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Hydrodesulfurization

I. Hydrogenolysis of Benzothiophene and Dibenzothiophene over $CoO–MoO_3–Al_2O_3$ Catalyst

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Hydrogenolysis of benzothiophene and dibenzothiophene dissolved in *n*-dodecane has been studied over a $CoO-MoO_3-Al_2O_3$ catalyst at atmospheric pressure using a fixed bed testing microunit. The products were ethylbenzene and biphenyl, respectively.

A kinetic expression describing the effects of temperature and space velocity was verified experimentally. The hydrogenolysis of benzothiophene is first order both in the organic compound and in hydrogen. The activation energies of both reactions are low (~5 kcal/mole), illustrating the importance of diffusion phenomena over this type of catalyst.

INTRODUCTION

In petroleum, benzothiophenes and dibenzothiophenes represent the major portion of the thiophenic sulfur compounds (*1*), but, compared to thiophene, there has been little work on their hydrogenolysis (*2*).

In this paper we report a study of benzothiophene and dibenzothiophene hydrogenolysis over $CoO–MoO_3–Al_2O_3$ catalyst at atmospheric pressure. The solvent employed, *n*-dodecane, allows chromatographic analysis of both the sulfur compounds and the hydrocarbons formed. The only previous work at atmospheric pressure (*3*) compares the ease of hydrodesulfurization at 400°C of thiophene, benzothiophene, and dibenzothiophene dissolved in isooctane, and makes no mention of the nature of the products.

Hydrogenolysis is normally first order with respect to the partial pressure of thiophenic compound (*4, 5*). Thus, if n is the order with respect to hydrogen, the rate of thiophenic compound disappearance is

$$v = -\frac{dp_s}{dt} = k_1 p_s p_H{}^n$$

or, integrating,

$$\ln\frac{p_s}{p_{s_0}} = -k_1 \cdot p_H{}^n \cdot t \simeq -\frac{kmP}{T(N_H + N_D)} \cdot p_H{}^n$$

with m = catalyst weight (g), P = total pressure of the system (atm), P_{s_0}, p_s = partial pressure of sulfur compound flowing up and down the catalytic bed, respectively, p_H = partial pressure of hydrogen, T = temperature in the reactor (°K), N_H, N_D = moles of hydrogen and dodecane passed over the catalyst per unit time, and

$$k = \frac{k_1 V_{\text{cata}}}{2.3\ Rm},$$

in which k_1 is the rate constant, V_{cata} is the void volume of the catalyst bed, and R is the gas constant.

Assuming that there is no change in volume during reaction (the concentration of thiophenic compound being small), we may write

$$\log_{10}\frac{N_s}{N_{s_0}} = -\frac{kmP}{T(N_H + N_D)}\,p_H{}^n,$$

where N_{s_0} and N_s are moles of thiophenic compound injected and collected during the time of an experiment.

Experimental

Apparatus

Experiments were carried out in a fixed bed microunit. The thiophenic compounds dissolved in *n*-dodecane (0.326% sulfur by weight) were pumped from a buret into the reactor, which consisted of a Pyrex glass tube (10-mm i.d. and 600-mm length), placed in an electrically heated metal block. Hydrocarbon was instantaneously vaporized at the entrance of the reactor tube and mixed with dried hydrogen, the flow rate being measured by a flowmeter. The mixture passed through a preheater section and then over the catalyst at a temperature controlled within ±2°C. Liquid reaction product was withdrawn from the bottom of a receiver, at room temperature, and the H_2S content of the noncondensable gases was estimated by absorption in NaOH solution followed by iodometric titration.

Materials

n-Dodecane (olefin free), benzothiophene (BT), and dibenzothiophene (DBT) were Fluka Purum grade and used as received. The catalyst was prepared in our laboratory as follows: γ-Al_2O_3 was impregnated with an aqueous solution of cobalt nitrate and ammonium paramolybdate. After evaporation of excess water in a Rotavapor, drying and calcining at 500°C for 5 hr, the catalyst powder was made into pellets, 2-

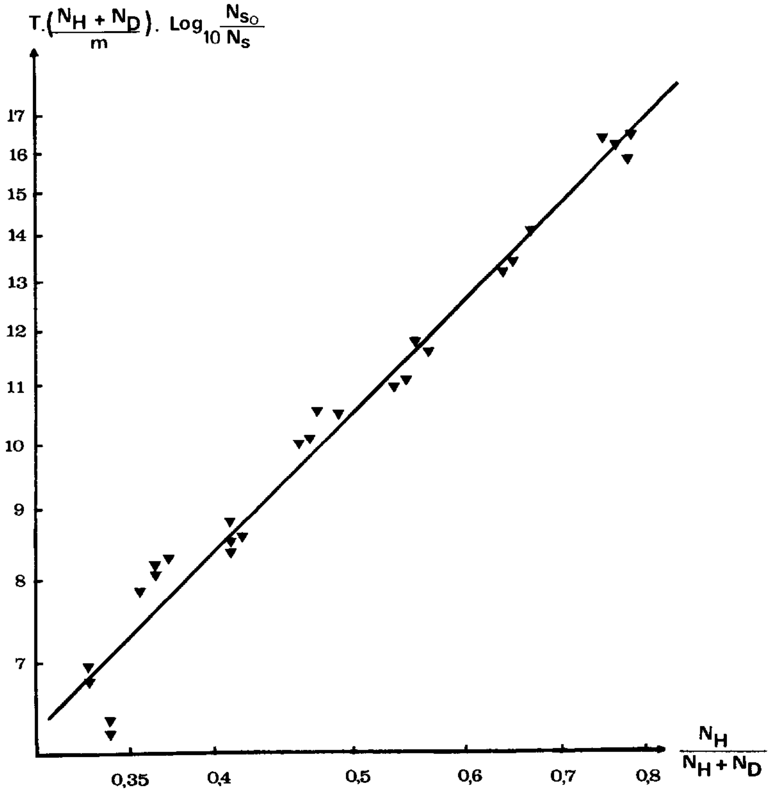

FIG. 1. Determination of the order with respect to hydrogen. Benzothiophene at 375°C.

mm diam × 2-mm length. The catalyst composition was 2% CoO, 10% MoO_3, 88% Al_2O_3, and its surface area was 95 m^2/g.

Experimental Procedure

The catalyst was presulfurized *in situ* in the reactor. It was reduced by a flow of hydrogen, the temperature being gradually raised to 400°C, and then sulfurized with a mixture of H_2 and H_2S (10% H_2S).

Hydrogenolysis experiments were made at temperatures decreasing from 400 to 300°C. The dodecane and hydrogen flow rates were controlled at the desired values. After a lapse of time the condensate receiver was discharged and the gaseous flow was connected with the soda absorption vessels. The time required to inject 4 ml of "sulfurized" dodecane was noted. The liquid product collected during this time in the condensate receiver at room tem-

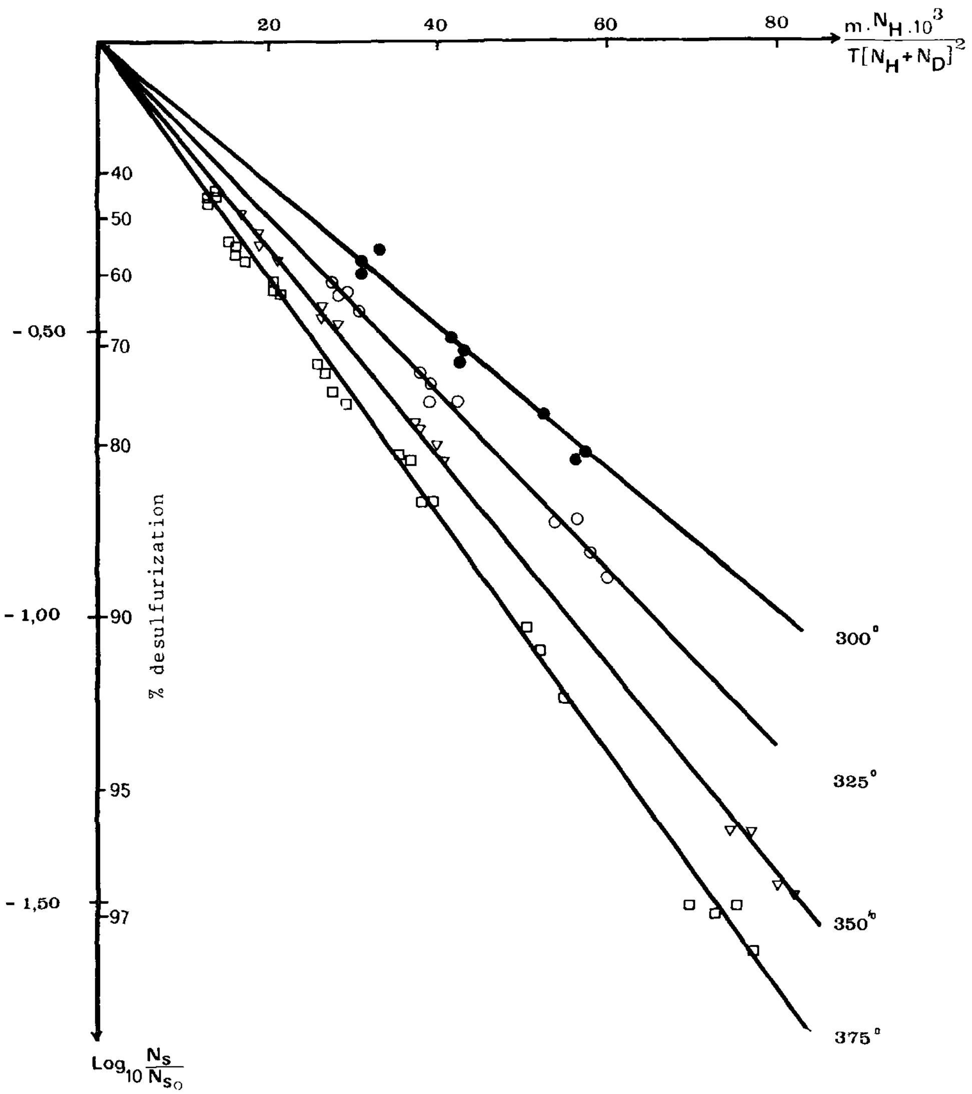

FIG. 2. Hydrogenolysis of benzothiophene over $CoO\text{-}MoO_3\text{-}Al_2O_3$ catalyst. Range of variation of p_{H_2}: 0.35-0.75 atm.

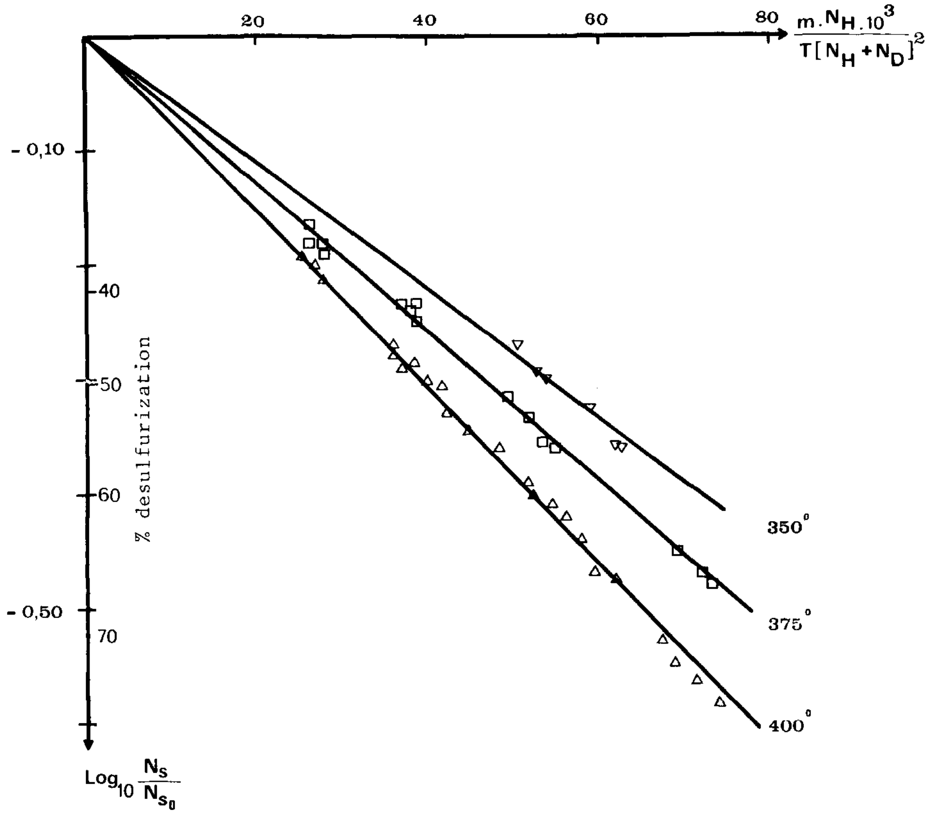

FIG. 3. Hydrogenolysis of dibenzothiophene over CoO–MoO$_3$–Al$_2$O$_3$ catalyst. Range of variation of p_{H_2}: 0.45–0.75 atm.

perature (20°C) was drawn off in a sample tube of known weight, then weighed exactly.

The sample was analyzed chromatographically using pseudocumene as internal standard.[1] The apparatus was supplied by F & M Scientific Corporation (Model 810 R-19 with two parallel columns and flame ionization detectors). The columns (2-m length and 0.25-in. diam) consisted of Chromosorb W (60–80 mesh) with 5% Apiezon L grease as stationary phase, and they were programed from 100 to 250°C (6°C/min).

RESULTS AND DISCUSSION

The conversion of the thiophenic compound was measured at different flow rates ($0.024 < N_D < 0.184$ mole/hr) and temperatures (300, 325, 350, 375, 400°C). 7.08 g of catalyst was used, and the flow rate of hydrogen was held constant at 2 liters/hr at 20°C ($N_H = 0.089$/mole/hr). Only ethylbenzene and biphenyl were detected as products.

To determine the order n with respect to hydrogen, values of

$$-\frac{T(N_H + N_D)}{m} \cdot \log \frac{N_s}{N_{s_0}}$$

were plotted against $p_H = N_H/N_H + N_D$ in a log–log graph (Fig. 1). In the case of benzothiophene hydrogenolysis at 375°C, the slope of the straight line was found to be unity. Hence the kinetic expression becomes

$$\log_{10} \frac{N_s}{N_{s_0}} = -\frac{k \cdot m \cdot N_H}{T(N_H + N_D)^2}.$$

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[1] This gives different values of N_s, N_{s_0} being equal to 3.08×10^{-4} mole BT or 3.06×10^{-4} mole DBT.

Figures 2 and 3 show plots of this relation to examine the order with respect to BT and DBT. In accordance with literature data (*4, 6, 7*), our results can be described by means of the first-order rate equation. The slopes of the straight lines represent the rate constant k. Arrhenius plots gave the following values of activation energy: $E = 4.9$ kcal/mole for benzothiophene; $E = 5.3$ kcal/mole for dibenzothiophene.

Pore diffusion limitations can be significant in distillate hydrodesulfurization (*8–10*) and are indicated by the effect of temperature on catalyst activity, since diffusion limitations are much less dependent on temperature than are the basic chemical reaction kinetics. This appears to be the case in our work. The apparent activation energies found are in accordance with literature data on thiophenic compound hydrogenolysis (*4, 6, 11–14*) with the exception of those of Mahugh (*15*) and Amberg *et al.* (*16*), who reported a value of 25 kcal/mole. Intermediate values are also found by Russian authors (*17, 18*).

According to our results, dibenzothiophene requires about three times as much catalyst as benzothiophene to be hydrogenolyzed to the same extent. This result is exactly that found by Obolentsev and Mashkina (*19*) at 40 atm pressure. This may indicate that diffusion limitations of sulfur compounds are not relatively greater at pressures higher than atmospheric.

The only work performed at atmospheric pressure (*3*) but unfortunately at only one temperature (400°C) and one liquid hourly space velocity (LHSV) gives values for percentage of sulfur converted, viz., BT 91, DBT 73, which are of the same order as ours (BT 98, DBT 73) but at a higher LHSV (6 vs 0.5–1 in our work). This can be ascribed either to a more active catalyst or to a lesser initial concentration of sulfur compound (0.22% S vs 0.326% S in our work).

Benzothiophene and dibenzothiophene give, respectively and in a quantitative way, ethylbenzene and biphenyl:

Benzothiophene + $3H_2 \rightarrow$ ethylbenzene + H_2S;

dibenzothiophene + $2H_2 \rightarrow$ biphenyl + H_2S.

The benzothiophene result is in good agreement with the literature (*20*). Moreover, it was verified under our experimental conditions that one of the possible intermediate products, i.e., styrene, was completely transformed into ethylbenzene.

The dibenzothiophene result is partially in disagreement with published data, since compounds with one or two saturated rings are reported. Thus, in gas oil hydrorefining on Co–Mo–Al_2O_3 catalyst, Drushel and Sommers (*21*) found compounds of the phenylcyclohexyl type, and Hoog (*22*) reported that in tridecane solution, at 375°C and under 50 atm, dibenzothiophene gives a mixture of 35% biphenyl and 65% phenylcyclohexane + bicyclohexyl. Moreover, in a batch reactor, on MoS_2 and under 100 atm hydrogen pressure, Landa and Mrnkova (*23*) found biphenyl (BP), phenylcyclohexane (PCH), bicyclohexyl (BCH), and dibenzothiophene (DBT) in the following percentages: at 300°C, BP 20.9, PCH 7.6, BCH 8.6, DBT 62.9; at 320°C, BP 18.0, PCH 32.0, BCH 24.2, DBT 25.8; at 340°C, BP 11.1, PCH 22.4, BCH 46.7, DBT 19.8.

Since temperature and hydrogen pressure increases favor the rate of aromatic ring saturation (*24*), biphenyl must be the only product initially formed. However, according to Obolentsev and Mashkina (*17*), 40 atm pressure should be inadequate (partial pressure hydrogen: 9–36 atm) to saturate biphenyl obtained by dibenzothiophene hydrogenolysis.

At atmospheric pressure, biphenyl is in fact the only product formed, because mixtures of dodecane–biphenyl or dodecane–phenylcyclohexane did not show any transformation in our experimental conditions. Therefore, contrary to what was thought (*20*), hydrogenation of an aromatic ring adjacent to the thiophenic one is not necessary in order to obtain easier opening and sulfur removal of the thiophenic ring.

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