

KINETICS OF HYDRODESULFURIZATION OF DIBENZOTHIOPHENE OVER NiO-MoO₃/γ-Al₂O₃ CATALYST

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Abstract—The kinetics of the hydrodesulfurization (HDS) of dibenzothiophene (DBT) has been studied over a NiO-MoO₃/γ-Al₂O₃ catalyst in the temperature range of 473-673 K for partial pressures of DBT from 20 × 10⁵Pa to 70 × 10⁵Pa. A form of the Langmuir-Hinshelwood type rate equation was used to describe the kinetics of the reaction. The reaction was carried out at low conversion level to obtain initial reaction rate data. From this study the rate equation giving the best fit to the data was $r = \frac{k_D P_D P_H}{[1 + K_D P_D + (K_H P_H)^{1/2}]^2}$, which suggests that DBT and hydrogen adsorb on the same type of active sites and that hydrogen adsorbs dissociatively.

INTRODUCTION

The HDS of hydrocarbon fuels is widely practiced in industrial processes to reduce sulfur content[1]. In petroleum thiophene compounds represent the major portion of the organosulfur compounds and among them DBT is one of the least reactive sulfur-containing constituents. Accordingly, the kinetics of DBT desulfurization has received increasing attention. The HDS of DBT has been studied by Hoog[2], Cawley[3], Obolentsev et al.[4], Landa et al.[5], Urimoto et al.[6], Bartsch et al.[7] and many other authors.

The results of these investigations, representing a variety of temperatures, hydrogen partial pressures, and catalyst compositions, fail to establish a unique reaction network. Cawley suggested that hydrogenolysis of the thiophenic ring is preceded by hydrogenation of one of the two benzenoid ring, giving cyclohexylbenzene(CHB) as a major product. Obolentsev et al., however, disagreed with Cawley's suggestion since they detected only biphenyl(BP) as the reaction product. Broderick et al.[8] reported that DBT reacted by two parallel routes: hydrogenolysis of the C-S bond to give H₂S and BP and hydrogenation of one of the benzoid rings followed by rapid hydrogenolysis of C-S bond to give CHB. Broderick[9] in a subsequent HDS study of DBT reported that hydrogenation and hydrogenolysis reactions occurred on different catalytic sites. The experiments reported here were performed to investigate the reaction kinetics of HDS of DBT.

EXPERIMENTAL

Dibenzothiophene(99.5%, Tokyo Chemical Company) was dissolved in n-heptane(Junsei Chemical Company). Both were used without purification. The reactant solution contained 0.25-1.5 mol% dibenzothiophene in n-heptane. The catalyst was a commercial NiO-MoO₃/γ-Al₂O₃(Cynamid Trilobe) which was crushed and sieved to 149-178 μm(80-100 mesh) particle size. Catalyst composition was 0.5 wt% NiO, 20.5 wt% MoO₃, 74.5% γ-Al₂O₃ and its surface area was 160 m²/g. The catalyst was presulfided in 10 vol% H₂S in H₂ flowing at the rate of 10 l/hr at atmospheric pressure and 673K for 3hr. Catalyst (1-3g) was mixed with carborundum, an inert reactor packing material.

The HDS of DBT was carried out in a fixed bed reactor(LPD Catastest Unit Model C manufactured by IFP). Reactant was pumped into the reactor, which consisted of a stainless steel tube(19 mm i.d. and 500mm length), placed in an electric furnace. Hydrocarbon was instantaneously vaporized at the entrance of the reactor tube and mixed with dried hydrogen of which the flow rate was measured by a flow meter. The mixture passed through a preheater section and then over the catalyst at a fixed temperature.

Reactions were run at temperatures of 473-673K and pressures of 20-70 × 10⁵ Pa with catalyst loading ranged 1 to 3g and its particle size of 20 to 100 mesh. Reactant solution was saturated with hydrogen before operation. Hydrogen partial pressure was varied from

6.7 to 60.7×10^5 Pa. The inverse of weight hourly space velocity (W/F) varied between 14.7×10^5 and 73.3×10^5 g of catalyst-h/g of feed.

Liquid reaction product was withdrawn from the bottom of a reactor. The sample was analyzed on a Shimadzu GC-7A gas chromatograph equipped with a flame ionization detector. The column was stainless steel tube having 3.5 m length and 3 mm i.d. It was packed with 1% OV-101 Chromosorb W, DMCS, A/W and maintained at 403K. Nitrogen carrier gas was employed with the flow rate of 30ml/min. For simplicity, no effort was made to analyze the gas products or to compute mass balances. The resultant experimental error introduced was thought to be trivial in view of the relatively low partial pressure of liquid products.

RESULTS AND DISCUSSION

1. Preliminary Experiments

Several preliminary experiments were carried out to check the influence on reaction rates. Firstly, blank runs with carborundum packing and no catalyst showed negligible activity. The lack of influence of an internal and an external mass transfer was confirmed by changing the particle size and the catalyst loading respectively. Rate data were obtained at steady state.

2. Reaction Route

The main products detected were biphenyl(BP) and cyclohexylbenzene(CHB) although trace amounts of bicyclohexyl were also detected. To find out the reaction route, three models in Table 1 were assumed. Two tests were made to find out the reaction route. First the concentration profiles for DBT and the two principal products were plotted. The shape of curves depicted in Fig. 1 suggested the typical serial reaction route.

Biphenyl yield versus DBT conversion data were obtained in order to test the validity of the reaction route by selectivity. In series reaction, differential equation is as follows.

Table 1. Reaction route models

Reaction	Reaction route
Serial reaction	$\text{DBT} \xrightarrow{k_1} \text{BP} \xrightarrow{k_2} \text{CHB}$
Parallel reaction	$\text{DBT} \begin{cases} \xrightarrow{k_1} \text{BP} \\ \xrightarrow{k_3} \text{CHB} \end{cases}$
Serial-parallel reaction	$\text{DBT} \begin{cases} \xrightarrow{k_1} \text{BP} \xrightarrow{k_2} \text{CHB} \\ \xrightarrow{k_3} \text{CHB} \end{cases}$

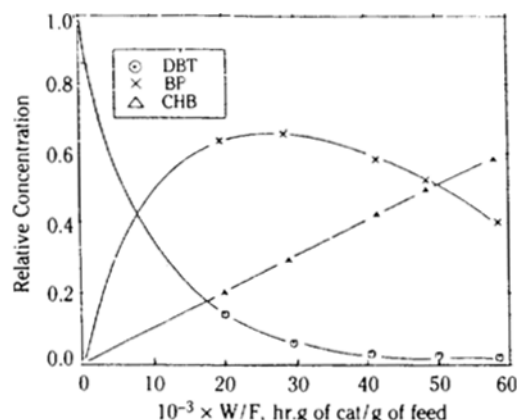


Fig. 1. Reactant and product concentration versus contact time data.

T: 300°C
 P: 40×10^5 Pa
 P_{DBT}/P_{H_2} : 9.3×10^{-3}

$$-\frac{d(1-X_D)}{dt} = k_1(1-X_D)$$

$$\frac{dY_B}{dt} = k_1(1-X_D) - k_2Y_B$$

As selectivity is $\frac{dY_B}{dX_D}$,

$$S = \frac{dY_B}{d(1-X_D)} = \frac{k_1(1-X_D) - k_2Y_B}{k_1(1-X_D)} = 1 - \frac{k_2}{k_1} \frac{Y_B}{1-X_D}$$

Experimental results, depicted in Fig. 2, fit serial reaction route.

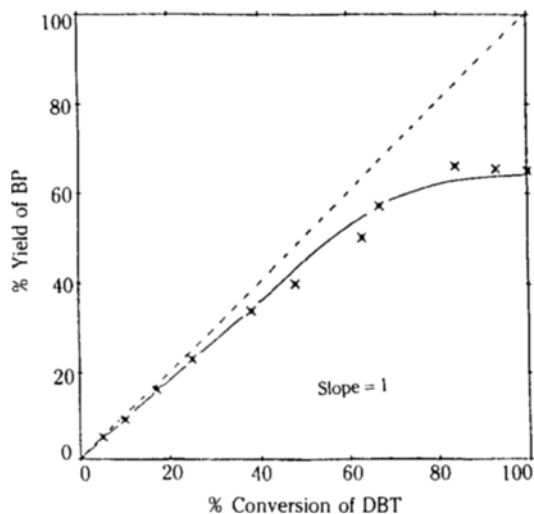


Fig. 2. Relation of DBT conversion and biphenyl yield for the test of reaction route by selectivity.

Table 2. Equation model and its linearization

	Rate equation	Linearization
Single type of site model	$r = \frac{K_D P_D P_H^a}{(1 + K_D P_D + (K_H P_H)^{1/c})^d}$	$Y = \left(\frac{P_D P_H^a}{r} \right)^{1/d} = \left(\frac{1}{K_D} \right)^{1/b} (1 + K_D P_D + (K_H P_H)^{1/c})$
Dual type of site model	$r = \frac{K_D P_D P_H^a}{(1 + K_D P_D)^b (1 + (K_H P_H)^{1/c})^d}$	$Y = \left(\frac{P_D P_H^a}{r (1 + (K_H P_H)^{1/c})^d} \right)^{1/b} = \left(\frac{1}{K_D} \right)^{1/b} (1 + K_D P_D)$

3. Rate Expressions

The HDS reaction rate of DBT depends on the partial pressure of products and reactants. In this study, two forms of Langmuir-Hinshelwood type rate equations were used to describe the kinetics of the reaction. Calculations of the best values of the constants were made at the reaction temperatures by multiple linear regression for a number of different combinations. Rate expressions are based on the assumption that the effect of hydrogen sulfide is negligible.

Broderick[9] found that the rate of hydrogenation was independent of the H₂S concentration. In order to apply this technique, the Langmuir-Hinshelwood equations were linearized after making the power of DBT unity as found by Broderick[9]. Equation model and its linearization form are shown in Table 2.

The sum of the squares of the differences between the experimental and the calculated reaction rates was computed for each rate equation, that is, for each combination of a, b, c, and d using the values of k_D , K_D , and K_H calculated by regression. Especially linear regression analysis were carried out for various values of K_H by trial-and-error in dual type of site model. The

rate equation with the lowest sum of squares was chosen as the best rate equation.

Multiple linear regression analysis such as those described above, when applied to Langmuir-Hinshelwood rate equation, has the drawback that deviations in the quantity Y in Table 2 are minimized, rather than the deviation in r as pointed out by Satterfield[10]. To avoid this kind of drawback Broderick[8] used a non-linear least squares(NLLS) regression analysis. In this study, however, NLLS analysis could not be applied due to the capacity limitation of our computer system. The data for the runs are given in Table 3-6.

Linear regression analysis were carried out for various sets of a, b, c and d values. Goodness of fit was assessed by the coefficient of determination(R²). The form represented by model S-1, D-1, and D-2 showed best satisfactory correlations, whereas the others did not. Parameter values for four temperatures are collected in Table 7.

Among the three models, the best is model S-1. The obtained rate equation is

$$r = \frac{k_D P_D P_H}{(1 + K_D P_D + (K_H P_H)^{1/2})^2}$$

Table 3. Kinetic data at 483K

No.	Pressure × 10 ⁵ Pa	Feed rate ml/hr	H ₂ flowrate //hr	W/F × 10 ⁻³ h·g cat/g feed	P _D ⁰ × 10 ³ Pa	P _{H₂} ⁰ × 10 ³ Pa	γ gmole/ hr·g cat	x _D converted fraction
1	30	70	14.4	20.9	3	1719	34	0.02
2	30	70	14.4	20.9	6	1719	36	0.02
3	30	50	7.9	29.3	3	1527	16	0.01
4	30	50	7.9	29.3	7	1527	16	0.01
5	30	30	7.9	48.9	3	1900	74	0.10
6	30	30	7.9	48.9	5	1900	87	0.12
7	30	25	7.9	58.6	2	2023	50	0.08
8	30	25	7.9	58.6	5	2024	45	0.07
9	30	20	7.9	73.3	2	2164	63	0.13
10	30	20	7.9	73.3	4	2164	76	0.15

Table 4. Kinetic data at 493K

No.	Pressure $\times 10^5$ Pa	Feed rate ml/hr	H ₂ flowrate l/hr	W/F $\times 10^{-3}$ h·g cat/g feed	P_D^0 $\times 10^3$ Pa	$P_{H_2}^0$ $\times 10^3$ Pa	γ gmole/ hr·g cat	x_D converted fraction
1	60	70	14.4	20.9	6	3437	77	0.04
2	60	70	14.4	20.9	13	3438	78	0.05
3	50	70	7.9	20.9	7	2126	63	0.04
4	50	70	7.9	20.9	14	2126	60	0.04
5	40	70	7.9	20.9	7	1701	40	0.02
6	40	70	7.9	20.9	14	1701	51	0.03
7	30	70	14.4	20.9	7	1719	40	0.04
8	30	70	14.4	20.9	14	1719	51	0.04
9	20	70	7.9	20.9	3	850	102	0.06
10	20	70	7.9	20.9	6	851	104	0.06

Table 5. Kinetic data at 513K

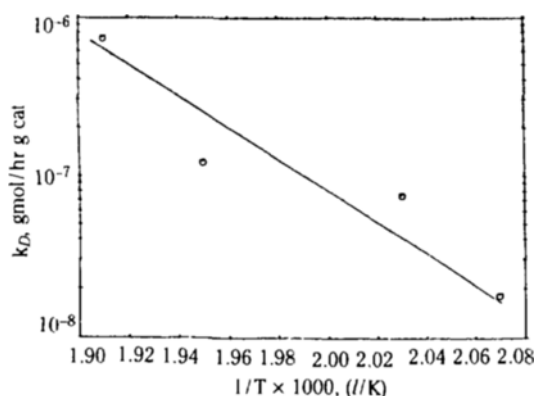
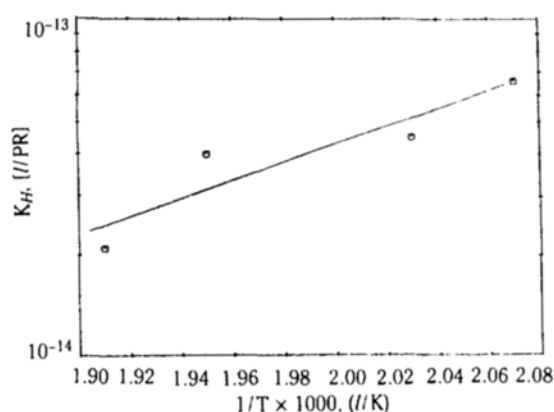
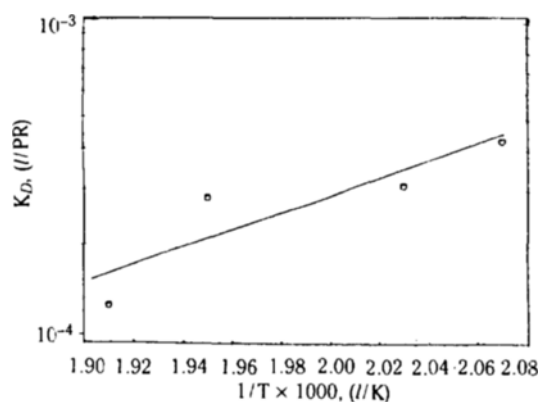
No.	Pressure $\times 10^5$ Pa	Feed rate ml/hr	H ₂ flowrate l/hr	W/F $\times 10^{-3}$ h·g cat/g feed	P_D^0 $\times 10^3$ Pa	$P_{H_2}^0$ $\times 10^3$ Pa	γ gmole/ hr·g cat	x_D converted fraction
1	30	70	14.4	20.9	3	1719	90	0.05
2	30	70	14.4	20.9	5	1719	90	0.05
3	30	50	7.9	29.3	4	1526	82	0.07
4	30	50	7.9	29.3	6	1526	86	0.07
5	30	35	7.9	41.9	3	1790	139	0.11
6	30	35	7.9	41.9	5	1790	140	0.11
7	30	30	7.9	48.9	3	1899	116	0.12
8	30	30	7.9	48.9	5	1899	121	0.12
9	30	20	7.9	73.3	2	2164	122	0.15
10	30	20	7.9	73.3	4	2164	136	0.15

Table 6. Kinetic data at 523K

No.	Pressure $\times 10^5$ Pa	Feed rate ml/hr	H ₂ flowrate l/hr	W/F $\times 10^{-3}$ h·g cat/g feed	P_D^0 $\times 10^3$ Pa	$P_{H_2}^0$ $\times 10^3$ Pa	γ gmole/ hr·g cat	x_D converted fraction
1	60	70	7.9	20.9	9	2551	211	0.09
2	60	70	7.9	20.9	13	2550	211	0.09
3	50	70	7.9	20.9	7	2126	195	0.11
4	50	70	7.9	20.9	11	2125	192	0.11
5	40	70	7.9	20.9	6	1701	143	0.08
6	40	70	7.9	20.9	11	1701	146	0.09
7	30	70	7.9	20.9	4	1526	203	0.15
8	30	70	7.9	20.9	7	1525	208	0.15
9	20	70	7.9	20.9	3	850	186	0.11
10	20	70	7.9	20.9	6	850	188	0.11

Table 7. Rate equations best fitting kinetic data

MODEL	a	b	c	d	T	k_D	K_D	K_H	R ²
S-1	1		2	2	483K	1.81×10^{-7}	4.25×10^{-4}	6.55×10^{-14}	0.782
					493K	6.64×10^{-7}	3.04×10^{-4}	4.51×10^{-14}	0.885
					513K	1.09×10^{-6}	2.88×10^{-4}	4.29×10^{-14}	0.885
					523K	5.37×10^{-6}	1.30×10^{-4}	3.05×10^{-14}	0.930
D-1	1	2	2	1	483K	3.40×10^{-8}	2.91×10^{-4}	4×10^{-12}	0.734
					493K	6.69×10^{-8}	3.69×10^{-4}	3×10^{-12}	0.833
					513K	7.56×10^{-8}	4.09×10^{-4}	2×10^{-12}	0.795
					523K	3.38×10^{-7}	5.05×10^{-3}	1×10^{-12}	0.897
D-2	2	2	1	1	483K	4.83×10^{-14}	2.71×10^{-4}	4×10^{-6}	0.732
					493K	9.06×10^{-14}	3.34×10^{-4}	3×10^{-6}	0.835
					513K	1.78×10^{-13}	5.51×10^{-4}	2×10^{-6}	0.760
					523K	7.97×10^{-13}	1.09×10^{-3}	1×10^{-6}	0.871

**Fig. 3. Arrhenius plot for rate constant of DBT HDS.****Fig. 5. van't Hoff for H₂ adsorption equilibrium constant.****Fig. 4. van't Hoff plot for DBT adsorption equilibrium constants.**

This rate expression suggests the single site mechanisms in which H₂ dissociatively adsorbs on the sites in competition with DBT. From Arrhenius and van't Hoff plots of Fig. 3-5, activation energy and heat of adsorption for each species were calculated. The kinetic parameters obtained are the following:

$$k_D = 6.72 \times 10^9 \exp(-36.48/RT)$$

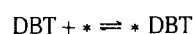
$$K_D = 1.45 \times 10^{-9} \exp(12.09/RT)$$

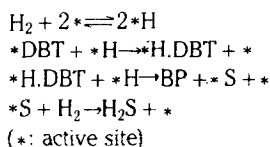
$$K_H = 1.58 \times 10^{-17} \exp(7.39/RT)$$

$$(R: \text{kcal/gmole}\cdot\text{K})$$

4. Reaction Mechanism

From the rate expression, a possible mechanism can be proposed as follows:





CONCLUSION

(1) HDS of DBT on NiO-MoO₃/γ-Al₂O₃ takes serial reaction route.



(2) Rate equation giving the best fit was:

$$r = \frac{K_D P_D P_H}{1 + K_D P_D + (K_H P_H)^{1/2}}$$

(3) The rate equation suggests that DBT and hydrogen adsorb on same type of site and hydrogen adsorbs dissociatively,

(4) The kinetics parameter in rate equation are given by:

$$k_D = 6.72 \times 10^9 \exp(-36.48/RT)$$

$$K_D = 1.45 \times 10^{-9} \exp(12.09/RT)$$

$$K_H = 1.58 \times 10^{-17} \exp(7.39/RT)$$

where T is in K and R is in kcal/g mole·K.

NOMENCLATURE

a, b, c, d : exponent constant of rate equation

BP : biphenyl

CHB : cyclohexylbenzene

DBT : dibenzothiophene

E_a : activation energy(kcal/gmole)

exp : exponent

F : flow rate (ml/hr)

k₁, k₂, k₃, k_d : rate constant(gmole/g.hr)

k_D, k_H : adsorption equilibrium constant(Pa⁻¹) of DBT and H₂

Pa, PA : Pascal in pressure unit

P_D, P_H(P_{H₂) : Partial pressure of DBT and H₂}

P_D⁰, P_{H₂}⁰ : initial partial pressure of DBT and H₂

r : reaction rate (gmole/g.hr)

S : selectivity

T : temperature

W : catalyst weight(g)

x_D : conversion of DBT

Y_B, Y_C : yield of BP and CHB

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