

## Hydrogenation of Aromatic Compounds Catalyzed by Sulfided CoO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

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Hydrogenation of aromatic compounds catalyzed by sulfided CoO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was investigated with batch and flow reactors at 275-350°C and pressures near 100 atm. The reactants included benzene, biphenyl, dibenzothiophene, naphthalene, 2-phenylnaphthalene, and benzo[*b*]naphtho[2,3-*d*]thiophene. The reactivity for ring saturation was about an order of magnitude greater for the latter three [(substituted) naphthalenes] than for the others [(substituted) benzenes]. Sulfur in a reactant molecule slightly increased the reactivity of a neighboring ring for hydrogenation. Dibenzothiophene hydrogenation was not inhibited by H<sub>2</sub>S, but biphenyl hydrogenation was moderately inhibited by H<sub>2</sub>S, and dibenzothiophene hydrogenolysis was strongly inhibited by H<sub>2</sub>S. These and other results suggest that the reactant to be hydrogenated is π-bonded at exposed Mo cations, where H<sub>2</sub>S undergoes weak competitive adsorption and bases like acridine undergo strong competitive adsorption.

### INTRODUCTION

The replacement of light petroleum feedstocks by coal, shale, and heavy oil is expected to require a great increase in applications of catalytic hydroprocessing for the production of clean liquid fuels. Since the heavier feedstocks have higher concentrations of aromatics than light petroleum feedstocks, and since they require more severe processing conditions, aromatic ring saturation reactions will take on increasing importance in catalytic hydroprocessing. There has been only little characterization of the aromatic hydrogenation reactions under conditions representative of industrial practice.

Here we summarize high-pressure reactivity data for hydrogenation of aromatic hydrocarbons and sulfur-containing aromatic compounds catalyzed by sulfided CoO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, a commercial hydro-

desulfurization catalyst. The data indicate patterns of reactivity as a function of reactant structure and provide measures of inhibition of reaction by H<sub>2</sub>S.

### EXPERIMENTAL

Hydrogenation reactions catalyzed by sulfided CoO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (American Cyanamid HDS 16A) were studied both in batch autoclave and steady-state flow reactors. In the batch reactor experiments, the catalyst was first sulfided outside the reactor and transferred to a charging vessel with minimal exposure to the atmosphere. Reactants in low concentration in *n*-hexadecane solvent were charged to the reactor, heated, and brought to pressure with H<sub>2</sub>; then the catalyst was injected into the mixture. Liquid samples were removed periodically and analyzed by glc and sometimes by <sup>1</sup>H NMR. The reactants included H<sub>2</sub> with benzene, biphenyl, naphthalene, 2-phenylnaphthalene, dibenzothiophene, or benzo[*b*]naphtho[2,3-*d*]thiophene (benzo-naphthothiophene). The conversion data were used to determine reaction networks and rates of individual reactions (2-4). The

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equipment (1) and methods (2-4) are described in detail elsewhere.

Detailed kinetics of the hydrogenation reactions of dibenzothiophene and of biphenyl (5, 6) were determined from differential conversion data obtained in a high-pressure flow microreactor (7). To stabilize the catalyst, it was necessary to add a source of sulfur to the reactant mixture, either as dissolved  $H_2S$  or  $CS_2$ . The latter reacted with  $H_2$  almost instantaneously to give  $H_2S$  and  $CH_4$ .  $H_2$  was initially dissolved in the reactant solution in an autoclave at 30-150 atm, and the solution was then pumped at a constant rate to the reactor, which operated at 60 to 70 atm (somewhat in excess of the saturation pressure) to ensure that no gas phase formed. Rates of reaction were measured for ranges of reactant and product concentrations. More complete presentations of the experimental methods and results are given elsewhere (5, 6, 8, 9).

## RESULTS AND DISCUSSION

### Hydrogenation Kinetics and Inhibition

The Langmuir-Hinshelwood rate equations selected as best fitting the hydrogenation kinetics data have been reported elsewhere (5, 6) and are shown in Table 1. For dibenzothiophene [Eq. (1)], the hydrogenation giving 1,2,3,4-tetrahydrodibenzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene (which accompanies

hydrogenolysis giving biphenyl) is first order in  $H_2$  concentration. The Langmuir dependence of rate on dibenzothiophene concentration suggests that saturation of the catalytic sites with dibenzothiophene was approached at the higher concentrations. The rate was virtually independent of the concentrations of biphenyl and of  $H_2S$  (Fig. 1). The lack of inhibition by  $H_2S$  is consistent with the observation that hexene hydrogenation was not inhibited by  $H_2S$  (10), and it is sharply in contrast to the results showing inhibition of hydrogenolysis by  $H_2S$  (5).

The kinetics of biphenyl hydrogenation is more complicated; the reaction is reversible, which is accounted for (but only roughly) in Eq. (2) (Table 1). At the higher  $H_2$  concentrations ( $>0.15$  mole/l), the reaction is nearly first order in  $H_2$  concentration. The Langmuir dependence of rate on biphenyl concentration suggests that saturation of the catalytic sites with biphenyl was approached at the higher concentrations.  $H_2S$  inhibited the reaction moderately (Fig. 1). It is evident from Table 1 that there are qualitative similarities between dibenzothiophene hydrogenation and biphenyl hydrogenation, but there are differences with respect to the influence of  $H_2S$ .

The literature provides some evidence of inhibition by nitrogen-containing compounds. Hydrogenation reactions of aromatic hydrocarbons and of dibenzothiophene are strongly inhibited by basic

TABLE I

Rate Equations for Hydrogenation and Hydrogenolysis Reactions Catalyzed by Sulfided  $CoO-MoO_3/\gamma-Al_2O_3$

Reaction	Rate equation <sup>a</sup>	Ref.
Dibenzothiophene $\xrightarrow{H_2}$ Hydrogenated products	$r = \frac{kK_{DBT}K_{H_2}C_{DBT}C_{H_2}}{1 + K_{DBT}C_{DBT}}$	(1) (5)
$3H_2 + \text{Biphenyl} \rightarrow \text{Cyclohexylbenzene}$	$r = \frac{kK_{BP}K_{H_2}^3[C_{BP}C_{H_2}^3 - (1/K_E)C_{CHB}]}{(1 + K_{BP}C_{BP} + K_{H_2S}C_{H_2S})^2(1 + K_{H_2}C_{H_2})^2}$	(2) (6)
$2H_2 + \text{Dibenzothiophene} \rightarrow H_2S + \text{Biphenyl}$	$r = \frac{kK_{DBT}K_{H_2}C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT} + K_{H_2S}C_{H_2S})^2(1 + K_{H_2}C_{H_2})}$	(3) (5)

<sup>a</sup> Parameter values are given in the cited references.

Notation. DBT = dibenzothiophene; BP = biphenyl; E = equilibrium.

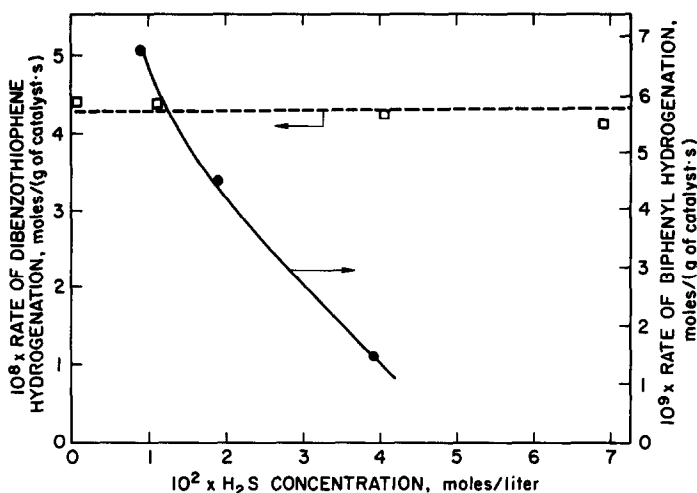


FIG. 1. Inhibition by hydrogen sulfide of dibenzothiophene hydrogenation and biphenyl hydrogenation at 300°C. The catalyst was sulfided CoO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (4, 5).

nitrogen-containing aromatic compounds such as quinoline (11), pyridine (12), and acridine (13). There is also strong inhibition by quinoline of the hydrogenation reactions which precede C-N bond breaking in hydrodenitrogenation of quinoline (11). In contrast, hydrogenolysis of dibenzothiophene is only modestly inhibited by these nitrogen-containing compounds (11, 13).

The inhibition effects of H<sub>2</sub>S are different for different hydrogenation reactions in the quinoline hydrodenitrogenation network (11). Pyridine hydrogenation is inhibited by H<sub>2</sub>S up to a certain concentration of H<sub>2</sub>S, with no further inhibition resulting from increased H<sub>2</sub>S concentrations (12). And increasing the concentration of H<sub>2</sub>S even increases the rate of hydrogenolysis (C-N bond breaking) of hydrogenated products formed from quinoline (11).

#### Reactivity Comparison

A summary of the available results allowing a quantitative comparison of the reactivities of the various reactants in hydrogenation catalyzed by sulfided CoO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> is shown in the Arrhenius plot of Fig. 2.

Each reaction has been represented as first order in the organic reactant, an ap-

proximation which is generally borne out by the data (2-4). For dibenzothiophene and biphenyl, the rate constants were calculated using Eqs. (1) and (2) in Table 1 for concentrations of H<sub>2</sub>, organic reactant, and inhibitor nearly equal to the corresponding concentrations used in the batch reactor experiments. For example, Eq. (1) was simplified to  $r = k_1 C_{\text{DBT}}$ , where

$$k_1 = \frac{kK_{\text{DBT}}K_{\text{H}_2}C_{\text{H}_2}}{1 + K_{\text{DBT}}C_{\text{DBT}}} \quad (3)$$

is the pseudo-first-order rate constant. The concentrations used in the calculations were the following:  $C_{\text{DBT}} = C_{\text{biphenyl}} = 0.02$ ;  $C_{\text{H}_2} = 0.2$ ; and  $C_{\text{H}_2\text{S}} = 0.02$  mole/l. The data from the batch reactor experiments had already been represented by pseudo-first-order kinetics (2-4); the points shown in Fig. 2 were corrected to 0.2 mole of H<sub>2</sub>/l by estimation of the actual H<sub>2</sub> concentration: Low-pressure Henry's law constants were extrapolated to the temperature and pressure of the batch reactor, and the H<sub>2</sub> concentrations were calculated from the fugacity of H<sub>2</sub> under the same conditions (8).

The data of Fig. 2 demonstrate good agreement between the batch- and flow-reactor data for biphenyl, and therefore we use the complete set of data to compare

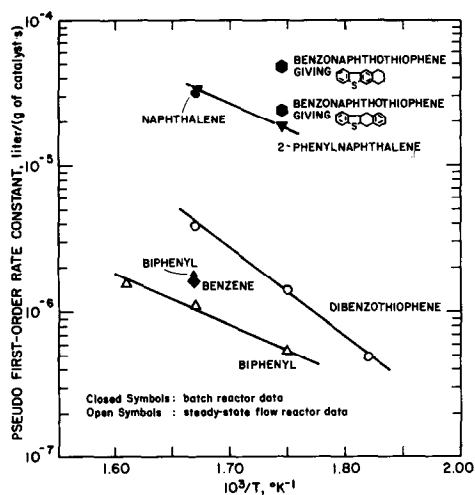


Fig. 2. Arrhenius plot: pseudo-first-order rate constants for hydrogenation of aromatic compounds, catalyzed by sulfided  $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ .

reactivities of the several reactants. The least reactive group of compounds, all having about the same reactivity, consists of benzene, biphenyl, and dibenzothiophene. We refer to these as (substituted) benzenes. Dibenzothiophene is the most reactive compound in this group. A more reactive group includes naphthalene, 2-phenylnaphthalene, and benzophenanthrothiophene, referred to as (substituted) naphthalenes. These are more than an order of magnitude greater in reactivity than the (substituted) benzenes.

The reactivity pattern shows that the naphthalene moiety, having a lower resonance energy per ring than benzene, undergoes hydrogenation more rapidly than the benzene moiety—and slightly more rapidly than similar compounds without sulfur. The pattern is evidently strongly dictated by electronic effects, since all of the compounds except 2-phenylnaphthalene are planar, and the observations cannot be accounted for by steric effects.

The pattern of reactivities in surface-catalyzed hydrogenation is qualitatively the same as that observed in homogeneous hydrogenation of aromatic hydrocarbons catalyzed by mononuclear cobalt complexes

(14). The results have been suggested to be consistent with a free-radical mechanism (14), but other mechanisms are not ruled out (15).

#### Catalytic Sites

In summary, a few characteristics of the sites of catalytic hydrogenation of aromatic compounds may be inferred from the aforementioned results, as follows: (1) the sites are acidic, being poisoned by such bases as pyridine, quinoline, and acridine; (2) the sites allow bonding of large heteroaromatics such as benzophenanthrothiophene, with no evidence of steric hindrance, which points to a "flat,"  $\pi$ -bonded structure of the adsorbed species as suggested earlier (16, 17); (3) thiophenic compounds like dibenzothiophene adsorb more strongly than hydrocarbons like biphenyl; (4)  $\text{H}_2\text{S}$  is adsorbed, but not as strongly as sulfur- and nitrogen-containing heteroaromatics; (5) adsorbed hydrogen is readily available as a reactant, but it does not exhibit site saturation at partial pressures up to about 100 atm.

It is also evident that the sites active for hydrogenolysis are different from those active for hydrogenation, as has been recognized before; the results of Stevens and Edmonds (18), for example, suggest that basal planes of  $\text{MoS}_2$  are preferentially active for hydrogenation of butenes, whereas surfaces of the crystal edges are preferentially active for hydrogenolysis of thiophene. The recent ESCA results of Okamoto *et al.* (19, 20) are consistent with these suggestions. We offer the further, speculative, suggestion that adsorption of aromatics leading to hydrogenation may involve an intercalation, whereby the flat aromatic molecule is inserted (at the crystal edge) between the parallel layers of sulfur ions in  $\text{MoS}_2$  (8). Similar spaces in  $\text{TaS}_2$  are known to intercalate compounds like pyridine (21); they may be roughly similar to the basal planes (where olefin hydrogenation seems to occur, presumably at exposed Mo ions) (18); and one might speculate that

they have little affinity for  $H_2S$ , which would explain the lack of inhibition by  $H_2S$ . We recognize, however, that the oxidic form of the molybdena catalyst is also active for hydrogenation of aromatics such as 1-methylnaphthalene (22), and some sites different from those on  $MoS_2$  must also be active.

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