JOURNAL OF CATALYSIS 51, 221–228 (1978)

Hydrodesulfurization of Benzothiophene over $CoO-MoO_3-Al_2O_3$ Catalyst

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Received June 27, 1977

Hydrodesulfurization of benzothiophene has been investigated over a $CoO-MoO_3-Al_2O_3$ catalyst. Studies were made with a stirred-batch minireactor at temperatures of 200 to 400°C and 1250 psig. The hydrodesulfurization of benzothiophene proceeds by two separate mechanisms, both pseudo-first order in benzothiophene. At increased hydrogen sulfide concentration levels, a back reaction occurs between styrene and hydrogen sulfide with the formation of 1-phenylethanethiol and 2-phenylethanethiol.

INTRODUCTION

Compared to thiophene little work has been done on the hydrodesulfurization of benzothiophene, one of the principal organosulfur compounds in coal hydrogenation (*1*). Characterization of the overall reaction mechanism has been minimal. Bartsch and Tanielian (*2*) reported that ethylbenzene was the only detectable reaction product formed, possibly by hydrogenation of an intermediate, i.e., styrene. Contrary to this Givens and Venuto (*3*) and DeBeer *et al.* (*4*) observed that hydrodesulfurization of benzothiophene did form ethylbenzene, but through the intermediate dihydrobenzothiophene. More recently Furimsky and Amberg (*5*) reported the appearance of styrene in the product stream during the hydrodesulfurization of benzothiophene and dihydrobenzothiophene over an unsupported MoS_2 catalyst promoted with Co.

Most of the previous work on the hydrodesulfurization of benzothiophene has been performed at atmospheric pressure in pulse and continuous-flow reactors. Since coal liquefaction–hydrodesulfurization processes operate at pressures greater than 1000 psig it was of interest to study the hydrodesulfurization of benzothiophene at elevated hydrogen pressures in a stirred-batch reactor. The principle objective was to elucidate the hydrodesulfurization reaction mechanism.

EXPERIMENTAL

Materials. Benzothiophene (97%) and styrene (99%) were obtained from Aldrich. Benzothiophene was recrystallized from 99+% *n*-dodecane (Matheson, Coleman and Bell) according to standard procedures. Gas chromatography (gc) suggested that the purity was over 99% for both stock and recrystallized compounds. Only low-boiling hydrocarbons with residence times less than 1 min were detected in either the stock or recrystallized compounds when dissolved in decalin. Separate hydrodesulfurization runs using both stock and recrystallized compounds resulted in no difference in the

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0021-9517/78/0512-0221$02.00/0

product distribution or rates of desulfurization. Therefore, all subsequent runs were performed using the stock benzothiophene as received.

Decahydronaphthalene (decalin), purchased from Eastman and reported to be a *cis–trans* mixture with a maximum of 0.01% tetralin, was used as received. 2-Phenylethanethiol, obtained from K & K, was also used as received. The catalyst was a commercial cobalt molybdate on alumina, Girdler 35 ($\frac{3}{16} \times \frac{3}{16}$ in.).

Instrumentation. Analysis of the samples was accomplished with a dual-column Perkin–Elmer Model 800 gas chromatograph equipped with a differential flame ionization detector and linear temperature programming. A 16-ft-long Dexil 300 gc column was used and permitted good separation.

Quantitative analysis of the chromatograms was obtained by electronic integration of the peak areas using the Perkin–Elmer M-1 Computing Integrator. Response factors were obtained, when possible, by integration of chromatograms of known amounts of commercial compounds.

Qualitative analysis of the samples was obtained from retention times and mass spectra. The gc–mass spectrometry (ms) instrument employed was equipped with a Varian Aerograph Series 2700 gas chromatograph and a Dupont Instruments 21-094b data acquisition system.

Apparatus and experimental technique. The minireactor used was a Parr Model 4561. Heat was supplied by an automatic temperature-controlled mantle. The reaction solution was continuously agitated by a mechanical stirrer. The reactor bomb was constructed of T 316 stainless steel with a capacity of 300 ml.

Approximately 7 g of fresh catalyst were used for each experiment. The catalyst, contained in a stainless steel basket attached to the stirrer shaft, was presulfided in the reactor according to the procedure described by Thomas (*6*). Reactant solutions (50 ml) consisting of a decalin-to-benzothiophene molar ratio of 1.9 (8 wt % sulfur) were added to the reactor bomb at room temperature. Nitrogen was passed over the presulfided catalyst while the solution was added to prevent exposure to the air.

The reactor was then charged from a regulated hydrogen cylinder to a pressure of 600 psig and was heated to the desired temperature. When the reactor temperature was reached, a 1- to 2-ml sample was collected, and the reactor was charged to 1250 psig and then closed off from the hydrogen cylinder. During the run the pressure in the reactor was recharged periodically, always before it dropped below 1200 psig.

Samples were collected periodically from a single-dip tube extended to the bottom of the reactor and attached to the gas inlet and liquid sampling valves. After the sample was collected the pressure was increased to 1250 psig. The samples collected were sealed and analyzed within 24 hr. The reaction times plotted in the graphs are with respect to the time of the first sample collected being at $t = 0$ and do not include the heat-up period of 20 to 30 min.

No effort was made to analyze the gas products or to compute mass balances. The principal goal was to perform a qualitative and quantitative analysis of the liquid products.

RESULTS AND DISCUSSION

Figure 1 illustrates the conversion–reaction period plots for benzothiophene from 200 to 400°C. It has previously been reported that the hydrodesulfurization of benzothiophene is first order in benzothiophene. To confirm this the integrated equation for a first-order reaction was put into a form in which a linear plot could be obtained:

$$k = 1/t \ln (a_o/a_o - x),$$

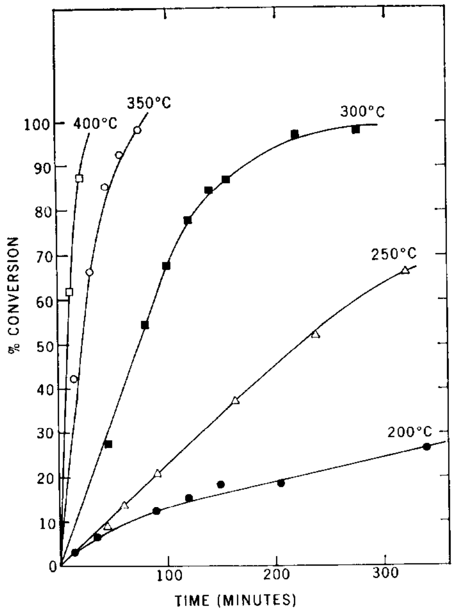


FIG. 1. The percentage conversion of benzothiophene as a function of reaction time at 200 (●), 250 (△), 300 (■), 350 (○), and 400°C (□). P = 1250 psig; 7 g of presulfided $CoO-MoO_3-Al_2O_3$.

where k is the rate constant, t is the reaction time, a_o is the concentration of benzothiophene at $t = 0$, and $a_o - x$ is the concentration at time t. Plots of ln $(a_o/a_o - x)$ vs t, illustrated in Fig. 2, gave straight lines suggesting a first-order reaction with respect to the benzothiophene concentration. The slopes of the straight lines represent the rate constant k as listed in Table 1.

An Arrhenius plot (Fig. 3) gave a value for the apparent activation energy of 16.1 kcal/mole. Though this value is in accordance with some reported data on thiophenic hydrodesulfurization (*7*), it is not the true activation energy for the hydrodesulfurization reaction mechanism. The apparent activation energy calculated by the Arrhenius plot reflects not only the temperature effect on the reaction rate constant but also the adsorption constants. However, an Arrhenius activation energy of this magnitude does strongly indicate that the reaction is not diffusion limited.

Addition of Hydrogen Sulfide

Gas chromatography–mass spectrometry data (Table 2) of the chromatogram illustrated in Fig. 4 suggest that the peaks at 2.1, 2.4, and 8.3 min are due to ethylbenzene, styrene, and dihydrobenzothiophene, respectively. In addition, the chromatogram peaks at 6.0 and 6.4 min are attributed to 1-phenylethanethiol and 2-phenylethanethiol, respectively. Figure 5 illustrates the conversion rates for the hydrodesulfurization products of benzothiophene at 250°C and 1250 psig.

The formation of 1-phenylethanethiol and 2-phenylethanethiol during the catalytic hydrodesulfurization of benzothiophene has not been previously reported. However, recently Yergey *et al.* (*8*) reported that hydrodesulfurization of coal, resulting in the formation of hydrogen sulfide, can cause a back reaction of the hydrogen sulfide with partially desulfurized coal.

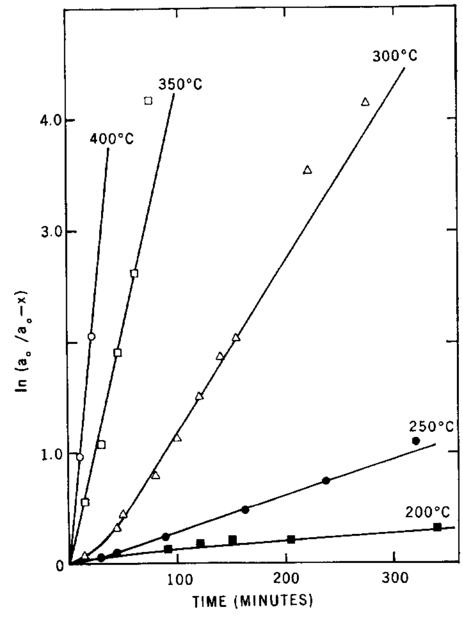


FIG. 2. Plot of ln $(a_o/a_o - x)$ vs reaction period for the hydrodesulfurization of benzothiophene at 200 (■), 250 (●), 300 (△), 350 (□), and 400°C (○). P = 1250 psig; 7 g of presulfided $CoO-MoO_3-Al_2O_3$.

TABLE 1

Reaction Rate Constants

Temperature (°C)	Rate constant (sec^{-1})
200	1.21×10^{-5}
250	5.67×10^{-5}
300	2.60×10^{-4}
350	7.60×10^{-4}
400	1.83×10^{-3}

They suggest that this sulfur-containing compound (referred to as Organic III), in which the sulfur is bound to the carbon, may not be present in the original coal but, rather, is formed during hydrodesulfurization. Consequently, several additional hydrodesulfurization experiments were performed to determine whether 1-phenylethanethiol and 2-phenylethanethiol were the result of a back reaction, possibly between styrene and hydrogen sulfide.

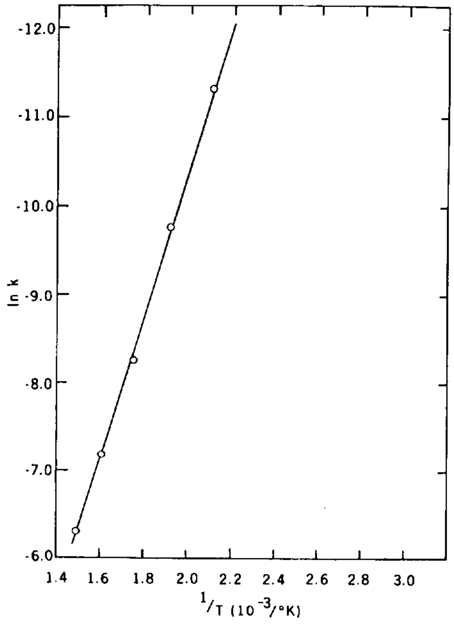


FIG. 3. Arrhenius plot for the hydrodesulfurization of benzothiophene. P = 1250 psig; 7 g of presulfided $CoO–MoO_3–Al_2O_3$.

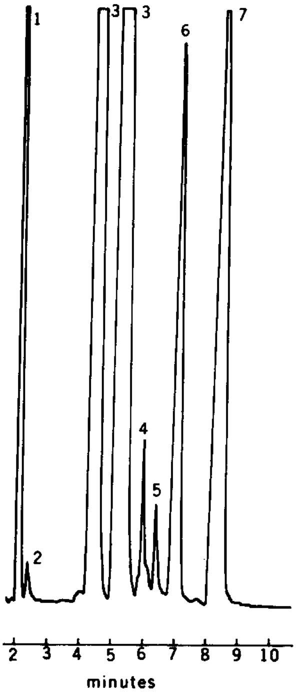


FIG. 4. Gas chromatogram of benzothiophene reaction solution after 320 min at 250°C and 1250 psig. (1) Ethylbenzene; (2) styrene; (3) decalin; (4) 1-phenylethanethiol; (5) 2-phenylethanethiol; (6) benzothiophene; (7) dihydrobenzothiophene. Temperature programmed at 7.5°C/min from 125 to 200°C.

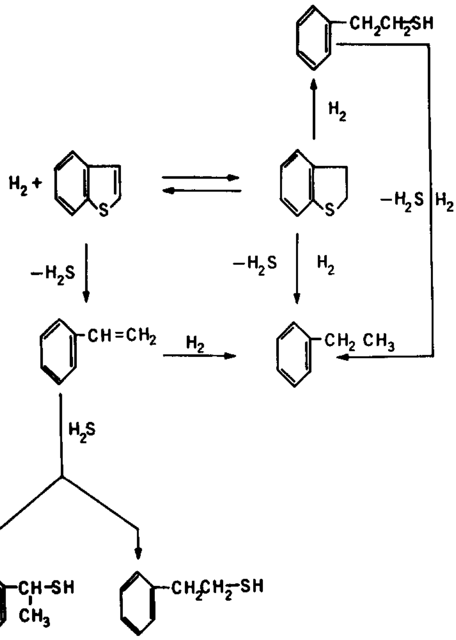
Since coal contains considerable amounts of pyrite (FeS_2), a mixture of benzothiophene and pyrite was hydrodesulfurized. It was anticipated that an increase in the hydrogen sulfide concentration would result from the hydrodesulfurization of pyrite. This increase in hydrogen sulfide would then result in an increase in the concentration of the back-reaction products, 1-phenylethanethiol and 2-phenylethanethiol. Figure 6, when compared to Fig. 5, illustrates that the rate of formation of the thiols increased with the addition of pyrite while the rate of conversion of benzothiophene decreased.

Jones and Reid (*9*) first reported that elemental sulfur positively catalyzed the reaction of hydrogen sulfide with olefins. When benzothiophene was desulfurized in the presence of sulfur the rate of formation of the thiols again increased while the rate of conversion of benzothiophene decreased in comparison to the desulfurization of benzothiophene alone (Fig. 7). This would suggest that a back reaction occurs between hydrogen sulfide and an unsaturated hydrocarbon, probably styrene.

Mechanism

The data presented suggest that the hydrodesulfurization of benzothiophene involves two different reaction mechanisms:

(i) the initial hydrogenation of the thiophene double bond followed by hydrodesulfurization, and (ii) hydrodesulfurization with the formation of unsaturated hydrocarbons followed by hydrogenation (see Scheme 1).



SCHEME 1

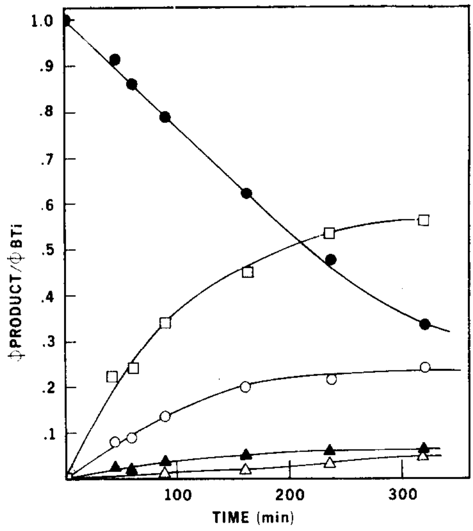


FIG. 5. The conversion of benzothiophene at 250°C and 1250 psig of hydrogen (7 g of presulfided CoO–MoO_3–Al_2O_3). (●) Benzothiophene; (□) Dihydrobenzothiophene; (○) Ethylbenzene; (▲) 1-phenylethanethiol; (△) 2-phenylethanethiol. ϕ Product/ϕ BTi is the ratio of the chromatogram peak area for the product plotted versus that for the initial concentration of benzothiophene.

This mechanism is in partial agreement with that recently proposed by Furimsky and Amberg (*5*) based on the detection of styrene and ethylbenzene during the hydrodesulfurization of benzothiophene over an unsupported MoS_2 catalyst promoted with Co. In a similar manner they proposed a mechanism in which ethylbenzene is formed through the hydrogenation of styrene and the hydrodesulfurization of dihydrobenzothiophene. However, they do not define the formation of ethylbenzene from dihydrobenzothiophene through the intermediate 2-phenylethanethiol. In addition they do not suggest the formation of either 1-phenylethanethiol or 2-phenylethanethiol by a back reaction of hydrogen sulfide.

Considerable efforts have been made by others to explain the catalytic nature of the CoO–MoO_3–Al_2O_3 during hydrodesulfurization. Desikan and Amberg (*10*) proposed a two-site theory for the sulfided cobalt molybdate catalyst during hydrodesulfurization. A strong acid site was attributed to hydrogenation of olefins. Hydrogen sulfide, thiophene, and pyridine were also strongly adsorbed on these sites and exerted a strong poisoning effect on the hydrogenation of olefins. A more weakly acidic site was identified with the bulk of the desulfurization.

Satterfield *et al.* (*11*) recently reported the interreactions between hydrodesulfurization of thiophene and hydrodenitrogena-

TABLE 2

Gas Chromatography–Mass Spectrometry Data

Benzothiophene (t_r = 7.0 min)[a]		Dihydrobenzothiophene (t_r = 8.3 min)		1-Phenylethanethiol (t_r = 6.0 min)		2-Phenylethanethiol (t_r = 6.4 min)	
m/e	Relative intensity	m/e	Relative intensity	m/e	Relative intensity	m/e	Relative intensity
136	65.0	136[b]	97.1	138[b]	31.0	138[b]	39.5
135	85.1	135	100.1	123	100.0	123	0.0
134[b]	100.0	134	48.1	105	46.5	105	4.9
91	3.7	91	90.2	91	6.0	91	100.0
90	44.4	90	8.2	47	0.0	47	4.3
89	34.1	89	33.3	45	6.5	45	4.5
47	1.5	47	1.7				
45	64.6	45	20.6				

[a] t_r is the retention time.

[b] Parent peak; ionization voltage = 70 V.

tion of pyridine using several catalysts including CoO–MoO$_3$. They observed that basic nitrogen compounds inhibit the hydrodesulfurization of thiophene on a sulfided cobalt molybdate catalyst. They postulated two hydrodesulfurization sites: one very active toward hydrodesulfurization, but sensitive to nitrogen bases, and the other site less active for hydrodesulfurization and pyridine poisoning, but responsible for hydrodesulfurization when the first type of site is poisoned.

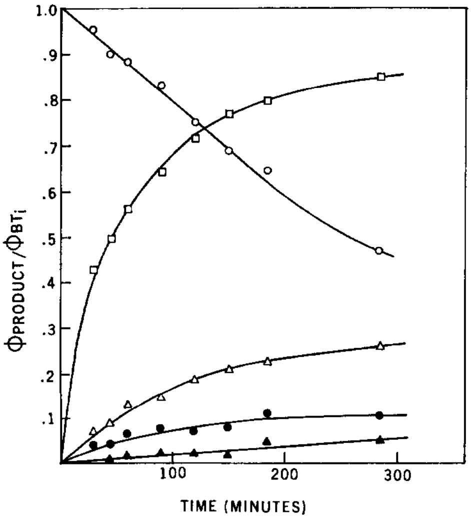


FIG. 6. The conversion of benzothiophene (10 g of pyrite) at 250°C and 1250 psig (7 g of presulfided CoO–MoO$_3$–Al$_2$O$_3$). (○) Benzothiophene; (□) dihydrobenzothiophene; (△) ethylbenzene; (●) 1-phenylethanethiol; (▲) 2-phenylethanethiol.

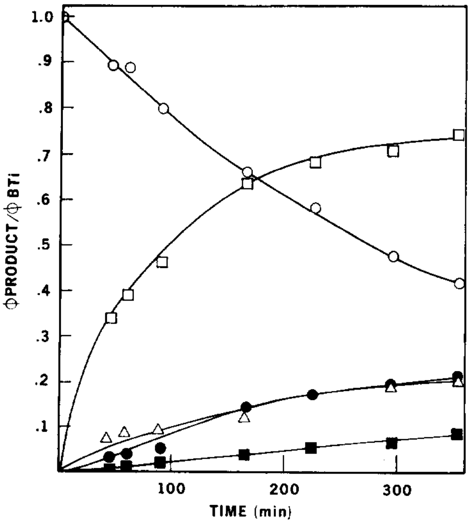


FIG. 7. The conversion of benzothiophene (2 g of sulfur) at 250°C and 1250 psig (7 g of presulfided CoO–MoO$_3$–Al$_2$O$_3$). (○) benzothiophene; (□) dihydrobenzothiophene; (△) ethylbenzene; (●) 1-phenylethanethiol; (■) 2-phenylethanethiol.

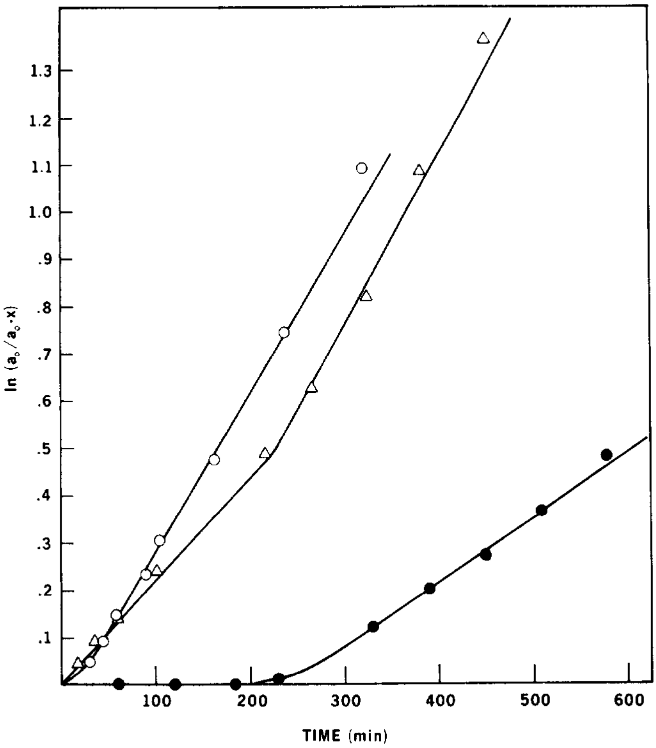


FIG. 8. Plot of ln $(a_0/a_0 - x)$ versus reaction period for the hydrodesulfurization of benzothiophene at 250°C and 1250 psig of (○) presulfided (H_2/H_2S) $CoO-MoO_3-Al_2O_3$, (△) prereduced (H_2) $CoO-MoO_3-Al_2O_3$, (●) unactivated $CoO-MoO_3-Al_2O_3$.

The two-site catalyst theory can be used to explain the reaction mechanism for the hydrodesulfurization of benzothiophene over a presulfided cobalt molybdate catalyst (*12*, *13*). Since benzothiophene is desulfurized by two different yet related mechanisms, it would seem reasonable that the molecule is actually adsorbed on two different sites.

Figure 8 illustrates a plot similar to that of Fig. 2 for an unactivated catalyst, a prereduced catalyst, and a presulfided catalyst in which benzothiophene was desulfurized at 1250 psig and 250°C. The plot for the unactivated catalyst shows little conversion of benzothiophene during the first 3 hr, but eventually achieves a rate constant equal to 2.27×10^{-5} sec^{-1}. The prereduced catalyst demonstrates an initial activity considerably greater than that of the unactivated catalyst ($k = 3.49 \times 10^{-5}$ sec^{-1}). After about 3 hr the reaction rate constant increases by about 70% ($k = 5.87 \times 10^{-5}$ sec^{-1}) to equal that of the presulfided catalyst ($k = 5.67 \times 10^{-5}$ sec^{-1}).

A comparison of the rates of formation of ethylbenzene showed a 64% increase in the initial rate for the presulfided versus the prereduced catalyst. It was also observed that little styrene or 2-phenylethanethiol was formed during the early stage of the reaction for the prereduced versus the presulfided catalyst. This possibly suggests that the sulfided catalyst (H_2/H_2S), in comparison to the reduced catalyst (H_2), enhances conversion of benzothiophene by direct desulfurization to styrene and eventually hydrogenation to ethylbenzene.

These results are in agreement with those of DeBeer *et al.* (*14*) who reported that the activity of the Co-promoted monolayer $CoO-MoO_3-Al_2O_3$ structure was substantially improved by presulfurization. The plot in Fig. 8 for the prereduced catalyst suggests that initially a hydrogenation site is available resulting in the formation of dihydrobenzothiophene. The slope eventually increases to that of the presulfided catalyst due to sulfurization of the catalyst by benzothiophene (*15*). The fact that the unactivated catalyst is eventually activated is also most likely due to sulfurization of the catalyst by benzothiophene.

CONCLUSION

The data presented permit the conclusion that hydrogenation of the aromatic ring is not necessary for hydrodesulfurization of benzothiophene. The reaction mechanism for desulfurization of benzothiophene consists of two different routes resulting in the same final product, ethylbenzene. Presulfiding the catalyst enhances the rate of desulfurization but contributes to the formation of styrene which can back react with hydrogen sulfide.

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