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NOTE

Kinetics of Dibenzothiophene Hydrodesulfurization

INTRODUCTION

Hydrotreating is a process in which organically bound sulfur and nitrogen compounds are removed from petroleum feedstocks to produce processible, stable, and environmentally acceptable liquid fuels or lubes (*1–3*). Essentially two types of catalysts, which differ in composition, are in use in current refineries: one is sulfided $CoO–MoO_3/\gamma–Al_2O_3$, the other sulfided $NiO–MoO_3/Al_2O_3$. The selection of these catalysts depends largely on the processing objectives and the nature of the feedstocks. Generally speaking, the NiMo catalysts are used for hydrodenitrogenation (HDN) and hydrodearomatization (HDA), while the CoMo catalysts are used for hydrodesulfurization (HDS).

Because of its industrial importance, hydrotreating catalytic chemistry has been a subject of a good deal of research. A common approach is to study the various hydrotreating reactions with model compounds which are representative of the least-reactive heterocyclic constituents of the feedstock. For example, HDS of dibenzothiophene (DBT) is a useful model reaction for HDS of commercial middle distillate feedstocks.

In a previous study, Ho *et al.* (*4*) quantified the interactions between HDN and HDA on a commercial NiMo catalyst by using a feed mixture containing 2,4-dimethyl pyridine and 2-methylnaphthalene. With *the same* catalyst, here we determine the kinetics of DBT HDS. We hope the results, when taken together with those in (*4*), give us some idea on how the various reactions compete with each other. Another reason for undertaking the present study is that *relatively* little attention has been paid to DBT HDS on NiMo catalysts. Most published DBT HDS studies have been done on CoMo catalysts (*2*).

EXPERIMENTAL

Catalyst

As noted, the catalyst used in this study was the same as that used in (*4*). Its composition and physical properties are: NiO, 3%; MoO_3, 16%; surface area, 180 m^2/g; and pore volume, 0.5 cc/g. Prior to use, the catalyst was screened to 20–40 mesh granules and then sulfided at 360°C for 1 h at atmospheric pressure with a 10% H_2S-in-H_2 gas mixture.

Apparatus and Analysis

Reactions were carried out in a cocurrent, downflow, fixed-bed reactor contained in a fluidized sand bath. The reactor was made of a $\frac{3}{8}$-in. i.d. 316 stainless-steel pipe and was equipped with a calibrated feed burette, pump, gas–liquid separator, and product collector. The reactor pressure and hydrogen flow were controlled by a computer.

In all runs a large excess of hydrogen was used, corresponding to a gas-to-liquid ratio of 32 kmol H_2/m^3 liquid feed. The feed consisted of a 10 wt% solution of DBT in tetralin. Both chemicals were purchased from Aldrich Chemical Company. After the reactor reached the steady state, the reaction was allowed to proceed for at least 2 to 3 days during which rate data were taken. Reaction conditions were 310–325°C, 6–48 LHSV, and 3.1 MPa. Under these conditions, the catalyst showed no signs of deactivation throughout the study.

The liquid products were quantified on an HP 5830A gas chromatograph equipped with a thermal conductivity detector with either a 10-ft, $\frac{1}{8}$-in.-o.d. column packed with

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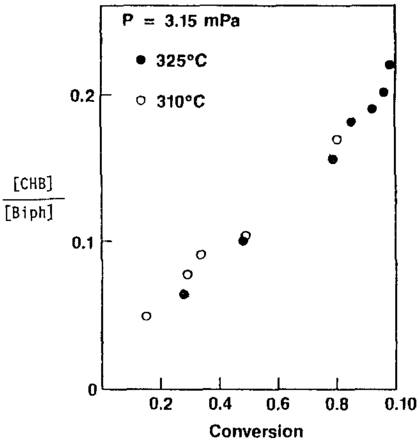

FIG. 1. Concentration ratio [CHB]/[BiPh] as a function of DBT conversion; T = 310°C and 325°C.

3% SP 2260 on 100/120 mesh Supelcoport or a 6-ft. column packed with 3% Dexsil 300 GC on 100/120 mesh Supelcoport.

RESULTS

The major reaction products were identified to be biphenyl (BiPh), cyclohexylbenzene (CHB), and H_2S. The disappearance of DBT takes a triangular pathway, as

$$\begin{tikzcd} & \text{BiPh} \arrow[dd] \\ \text{DBT} \arrow[ur] \arrow[dr] & \\ & \text{CHB} \end{tikzcd} \tag{1}$$

The reaction DBT-to-CHB has been found to involve the reactive intermediate tetrahydro-DBT (*1*). The above reaction scheme was based on the following observations:

(1) Experiments at 325°C showed that CHB formed at very early stages of the reaction.

(2) As Fig. 1 shows, the ratio [CHB]/[BiPh] increases with increasing DBT conversion through changes in LHSV. And the pseudo-reaction orders for the two reactions DBT → BiPh and DBT → CHB are the same (*1, 5*).

The above triangular scheme has also been used by others for HDS of DBT on CoMo catalysts (*6, 7*). It should be mentioned that Singhal *et al.* (*8*) proposed a parallel scheme for DBT HDS on a CoMo catalyst. In this regard, we comment that NiMo in general is a stronger hydrogenation catalyst than CoMo, as already mentioned.

KINETIC MODELING

The rate data were correlated with a Langmuir–Hinshelwood kinetic model, with the following assumptions:

(1) The adsorptions of organics and hydrogen involve two different types of catalytic sites.

(2) Surface reactions, not adsorption or desorption, are rate-limiting.

(3) The reaction products compete with DBT for catalytic sites.

(4) Hydrogen concentration is essentially constant across the reactor, thus allowing the hydrogen concentration term to be incorporated in the rate constants of surface reactions.

It should be pointed out that while there are significant discrepancies among the published HDS kinetic models, most of the literature data can be fitted rather well by models based on the above assumptions (*2*, and references therein). Finally, we note that the active sites for the organics are commonly accepted to be sulfur anion vacancies associated with exposed Mo cations. It is not our intent here to distinguish different kinds of vacancies which may have different degrees of reactivities for hydrogenation and hydrogenolysis.

The above assumptions lead to the mass balance equations for DBT, BiPh, and the total reaction products,

$$\frac{dC_d}{d\xi} = -\frac{(k_{d1} + k_{d2})K_dC_d}{1 + K_dC_dC_{do} + K_pC_pC_{do}} \tag{2}$$

$$\frac{dC_b}{d\xi} = \frac{k_{d1}K_dC_d - k_bK_bC_b}{1 + K_dC_dC_{do} + K_pC_pC_{do}} \tag{3}$$

$$\frac{dC_p}{d\xi} = \frac{2(k_{d1} + k_{d2})K_dC_d}{1 + K_dC_dC_{do} + K_pC_pC_{do}} \tag{4}$$

with boundary conditions

$$\xi = 0, \quad C_d = 1.0, \quad C_b = C_p = 0.0, \qquad (5)$$

where

C_{do} = concentration of DBT in the feed (mol/liter)

C_d = DBT concentration normalized with respect to C_{do}

C_b = normalized BiPh concentration

C_p = sum of normalized concentrations of BiPh, CHB, and H_2S

ξ = contact time (1/LHSV).

Thus, we see that the performance of the catalyst is characterized by the following parameters: k_{d1} and k_{d2}, the HDS surface rate constants for DBT-to-BiPh and DBT-to-CHB, respectively; K_d, the adsorption equilibrium constant for DBT; k_b, the hydrogenation surface rate constant for BiPh-to-CHB; and K_p, the lumped adsorption equilibrium constant for the reaction products. The model parameters were determined by a nonlinear-squares fit using the Levenberg–Marquardt algorithm. In so doing, Eqs. (2)–(4) were numerically integrated by means of a fourth-order Runge–Kutta method. The best sets of parameters so found for 310°C are

$$\begin{array}{ccccc} k_{d1} & k_{d2} & K_d & K_p & k_bK_b \\ \hline 11.6 & 2.69 & 1.26 & 1.32 & 1.0 \end{array},$$

where units of k's and K's are, respectively, mol liter^{-1} h^{-1} and liter/mol. The results of the fit are shown in Fig. 2 where the solid curves are model predictions using the above parameter values.

The above results indicate that DBT-to-BiPh is the most important pathway in DBT HDS, as is the case in DBT HDS on sulfided $CoO–MoO_3/Al_2O_3$ catalysts. Over the conditions studied, the adsorption equilibrium constant for total reaction products, K_p, is found to be comparable to that of DBT, K_d.

Before making a comparison between the present result with those of Ho *et al.* (*4*), two points should be made. One is that the kinetic model used by Ho *et al.* is identical in structure to the one used here. In the study of Ho *et al.*, the model passed a critical test: the same rate constants and adsorption coefficients were obtained—whether the HDN and HDA reactions were carried out individually or competitively. The other point is that Ho *et al.* found virtually no effects of hydrogen pressure on the HDN and HDA kinetics over the 4 to 13 MPa range, indicating that hydrogen is readily available on the catalyst surface. This probably reflects that the NiMo catalyst is quite effective in activating hydrogen.

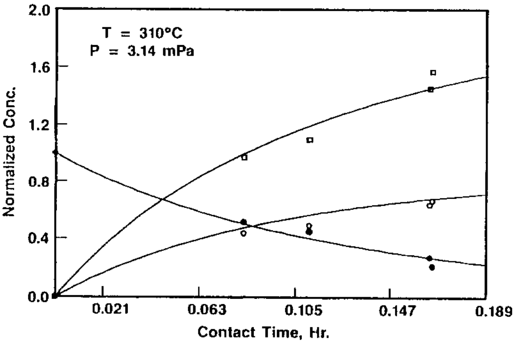

FIG. 2. Product distribution as a function of contact time; T = 310°C. Solid lines are model predictions.

Comparing the present results with those of Ho *et al.*, *qualitatively*, one notes that the rankings

$$K_n \gg K_s \gg K_a \qquad (6)$$

$$k_a \gg k_s \gg k_n, \qquad (7)$$

where the subscripts n, s, and a denote nitrogen, sulfur, and aromatic compounds, respectively. The variations of k and K in going from HDN to HDS to HDA are quite significant. However, the product kK does not vary much on a relative basis; i.e., a sort of "compensation effect." It is unclear to us as to how general this finding is. More work along this line is needed.

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