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Interactions between Catalytic Hydrodeoxygenation of Benzofuran and Hydrodesulfurization of Dibenzothiophene

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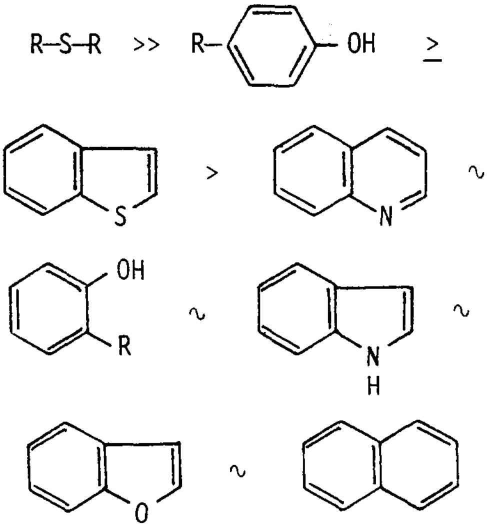
The catalytic removal of oxygen from benzofuran (BF) is much more difficult than the catalytic removal of sulfur from dibenzothiophene (DBT) under the same conditions in an equimolar feedstream. The oxygenate, benzofuran, inhibits dibenzothiophene hydrodesulfurization (HDS) relatively strongly. In contrast, at low levels (0.–0.075 *M*) of dibenzothiophene, benzofuran hydrodeoxygenation is enhanced; further increases in the dibenzothiophene level inhibit hydrodeoxygenation, though not severely. A Langmuir–Hinshelwood model provides a satisfactory form of the kinetic behavior, rationalizing the relationships between the binding strength, reactivities, and inhibition effects.

INTRODUCTION

The simultaneous catalytic removal of heteroatoms from petroleum residue, shale oils, and coal oils was studied by Rollmann (*1*). His results show a decreasing reactivity, over conventional CoMo catalysts, in the following order:



This pattern observed in simultaneous conversion experiments must include competition and inhibition interactions between sulfur-, nitrogen-, and oxygen-containing compounds, as well as the influence of (all) reactants and products on the catalyst activation. Nitrogen-containing compounds in the feedstock have been claimed to be the most important variable affecting the catalyst's HDS reactivity (*2*). Several reports (*3–6*) reveal common and severe inhibitory effect of nitrogen-containing compounds on the catalytic removal of sulfur.

Satterfield and co-workers have clearly demonstrated the *mutual* interactions between catalytic hydrodesulfurization of thiophene and hydrodenitrogenation of pyridine (*7*). Pyridine severely inhibits the catalytic removal of sulfur on sulfided cobalt–molybdate catalysts, in agreement with previous reports, but sulfur-containing compounds were found to have dual effects on catalytic nitrogen removal. At temperature lower than 325°C, thiophene inhibited the conversion of pyridine by competing with pyridine on the catalytic sites of the catalyst. At higher temperature (325–400°C), thiophene enhanced the HDN rate, apparently by interaction of an HDS reaction product, H_2S, with the catalyst. This postulate was confirmed by experiment with a pure pyridine feedstock at 10.3 bars

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total pressure but with a hydrogen sulfide partial pressure of 0.358 and 0.0046 bar in the reaction gas. An analogous result for HDN was reported earlier by Goudriaan *et al.* (*8*), who demonstrated that catalytic HDN/reactivity was increased in the presence of hydrogen sulfide in molar excess over pyridine; these authors argued that this result was due to the enhancement of hydrocracking reactivity of the catalyst by the hydrogen sulfide.

The presence of appreciable oxygenates in coal- and shale-derived liquids suggests that analogous interactions may occur in simultaneous HDO–HDN or HDO–HDS operations. Our recent study of a supported commercial cobalt–molybdate catalyst shows mutual inhibition of cresol on HDS and of the benzothiophenes on HDO (*9*), as well as mutual inhibition of indole (and indoline) on HDO and of *m*-cresol on HDN (*10*).

In the present paper, we establish the *mutual* influence of benzofuran on dibenzothiophene HDS and of dibenzothiophene on benzofuran HDO.

EXPERIMENTAL DETAILS

Equipment

Experiments were carried out in the same continuous trickle reactor described in the previous paper (*11*).

Catalyst

Ninety milligrams of CoO–$MoO_3/\gamma Al_2O_3$ (American Cyanamid Co.), crushed and sieved to 40 mesh, were loaded with 1 g of 40-mesh quartz chips into a $\frac{1}{4}$-in. stainless-steel reactor. Both ends of the reactor were packed with 40-mesh quartz chips to prevent escape of the catalyst from the high-temperature reaction zone. The catalyst was activated by 17 hr of prereduction with hydrogen, then 3 hr of presulfiding with hydrogen sulfide (10% of H_2S in H_2 by volume) at 400°C; subsequently, the catalyst was cooled to the desired temperature (325°C) under pure argon.

Chemicals

Benzofuran, dibenzothiophene, *n*-heptylmercaptan, and hexadecane were obtained from Aldrich Chemical Company and used without further purification. All gases were supplied by Matheson in ultrahigh purity.

Procedure and Analysis

To maintain the sulfided form of the catalyst, *n*-heptylmercaptan was added to every feedstock in a concentration of 0.0075 *M*. The concentrations of benzofuran and dibenzothiophene ranged from zero to 0.20 *M* in either mixed feed or single feed. Two fixed temperatures employed were 325 and 310°C. Study of the enhancement and the inhibition of dibenzothiophene on HDO of benzofuran was done at 325°C with fixed liquid flow rate 5 cc/hr. Usually, liquid flow rate from 5 to 15 cc/hr was chosen. Kinetic data were obtained from the analysis of liquid samples on a Perkin–Elmer Sigma 1 gas chromatograph; component identification was established on a Finnigan GC/MS.

Kinetic Analysis and Results

The kinetics of catalytic hydrodesulfurization of dibenzothiophene was examined on CoO–$MoO_3/\gamma Al_2O_3$ catalyst by Singhal *et al.* (*12*). Their results followed a Langmuir–Hinshelwood kinetic form with competitive adsorption of dibenzothiophene and products on one site, and noncompetitive adsorption of hydrogen on the other site. Massoth (*13*) as well as Kilanowski and Gates (*14*) have observed the same type of kinetic model for hydrodesulfurization of thiophene and benzothiophene, respectively.

In mixed-feed kinetic studies, Odebunmi and Ollis (*9, 10*) interpreted their mixed reactant data with a Langmuir–Hinshelwood kinetic model. In the present paper, we continue use of this convenient form to represent two types of sites on the catalyst: one for competitive adsorption of all heteroatom reactants (C_R) and products (C_P)

and the other site for noncompetitive adsorption of hydrogen. We may write a differential rate expression for this model as

$$F \cdot dX_{\rm R} = \frac{kK_{\rm R}C_{\rm R}}{1 + \Sigma(K_{{\rm R}i}C_{{\rm R}i}) + \Sigma(K_{{\rm P}i}C_{{\rm P}i})} f({\rm H_2})\, dw.$$

An equation for the hydrodesulfurization of dibenzothiophene in single feed and mixed feed could be written as:

for single-feed dibenzothiophene only,

$$F \cdot dX_{\rm DBT} = \frac{k_{\rm HDS}K_{\rm DBT}C_{\rm DBT}f({\rm H_2})\, dw}{[1 + K_{\rm DBT}C^0_{\rm DBT}(1 - X_{\rm DBT}) + K_{\rm H_2S}C_{\rm S} + K_{\rm H_2S}X_{\rm DBT}C^0_{\rm DBT}]}; \quad (1)$$

for mixed-feed dibenzothiophene and benzofuran,

$$F\frac{dX_{\rm DBT}}{dw} = \frac{k_{\rm HDS}K_{\rm DBT}C_{\rm DBT}f({\rm H_2})}{[1 + K_{\rm DBT}C^0_{\rm DBT}(1 - X_{\rm DBT}) + K_{\rm H_2S}X_{\rm DBT}C^0_{\rm DBT} + K_{\rm H_2S}C_{\rm S} + K_{\rm BF}C_{\rm BF} + K_{\rm DHBF}C_{\rm DHBF} + K_{\rm ETPH}C_{\rm ETPH} + K_{\rm w}C^0_{\rm BF}X_{\rm BF}]}, \quad (2)$$

where

$X_{\rm DBT}$ = Σ feed dibenzothiophene hydrodesulfurized products,
$X_{\rm BF}$ = Σ feed benzofuran hydrodeoxygenated products,
$C^0_{\rm DBT}$ = dibenzothiophene feed concentration,
$C^0_{\rm BF}$ = benzofuran feed concentration,
$C_{\rm DHBF}$ = concentration of 2,3-dihydrobenzofuran,
$C_{\rm ETPH}$ = concentration of *o*-ethylphenol,
$C_{\rm S}$ = *n*-heptylmercaptan feed concentration.

Under the assumption that all S- or O-containing molecules have similar binding constants, as mentioned in a previous paper (*11*), a simplified integrated form is obtained:

$$-\ln(1 - X_{\rm DBT}) = \frac{k_{\rm HDS}K_{\rm DBT}C^0_{\rm BBT}}{1 + K_{\rm BF}C^0_{\rm BF} + K_{\rm DBT}C^0_{\rm DBT} + K_{\rm DBT}C_{\rm S}} \cdot f({\rm H_2}) \cdot w/F. \quad (3)$$

Using a volumetric feed basis ($Q = F/C^0_{\rm DBT}$), plots of (nearly) differential conversion data as $-\ln(1 - X_{\rm DBT})$ against reciprocal of space velocity w/Q provide a set of apparent rate constants (slopes), which are then used to evaluate the individual rate and equilibrium constants from the relationship

$$\text{experimental slope} \equiv k'_{\rm HDS(m)} = \frac{k_{\rm HDS}K_{\rm DBT}}{[1 + K_{\rm DBT}C^0_{\rm DBT} + K_{\rm BF}C^0_{\rm BF} + K_{\rm DBT}C_{\rm S}]} f({\rm H_2}).$$

Since the hydrogen pressure and gas flow rate have been kept constant throughout the experiment, the function $f({\rm H_2})$ of hydrogen is henceforth included in the intrinsic rate constant $k_{\rm HDS}$. The reciprocal of the apparent rate constant plotted vs concentration or inverse concentration of benzofuran and dibenzothiophene, as appropriate, in mixed-feed experiments is:

constant dibenzothiophene (DBT), variable benzofuran (BF),

$$\frac{1}{k'_{\rm HDS(m)}} = \frac{1 + K_{\rm DBT}(C^0_{\rm DBT} + C_{\rm S})}{k_{\rm HDS}K_{\rm DBT}} + \left(\frac{K_{\rm BF}}{k_{\rm HDS}K_{\rm DBT}}\right) C^0_{\rm BF}; \quad (4)$$

constant BF, variable DBT,

$$\frac{1}{k'_{\rm HDS(m)}} = \frac{1 + K_{\rm DBT}C_{\rm S} + K_{\rm BF}C^0_{\rm BF}}{k_{\rm HDS}K_{\rm DBT}} + \left(\frac{1}{k_{\rm HDS}}\right) C^0_{\rm DBT}. \quad (5)$$

Equations (4) and (5) enable us to evaluate the intrinsic rate constant $k_{\rm HDS}$ and the equilibrium adsorption coefficients $K_{\rm BF}$ and $K_{\rm DBT}$.

The intrinsic rate constant $k_{\rm HDS}$ and equilibrium adsorption coefficient $K_{\rm DBT}$ were also evaluated from single-feed experiments of dibenzothiophene as

$$\frac{1}{k'_{\mathrm{HDS(s)}}} = \frac{1 + K_{\mathrm{DBT}}C_{\mathrm{S}}}{k_{\mathrm{HDS}}K_{\mathrm{DBT}}} + \frac{1}{k_{\mathrm{HDS}}} C^{0}_{\mathrm{DBT}}. \quad (6)$$

HDS of Dibenzothiophene Single Feed

A simple test of the linear relation between $-\ln(1 - X_{\mathrm{DBT}})$ and w/Q is available from dibenzothiophene single-feed experiments. Results shown in Fig. 1 indicate that the assumption $K_{\mathrm{DBT}} \approx K_{\mathrm{H_2S}}$ is valid, since otherwise the date plot would not be linear over the entire range of conversion of dibenzothiophene from zero to 70%. The corresponding apparent rate constants, intrinsic rate constants, and equilibrium adsorption coefficients for two temperatures are tabulated in Table 1. These values will be compared below with the results from mixed-feed experiments.

TABLE 1

Empirical Rate Constants, Intrinsic Rate Constants, and Equilibrium Adsorption Coefficients for Dibenzothiophene Single-Feed Experiment

DBT feed concentration (M)	$k' \times 10^2$	$1/k'$
Empirical rate constants k' (liters hr^{-1} (g-cat)$^{-1}$) at 325°C		
0.05	13.16	7.60
0.15	7.75	12.90
Empirical rate constants k' (liters hr^{-1} (g-cat)$^{-1}$) at 310°C		
0.05	9.18	10.90
0.15	5.27	18.97
Temp. (°C)	**Intrinsic rate constants k_{HDS} (moles hr^{-1} (g-cat)$^{-1}$)**	**Equilibrium adsorption coefficient K_{DBT} (liters mole^{-1})**
325	1.88×10^{-2}	11.65
310	1.24×10^{-2}	12.89

HDS of Dibenzothiophene in DBT and BF Mixed Feed

A very strong inhibition of benzofuran on the HDS of dibenzothiophene was observed in the mixed-feed experiment. Conversion of dibenzothiophene is less in 0.15 M DBT with 0.025 M BF by 46% than that in 0.15 M DBT only, as shown in Fig. 2 and Table 2. Variation of dibenzothiophene concentration, as shown in Fig. 3, also produced a diminished apparent first-order rate constant, as expected from a surface capable of becoming saturated in reactant. With

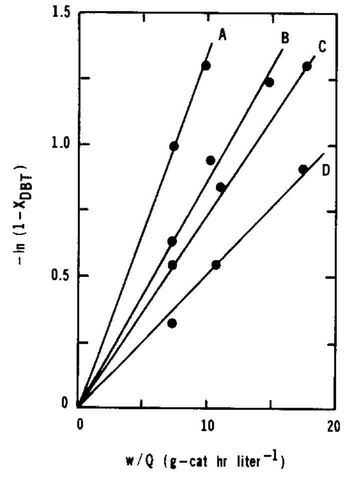

FIG. 1. Plot of $-\ln(1 - X_{\mathrm{DBT}})$ vs w/Q for the hydrodesulfurization of dibenzothiophene in single feed. (A) 0.05 M DBT at 325°C; (B) 0.15 M DBT at 325°C; (C) 0.05 M DBT at 310°C; (D) 0.15 M DBT at 310°C.

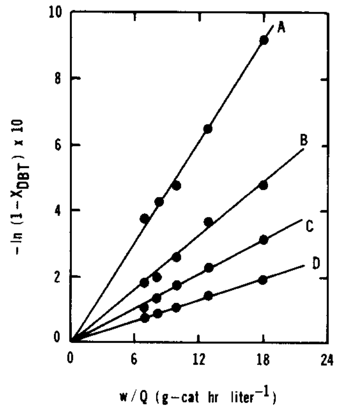

FIG. 2. Plot of $-\ln(1 - X_{\mathrm{DBT}})$ vs w/Q for the hydrodesulfurization of dibenzothiophene in DBT and BF mixed feed with fixed concentration of 0.15 M DBT and (A) 0.0 M BF, (B) 0.025 M BF, (C) 0.075 M BF, and (D) 0.15 M BF.

TABLE 2

Empirical Rate Constants, Intrinsic Rate Constants, and Equilibrium Adsorption Coefficients for HDS of DBT in Dibenzothiophene and Benzofuran Mixed-Feed Experiments

Feed concentration	$k' \times 10^2$	$1/k'$
Empirical rate constants k'_{HDS} (liters hr^{-1} (g-cat)$^{-1}$) at 325°C		
0.15 *M* DBT + 0 *M* BF	5.06	19.75
0.15 *M* DBT + 0.025 *M* BF	2.73	36.60
0.15 *M* DBT + 0.075 *M* BF	1.79	55.91
0.15 *M* DBT + 0.15 *M* BF	1.08	92.19
0.15 *M* BF + 0.075 *M* DBT	1.99	50.31
0.15 *M* BF + 0.11 *M* DBT	1.93	51.80
0.15 *M* BF + 0.15 *M* DBT	1.76	56.77

Temp. (°C)	Intrinsic rate constant k_{HDS} (moles hr^{-1} (g-cat)$^{-1}$)	Equilibrium adsorption coefficient K (liters $mole^{-1}$)
325	1.11×10^{-2}	$K_{DBT} = 11.86$ $K_{BF} = 61.70$

Eqs. (4) and (5), the intrinsic rate constant k_{HDS} and equilibrium adsorption coefficients K_{DBT} and K_{BF} were evaluated from Fig. 4; these mixed-feed results are listed in Table 2.

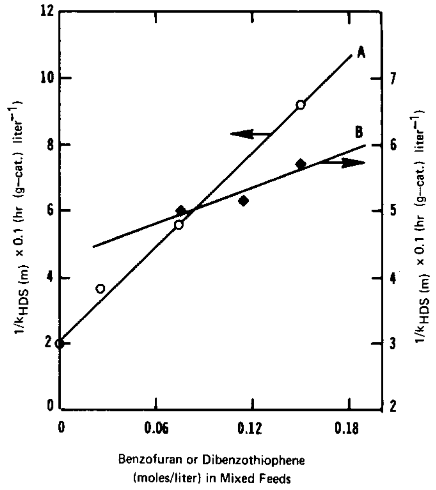

FIG. 4. Plot of $1/k'_{HDS(m)}$ vs concentration of benzofuran or dibenzothiophene in mixed-feed experiments. (A) 0.15 *M* DBT with vari-BF concentration; (B) 0.15 *M* BF with various DBT concentration.

HDO of Benzofuran in BF and DBT Mixed Feed

The hydrodeoxygenation activity was enhanced when the concentration of dibenzothiophene was increased from zero to 0.075 *M*. An inhibitory effect appeared when a concentration of dibenzothiophene was greater than 0.075 *M* (Fig. 5). The corresponding apparent rate constants are listed

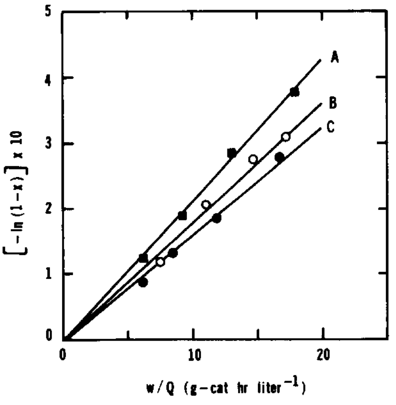

FIG. 3. Plot of $-\ln(1 - X_{DBT})$ vs w/Q for the hydrodesulfurization of dibenzothiophene in DBT and BF mixed feed with fixed concentration of 0.15 *M* BF and (A) 0.075 *M* DBT, (B), 0.11 *M* DBT, and (C) 0.15 *M* DBT.

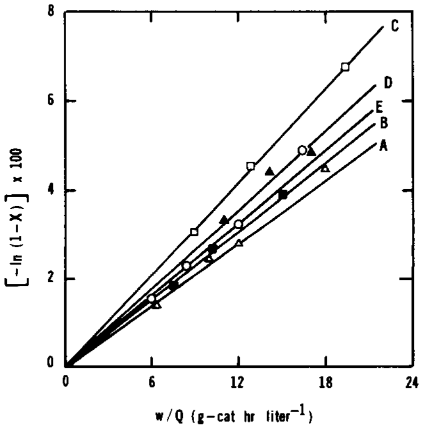

FIG. 5. Plot of $-\ln(1 - X_{BF})$ vs w/Q for the hydrodeoxygenation of benzofuran in BF and DBT mixed feed with fixed concentration of 0.15 *M* BF and (A) 0 *M* DBT, (B) 0.025 *M* DBT, (C) 0.075 *M* DBT, (D) 0.11 *M* DBT, and (E) 0.15 *M* DBT.

TABLE 3

Empirical Rate Constants for HDO of BF in Benzofuran and Dibenzothiophene Experiments

Feed concentration	$k'_{\mathrm{HDO}} \times 10^3$
Empirical rate constants k'_{HDO} (liters hr^{-1} $(\text{g-cat})^{-1}$) at 325°C	
0.15 *M* BF + 0 *M* DBT	5.68
0.15 *M* BF + 0.025 *M* DBT	5.85
0.15 *M* BF + 0.075 *M* DBT	7.89
0.15 *M* BF + 0.11 *M* DBT	6.30
0.15 *M* BF + 0.15 *M* DBT	6.18

in Table 3. The enhancement and then inhibition of HDO of benzofuran by dibenzothiophene was confirmed by experiment with fixed liquid flow rate of 5 cc/hr. These results are compared in Fig. 6 with benzofuran inhibition on hydrodesulfurization.

CONCLUSION

The remarkable inhibition of benzofuran on hydrodesulfurization of dibenzothiophene indicates that the binding strength of benzofuran must be much greater than that of dibenzothiophene, as indicated by the equilibrium adsorption coefficients obtained from mixed-feed experiments. The severity of the inhibition of benzofuran on HDS is clearly not less severe than pyridine on HDS (*4–6*).

The phenomenon that we observed in interactions of the hydrodeoxygenation of benzofuran and hydrodesulfurization of dibenzothiophene may be interpreted as follows: at lower DBT concentration, the higher conversion of DBT to desulfided products and H_2S results in promoting the catalyst reactivity by interaction of the catalyst with H_2S; at higher DBT concentration, the dominant effect is the competition between benzofuran and dibenzothiophene for the catalytic sites.

The nearly identical equilibrium adsorption coefficients determined from single-feed and mixed-feed Tables 1 and 2 confirm the unique catalytic site which is independent of the second component in the feed.

Note. In a paper appearing after our submission, Krishnamurthy and Shah (*20*) found diminution of dibenzofuran HDO rate by the presence of dibenzothiophene. Similarly, DBT retarded the HDS rate. A detailed kinetic analysis was not presented.

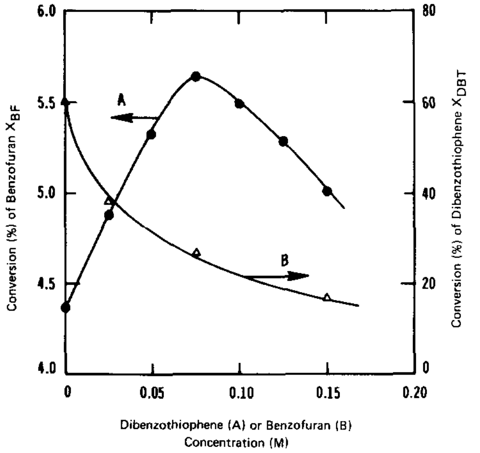

FIG. 6. Conversions vs concentration of second component in the mixed feed. (A) Conversion of benzofuran X_{BF} vs concentration of dibenzothiophene as second component. (B) Conversion of dibenzothiophene X_{DBT} vs concentration of benzofuran as second component in the mixed-feed stock.

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