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Hydrodesulfurization

II. Hydrogenolysis of Benzothiophene and Dibenzothiophene over Prereduced Fe_2O_3–Al_2O_3 Catalysts

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Hydrodesulfurization of benzothiophene (BT) and dibenzothiophene (DBT) dissolved in *n*-dodecane has been studied over several prereduced Fe_2O_3–Al_2O_3 catalysts. Compared to CoO–MoO_3–Al_2O_3, iron catalysts appear less active in BT hydrogenolysis, but the same activities are noticed at 400°C in the case of the higher condensed thiophenic compound, DBT. The appearance of styrene, formed as an additional product of BT during the activation of the catalyst at 300°C, supports the view that the initial step in the reaction sequence is C–S cleavage rather than thiophenic ring hydrogenation, at least under atmospheric pressure. The disappearance of styrene with catalyst aging was ascribed to the formation of sulfurized sites which improve the hydrogenation function of the catalyst.

INTRODUCTION

Desulfurization of hydrocarbons is carried out over metallic oxides or sulfides which may be classified as follows into three kinds: (i) Simple absorbents such as iron or zinc oxide. Used in natural and synthetic gas desulfurization only (*1*), they involve a noncatalytic process: The nature of the organosulfur compounds allows elimination of sulfur through a simple exchange reaction with oxygen atoms of the metal oxide. (ii) Hydrodesulfurization catalysts used in petroleum refining. Multicomponent oxide catalysts such as CoO–MoO_3–Al_2O_3 are partly converted to the sulfide form prior to or during hydrocarbon processing. (iii) Bifunctional catalysts on which hydrogenation and hydrogen sulfide adsorption are simultaneously performed. This is the case for Cu–ZnO (*2*) and ZnO–MoO_3–CuO (*3*). The present paper deals with the last kind.

Utilization of iron as a desulfurizing agent for petroleum fractions is described in the patent literature (*4*). However, studies on pure thiophenic compound desulfurization were limited to thiophene only, in purification of benzene (*5, 6*) and coke oven gas (*7*), with no mention of higher condensed thiophenes such as benzothiophenes or dibenzothiophenes.

The mechanism of hydrogenolysis of thiophenic compounds has received much attention in the literature and there are various opinions about the exact sequence of steps involved. Thus, the reaction scheme for thiophene hydrogenolysis proposed by one group of authors involves ring saturation to tetrahydrothiophene as the first process (*8–10*) and another group supports ring opening to form 1-butadienethiol (*11–13*), 1-butene (*14, 15*) or 1,3-butadiene (*16–19*). According to Schuit and Gates (*20*), the attachment of a ben-

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zene ring to the thiophene ring (giving benzothiophene) lowers the rate of hydrodesulfurization more than the rate of hydrogenation of the thiophene ring, so that hydrogenated compounds may be intermediates. Evidence of 2,3-dihydrobenzothiophene formation in benzothiophene hydrogenolysis, as conjectured some years ago by Cawley (*21*), has now been given by Givens and Venuto (*22*) who studied the reaction at atmospheric pressure, 300°C, and high space velocity.

The present paper reports a kinetic study of benzothiophene and dibenzothiophene hydrodesulfurization over several Fe_2O_3–Al_2O_3 catalysts, with additional information about the BT reaction network.

EXPERIMENTAL

Two procedures were used for Fe_2O_3–Al_2O_3 preparation. (i) The first was precipitation of ferric hydroxide on alumina carrier. Thus, γ-alumina powder (surface area 155 m^2/g) was mixed with an aqueous solution of ferric nitrate, the mixture was well stirred, and the hydroxide precipitated with a slight excess of ammonia. The solid mass was filtered, washed, dried at 120°C and calcined at 500°C for 6 h. The powder obtained was pelleted in the form of cylinders of 2-mm diameter and length. Catalysts so prepared are called F_I (25% Fe_2O_3 by weight, surface area 90 m^2/g) and F_{II} (10% Fe_2O_3 by weight, surface area 95 m^2/g). (ii) The second procedure was impregnation of alumina carrier with ferric nitrate. The mixture of alumina and aqueous ferric nitrate solution was slowly evaporated to dryness in a Rotavapor. The powder was then calcined at 500°C to obtain ferric oxide and treated as above. It is called F_{III} (25% Fe_2O_3 by weight, surface area 83 m^2/g).

The experimental procedure and effluent analysis were the same as in Part I of this study (*23*). Before contacting the feed (*n*-dodecane with 0.326% sulfur by weight), each iron oxide catalyst was prereduced *in situ* in the reactor with the standard flow of hydrogen (2 liters/h at 20°C) at 300, 400, or 500°C. It is known that hydrogen reduction of Fe_2O_3 powder leads to a mixture of Fe_3O_4, FeO, and Fe (*24*), the ratio depending upon temperature treatment. At 300°C Fe_3O_4 alone is formed, and Fe appears only at temperatures higher than 350°C (*25*). Moreover, as Al_2O_3 diminishes the overall rate of reduction (*26*) and as Fe_2O_3 is not completely reduced at 450°C after 26 days (*27*), we limited the reduction time to an overnight period.

RESULTS

In order to obtain some preliminary data about the conditions and limitations of desulfurization over iron catalysts, experiments were performed on pure metallic iron, using benzothiophene (BT) dissolved in *n*-dodecane. Thus, iron powder (hydrogen reduced, Prolabo RP) pelleted in the form of cylinders of 2-mm diameter and length was found to have no activity between 300 and 400°C, when no hydrogen flow was introduced in the reactor simultaneously with the feed. On the other hand, BT is effectively desulfurized when hydrogen is present, but the iron catalyst unfortunately suffers too rapid a deactivation to be used in a kinetic study involving contact time variations at several temperatures. To avoid such rapid deactivation, iron was deposited on a porous carrier of alumina in order to allow easier exchange between reagent and absorbent and to operate within a period of more stable desulfurizing activity.

A kinetic treatment, similar to that employed for a CoO–MoO_3–Al_2O_3 catalyst (Part I), was applied to all iron catalysts. For catalyst F_I, prereduced at 400°C, the experimental data (Fig. 1) may be correlated by the following equation:

$$\log_{10}\frac{Ns}{Ns_0} = -134{,}500e^{-12,500/RT}\frac{mN_{\mathrm{H}}}{T(N_{\mathrm{H}}+N_{\mathrm{D}})^2},$$

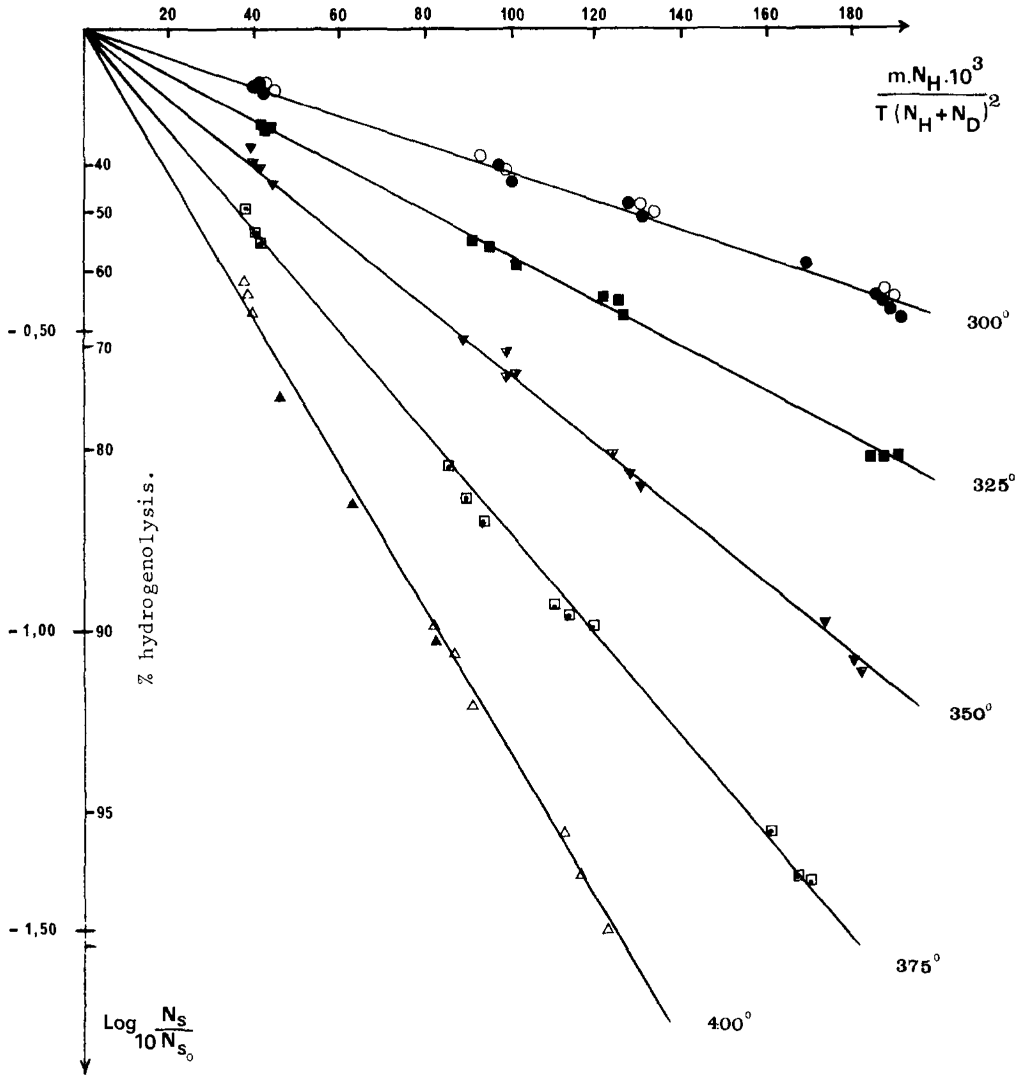


Fig. 1. Kinetics of BT hydrogenolysis over Fe_2O_3–Al_2O_3. (3.65–7.52–10.75–15.10 g F_I prereduced at 400°C, but first contact with feed was made at 300°C). Feed was injected at three or four slightly different velocities. Hydrogen flow was held constant at 2 liters/h at 20°C (partial pressure >0.75 atm) except in three experiments at 400°C (black triangles). Each series of experiments for each amount of catalyst was performed at temperature increasing from 300 to 400°C.

where Ns_0 and Ns are the moles of BT injected and collected during the time of an experiment, m is the catalyst weight (g), N_H and N_D are the moles of hydrogen and dodecane passed through the catalyst bed per hour; and the energy of activation and preexponential factor were determined from an Arrhenius plot.

The kinetic parameters obtained for all iron catalysts used in this work are given in Table 1, together with those already found for CoO–MoO_3–Al_2O_3 (Part I).

By plotting the values of $k = k_0e^{-E/RT}$ versus temperature, one obtains an activity scale for all the temperatures tested (Fig. 2).

As can been seen, better hydrodesulfurization activity is observed for the

TABLE 1

Hydrodesulfurization Kinetic Parameters for Fe_2O_3–Al_2O_3 and CoO–MoO_3–Al_2O_3 Catalysts

Contact mass and compound hydrogenolyzed		Energy of activation E(kcal/mol)	Preexponential factor k_0 (°K mol)/(h·g catalyst)
1. CoO–MoO_3–Al_2O_3	BT	4.9	955
2. F_I reduced at 300°C	BT	7.9	2,290
3. F_I reduced at 400°C	BT	12.5	134,500
4. F_{III} reduced at 400°C	BT	14.0	399,000
5. F_{II} reduced at 400°C	BT	12.5	88,000
6. F_I reduced at 500°C	BT	12.6	42,400
7. F_{III} reduced at 400°C	DBT	14.1	268,000
8. CoO–MoO_3–Al_2O_3	DBT	5.3	405

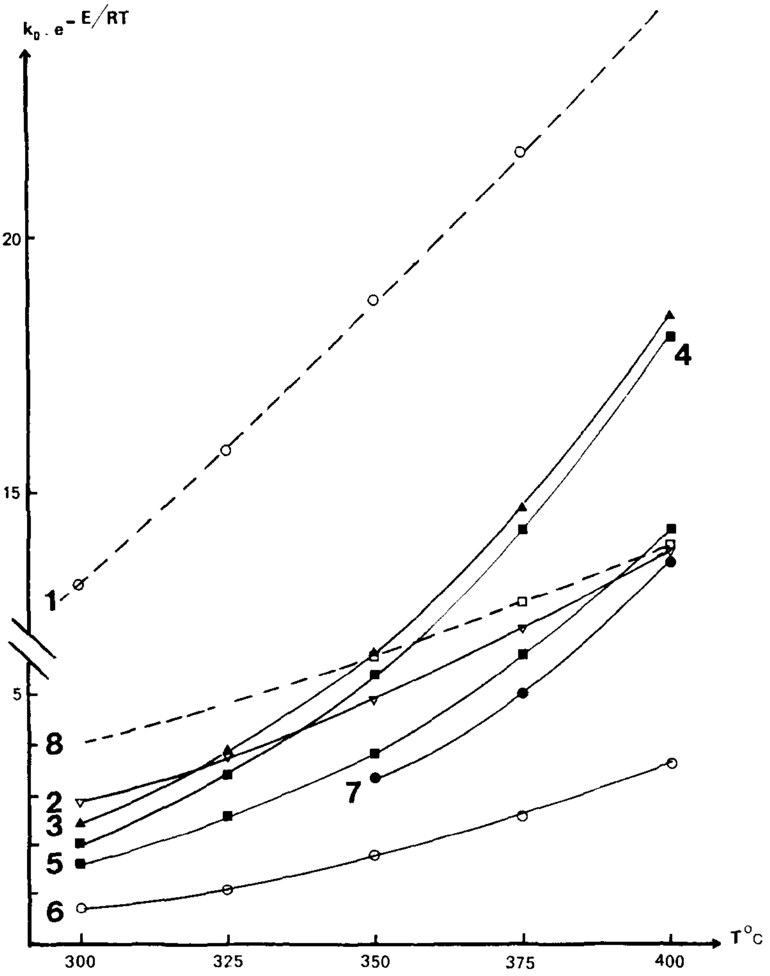


Fig. 2. Velocity constants $k_0 \cdot e^{-E/RT}$ versus temperature. (1) CoO–MoO_3–Al_2O_3, BT; (2) F_I reduced at 300°C, BT; (3) F_I reduced at 400°C, BT; (4) F_{II} reduced at 400°C, BT; (5) F_{II} reduced at 400°C, BT; (6) F_I reduced at 500°C, BT; (7) F_{III} reduced at 400°C, DBT; (8) CoO–MoO_3–Al_2O_3, DBT. Numbers as in Table 1.

TABLE 2

Composition of the Reaction Mixture Initially Obtained in BT Hydrogenolysis at 300°C

Weight of Fe_2O_3–Al_2O_3 used (g)	Reduction temperature (°C)	Order of samples withdrawn	Sty[a]/(Sty + EB) (%)	(EB + Sty)/BT (%)	Desulfurization (%)
3.69 F_{I}	300	1	65	54	26
		2	35	47	26
		3	—	66	25
		4	—	88	25
6.56 F_{III}	300	1	61	59	39
		2	35	48	36
		3	—	53	35
		4	—	82	35
3.65 F_{I}	400	1	39	81	20
		2	19	79	20
		3	—	81	22
		4	—	96	22
7.52 F_{I}	400	1	35	81	62
		2	16	92	41
		3	—	96	41
10.75 F_{I}	400	1	30	82	70
		2	13	89	48
		3	—	93	49
		4	—	98	49
15.10 F_{I}	400	1	18	94	92
		2	—	93	60
		3	—	98	59
16.70 F_{III}	400	1	30	92	71
		2	20	90	48
		3	—	95	54
		4	—	95	54
3.70 F_{I}	500	1	46	49	16
		2	35	73	6
		3	—	75	6
		4	—	91	6

[a] Sty, EB, BT: Amounts of styrene, ethylbenzene formed, and benzothiophene consumed, respectively, in a condensed sample.

CoO–MoO_3–Al_2O_3 catalyst, especially in BT hydrogenolysis, but the difference is lower at higher temperatures. In DBT hydrogenolysis, Fe_2O_3–Al_2O_3 becomes just as active as CoO–MoO_3–Al_2O_3 at 400°C (curves 7 and 8). This may indicate that higher condensed thiophenic compounds (than BT) could be quite well desulfurized by iron catalysts.

With all Fe_2O_3–Al_2O_3 catalysts tested initially at 300°C, but only during about the first hour after they were contacted with the feed, styrene was detected in the liquid effluent, together with ethylbenzene, the only product which exists at the steady state.

Table 2 gives the composition of the reaction mixture in the first three or four samples collected on each quantity of catalyst used.

Finally we have checked if iron catalyst is still able to desulfurize BT when fully presulfided. Presulfidation was effected with an H_2–H_2S mixture (10% H_2S) applied for 5 h. It was verified that no BT conversion arises when feed was injected along with H_2S; however, when H_2S supply was stopped, positive hydrogenolysis was shown as soon as excess H_2S was evacuated from the catalyst. No styrene was detected and the ethylbenzene formed corresponds thoroughly to the BT consumed. Moreover, the catalyst so obtained completely hydrogenates styrene (as a 2% solution in *n*-dodecane) into ethylbenzene.

DISCUSSION

It must be emphasized that sulfur produced from BT hydrogenolysis remains bound on the catalyst surface and never appears as H_2S in the exit gas. However, under the experimental conditions investigated, the activity of each catalyst sample decreases only slightly during use, as shown by control tests systematically performed at the end of each series of experiments by lowering the temperature to the initial one, 300°C (tests symbolized by circles in Fig. 1, 300°C). Similar behavior was observed by Gaur *et al.* (*28*) who found that the activity of alkalized iron pellets remained unaffected during naphtha-thiophene hydrodesulfurization. As preliminary work on bulk-reduced iron has shown, thiophenic sulfur occupies active sites, thus preventing further hydrodesulfurization reaction. When supported on alumina, reduced iron oxide is believed to have similar behavior, but the high catalytic surface does not allow evidence of such a poisoning effect.

The temperature of reduction seems to be rather important, since prereduction at 400°C leads to the best activity at high temperature (curve 3, Fig. 2). Active hydrodesulfurization sites are formed by reduction, for catalyst prereduced at 300°C never reaches the same activity (at any higher temperature tested) as catalyst prereduced at 400°C (curve 2 compared to 3). As already reported by Szayna (*29*), pretreatment at 500°C gives rise to a catalyst with reduced hydrodesulfurization performance (curve 6), probably through overreduction which decreases the hydrogenation activity (*30*) and/or through surface area lowering by the high reduction temperature used.

When less iron oxide is deposited on the carrier (F_{II}), the quality of the surface is unchanged (same activation energy as F_I, Table 1), but the density of active sites varies. It appears that F_I is only 1.5 times more active than F_{II}, although the iron weight percentage is 2.5 times greater. This relatively lower desulfurization activity of F_I could be ascribed to the formation of more than a monolayer Fe_2O_3 on some parts of the alumina surface.

Kinetic parameters determined on an alumina-impregnated iron catalyst (F_{III}) are indicative of a higher density of active sites but the HDS reaction is more difficult to activate. The net result is that F_{III} is slightly less active than F_I (curves 4 and 3, Fig. 2). A possible explanation can be found in the catalyst preparation: Thus, during drying in the Rotavapor, ferric nitrate solution may continuously migrate from the interior of the pores to the external surface of the support; therefore, ferric nitrate deposits preferentially near or on the external surface, a situation which after calcination and hydrogen treatment probably leads to a higher superficial density of active sites than in case F_I.

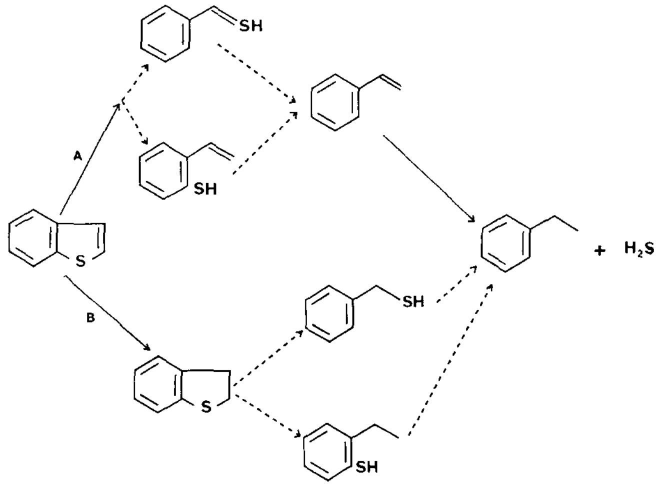
With regard to the behavior of catalysts used at 300°C for the first contact with the feed, data from Table 2 show that the relative yield of styrene is smaller with larger amounts of catalyst, a fact probably due to longer residence of styrene in the catalyst bed leading to increased hydrogenation. Also relevant to this are the poorer values of (ethylbenzene + styrene)/(BT consumed) obtained on the smallest catalyst beds. On the other hand, the degree of desulfurization decreases with time of use of the catalyst, especially between the first and second samples withdrawn, and more with the larger catalyst bed: Such behavior does not point to a decrease of the hydrogenation function, but can rather be ascribed to the initial working of the more active hydrodesulfurization sites, i.e., the sites located on the external surface of the pellets.

It is noteworthy that the degree of desulfurization has already reached a stable state when styrene disappears from the condensed effluent. In the meantime, the hydrogenation activity increases until quasistoichiometric BT conversion to ethylbenzene is obtained after the fourth sample (values then used for the kinetic treatment). As the same picture is observed with catalysts reduced at 300, 400, or 500°C, i.e., as it seems independent of the state of prereduction, it may be that the styrene disappearing with time of use of the catalysts is related to the formation of sulfurized sites which improve their hydrogenation function.

On prereduced catalysts it is obvious that reduced iron centers are the adsorption sites of thiophenic sulfur. Further hydrogenolysis requires adjacent hydrogen which may be adsorbed on Fe–O and later on Fe–S groups.

When an iron catalyst is presulfided, the picture becomes more complex. According to Ivanovskii *et al.* (*31*), dissolved nonstoichiometric sulfur should be present for hydrodesulfurization activity: BT is hydrogenolized in two steps, viz., formation of catalytically active centers in places where dissolved sulfur is removed by hydrogenation, and then bonding of thiophenic sulfur to the reduced Fe center and splitting of the thiophenic ring.

With regard to the hydrodesulfurization mechanism, two possible reaction schemes may be expected, viz., C–S bond cleavage with the participation of hydrogen reactant as the initial step (Scheme 1, route A), or intermediate ring saturation of the BT hetero-ring into dihydrobenzothiophene (DHBT) followed by desulfurization (Scheme 1, route B).



SCHEME 1

Under the present experimental conditions, DHBT was not detected, though it was detected in the work of Givens and Venuto (*22*). Possibly in our case, the hydrogenation rate of BT to DHBT is far slower than the desulfurization rate;

it is therefore very likely that under rather higher hydrogen pressure DHBT appears as an intermediate, as reported by De Beer *et al.* (*32*).

The fact that the styrene yield progressively drops may suggest that route A is operative during the activation stage of the catalyst, with this route being less and less effective when the catalyst reaches a more stable state. It is noteworthy that sulfidation during the first stage forms new sites, the proportion of which increases when the catalyst ages. These sites may have quite different selectivities. We believe, however, that route A remains operative, styrene being now hydrogenated too rapidly to be detected. Such a statement would be in agreement with the findings of Furimsky and Amberg on BT hydrogenolysis over an unsupported MoS_2 catalyst promoted with cobalt (*33*).

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