ln(1 - X_B). \tag{8b}$$

In these equations the subscript Bo and Co indicate feed composition. Note that Eqs. (5b), (6b), (7b), and (8b) are written to contain an apparent first-order rate constant k'_{HDO} or k'_{HDS}. The additional subscript m denotes k' from a mixed-feed experiment. The apparent rate constant values (k'_{HDO}, k'_{HDO_m}, k'_{HDS}, k'_{HDS_m}) were summarized in Tables 2 and 3.

The rate equation parameters were evaluated as follows:

(a) From Eqs. (8a) and (8b) a plot of (1/k'_{HDS_m}) vs C_{BO} (Fig. 6, HDS data) gives a line of slope S_1,

$$S_1 = \frac{1}{k_{HDS}}. \tag{9a}$$

The intercept i_1 for this first plot is

$$i_1 = \frac{1 + K_c C_{co}}{k_{HDS} K_B}. \tag{9b}$$

Thus $K_B = \dfrac{1 + K_c C_{co}}{(i_1 k_{HDS})}$ = benzofuran binding constant.

(b) From Eqs. (7a), (7b), and (8a), (8b),

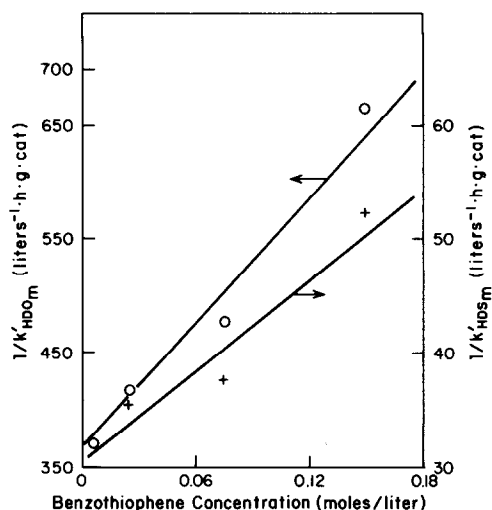$$\frac{1}{k'_{HDS_m}} = \frac{1}{k'_{HDS}} + \frac{K_c C_{co}}{k_{HDS} K_B}.$$

FIG. 6. Inverse apparent first-order rate constants vs benzothiophene feed concentration. $T = 400°C$, 0.15 M CRE: BT HDS (O), m-CRE HDO (+).

Thus

$$K_c = K_B \left[\frac{1}{k'_{HDS_m}} - \frac{1}{k'_{HDS}}\right] \frac{k_{HDS}}{C_{co}}$$
$$= \text{cresol binding constant.} \tag{10}$$

With k'_{HDS}, k'_{HDS_m}, k_{HDS}, C_{co}, S_1 and i_1 known, Eqs. (9b) and (10) provide two equations and the two unknowns, K_c and K_B.

(c) From Eqs. (6a) and (6b) a plot of (1/k'_{HDO_m}) vs C_{BO} (Fig. 6, HDO data) gives a slope S_2,

$$S_2 = \frac{K_B}{k_{HDO} K_c} \tag{11a}$$

TABLE 4

Rate Equation Parameters for CRE and BT

Temperature (°C)	$-\ln k_{HDO}$ (HDO)	$-\ln k_{HDS}$ (HDS)	K_c (CRE) (liters/mole)	KL_B (BT) (liters/mole)
375	6.662	3.725	8.42	16.45
400	6.079	3.164	6.20	9.51
E_a (kcal/mole)	20.2	19.5	$\Delta H_c{}^a$ = kcal/mole	$\Delta H_B{}^b$ = kcal/mole
$-\ln A$	9.0	9.5	$\Delta H_c{}^a$ = −11 kcal/ mole	$\Delta H_B{}^b$ = −19 kcal/mole

[a] Present results.
[b] From Ref. (15) data.

and intercept i_2,

$$i_2 = \frac{1 + K_c C_{co}}{k_{HDO} K_c}.$$

Thus

$$k_{HDO} = \frac{K_B}{S_2 K_c}. \qquad (11b)$$

These Eqs. (9a), (9b), (10), (11a), and (11b) were used to evaluate k_{HDO}, k_{HDS}, K_B, K_S. The results are summarized in Table 4.

The magnitude of the equilibrium constants provides an indication of the true reaction orders. For example, at 400°C (Table 4), the product of binding constant (K_c) times cresol feed level (C_{co}) is 6.2 (liters/mole) × 0.15 (moles/liter) = 0.93, indicating that the surface coverage by cresol would be about one-half, corresponding to a rate of fractional order near one-half. The linearity of the $\ln(1 - x)$ vs W/F plots is largely a consequence of the typically differential conversions (as we noted in paper I, both a zero-order and a first-order reaction will exhibit linear $\ln(1 - X)$ vs W/F plots under differential conversion conditions, as will all fractional orders). The very clear inhibition effects noted by benzothiophene and dibenzothiophene here provide evidence of the need to interpret these "first"-order plots with Langmuir–Hinshelwood forms.

The results of Gates et al. (10a) indicate that in HDS conversions, the less reactive compound is less strongly adsorbed, thus less effective as an inhibitor. Thus the more reactive 3,7-dimethyl DBT and 2,8-dimethyl DBT are more strongly adsorbed than DBT, while the less reactive 4,6-dimethyl DBT is less strongly adsorbed than DBT.

The relative reactivity which we have observed for m-cresol and benzothiophene and the inhibiting effect that each of these has on the conversion of the other support a similar correlation between reactivity and the relative strength of adsorption of these compounds on the catalyst surface. Thus the more reactive BT is also more strongly

adsorbed, and CRE is less reactive and has the smaller binding constant (Table 4).

The rate constants (Tables 2, 3) and Fig. 5 show the following decreasing order of reactivity:

benzothiophene >

dibenzothiophene > m-cresol.

Since we found previously (23) that m-cresol is somewhat more reactive than p-cresol, these results do not parallel Rollmann's (3) note that on conventional CoMo catalysts the order of reactivity is

p-cresol ≳ benzothiophene.

However, our results do agree with those of Whitehurst et al. (4), who found that for four different hydrotreating catalyst systems the BT HDS reaction is faster than the p-cresol HDO reaction.

The observation in the present study of the high-temperature insensitivity of the product ratio ([MCH]/[TOL]) to the m-cresol conversion agrees with our previous paper (19). Thus the high-temperature pathway cited previously, involving parallel decomposition of a surface intermediate into toluene or methylcyclohexane, appears to be appropriate in the presence of benzothiophene and dibenzothiophene.

Ethylbenzene and biphenyl are the only major products observed for the HDS of BT and DBT, respectively, on our sulfided CoMo. This suggests that the HDS of BT and DBT proceeds by a simple sulfur extrusion, presumably through partially hydrogenated intermediates, to give ethylbenzene and biphenyl, respectively. These are the products commonly observed under reaction conditions less severe than ours (lower temperatures and pressures). On the aged catalysts used in our studies further hydrogenation of ethylbenzene and biphenyl did not take place.

CONCLUSIONS

This study investigated the influence of benzothiophene (BT) and dibenzothio-

phene (DBT) on the HDO of *m*-cresol (CRE), and the influence of *m*-cresol on the HDS of BT and DBT as the liquid flow rates, reactant concentrations, and reaction temperatures vary. Single-feed and mixed-feed differential results show that for the HDO of *m*-cresol, and the HDS of BT and DBT, linear plots of ln(1 − *X*) vs *W/F* are routinely obtained.

Hydrodeoxygenation of the single-ring alkyl phenol, *m*-cresol, is inhibited by BT and DBT. In a similar fashion *m*-cresol inhibited the HDS of BT and DBT. The distribution of products in the HDS of BT and DBT, and the HDO of *m*-cresol, and the pattern of inhibition may be represented by a single HDS/HDO site. (If our catalyst initially contained a second HDS/HDO site of appreciable hydrogenation activity, as proposed earlier for CoMo catalysts (*2*), this site has been deactivated in the aged catalysts used for part of the HDO studies reported previously (*19*) and the HDO–HDS studies reported in this paper.)

The formulation and analysis of the kinetic model using a Langmuir–Hinshelwood form yielded the intrinsic rate constants for the HDO and HDS reactions, the equilibrium adsorption coefficients (K_C, K_B) for *m*-cresol and benzothiophene, respectively, and the heat of adsorption of *m*-cresol.

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