Factors in Sulfur Poisoning of Iron Catalysts in Fischer-Tropsch Synthesis

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Poisoning of catalysts in the Fischer-Tropsch synthesis by sulfur compounds has been investigated at the U.S. Bureau of Mines as part of its program on the conversion of coal to liquid and gaseous fuels. The effects of alkali content, initial surface area, and particle size on the poisoning of fixed beds of reduced fused iron oxide catalysts are reported for synthesis tests with $1 H_2 + 1 CO$ gas containing 69 mg S as H_2S/m^3 at 21.4 atm.

Chemisorption studies of CO at $-195°C$ and CO_2 at $-78°C$ on reduced catalysts on which H_2S was adsorbed indicate that sulfur chemisorbs on both metallic iron and on alkali promoter if present. However, the decrease in the moles of CO plus CO_2 chemisorbed was only 14 to 29% of the moles of H_2S chemisorbed on the catalyst. Alkali promoters increase both the activity of the catalyst and its resistance to poisoning. Addition of 0.51 g $K_2O/100$ g Fe to an alumina-promoted catalyst increased activity about sixfold and resistance to poisoning about fivefold.

In the early and intermediate stages of poisoning, the selectivity was not significantly changed. The relative amounts of products in different boiling fractions and the concentrations of olefins and oxygenated molecules in these fractions remained essentially constant.

Initial surface area of reduced catalysts was not an important factor in determining either activity or resistance to poisoning. Decreasing particle size from 6–8 mesh to 28–32 mesh (a fivefold increase in external area) increased the activity and the resistance to poisoning more than threefold. Apparently poisoning occurs in a thin active layer near the external surface of the particles. Previous work from this laboratory has shown the depth of this active layer to be about 0.1 mm. In three fixed-bed poisoning tests, the concentration of sulfur in the catalyst was determined as a function of bed length. Most of the sulfur was found in the inlet third of the catalyst.

INTRODUCTION

Sulfur poisoning of iron catalysts in the ammonia synthesis was observed about 50 years ago (1), and in 1935 a practical upper limit for sulfur concentration, 1 to 2 mg S/m^3 of synthesis gas, for the Fischer-Tropsch synthesis was given by Fischer (2). U.S. Bureau of Mines' papers on poisoning of iron Fischer-Tropsch catalysts include prepoisoning experiments (3), and *in situ* poisoning by H_2S in synthesis gas (4, 5).

The literature on sulfur poisoning of iron

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catalysts in the ammonia and the Fischer-Tropsch syntheses has been reviewed (3, 6). Only two papers are pertinent to the present work. Brill (7) found that the resistance of iron catalysts to poisoning in the atmospheric pressure synthesis of ammonia increased in the following order: Pure iron, $Fe-K_2O$, $Fe-Al_2O_3-K_2O$, $Fe-Al_2O_3-CaO-K_2O$. More recently Bulstuikova, Apel'baum, and Temkin (8) investigated the poisoning of iron catalysts by hydrogen sulfide in the ammonia synthesis at atmospheric pressure. Potassium oxide, either alone or in the presence of alumina, increased the resistance of the catalysts to poisoning.

The present paper considers the effect of

alkali promoters on activity and resistance to poisoning and the influence of catalyst geometry in poisoning. The effect of chemisorbed H_2S on the chemisorption of CO and CO_2 is reported for several reduced catalysts.

In the Fischer-Tropsch tests, catalytic activity, A_{Fe}, is expressed as cubic centimeters (STP) of synthesis gas consumed per hour-gram of iron at 240°C, when the space velocity is adjusted to provide conversions of H_2 + CO of 65%. The activity for these conditions was calculated by use of the empirical rate equation (9) $-\ln(1 - x)$ $= (A/S) \exp(-E/RT)$, where x is the fraction of H_2 + CO reacted; S, the hourly space velocity; A is a constant; and the activation energy E has a value of 19 kcal/mole. Hourly space velocity is defined as volumes of synthesis gas (STP) introduced per hour per volume of catalyst space.

EXPERIMENTAL

Analytical data for principal components of catalysts described in this paper are given in Table 1. All preparations were of the fused-magnetite type. Catalyst D3001 was a commercial preparation, and the remainder of the catalysts were prepared in our laboratory by electrical fusion (10). The materials used in the fusion contained no added alkali, and sized samples of crushed fused oxides were impregnated with aqueous solutions of the alkali promoter, usually K_2CO_3.

Synthesis gas, $1 H_2 + 1 CO$, essentially free of sulfur, was prepared by reforming natural gas with steam and CO_2, and was available in standard carbon steel gas cylinders. Mixtures of H_2S in this gas containing 69 ± 5 mg S/m^3 were prepared in special cylinders, plastic-lined carbon steel, stainless steel, or aluminum (11). Each type of cylinder was effective in storing mixtures of sulfur compounds in synthesis gas, provided that carbonyls, produced during the storage of the pure gas in carbon steel cylinders, were first removed.

All tests were made at 21.4 atm in stainless steel fixed-bed reactors similar in design to reactors described previously (10). Stainless steel tubing and valves were used throughout the inlet system employed for

TABLE 1

CATALYST COMPOSITION

Catalyst number	Composition, parts by weight per 100 Fe				
	K_2O	MgO	Al_2O_3	Other	
D3001	0.85	6.84	—	1.05	SiO_2
				0.96	Cr_2O_3
D3001X[a]	0.25	6.84	—	1.05	SiO_2
				0.96	Cr_2O_3
D3001K[b]	1.32	6.84	—	1.05	SiO_2
				0.96	Cr_2O_3
L2021	—	2.77	—	—	
P2007	0.04	—	3.52	0.28	SiO_2
P2007.6	—	—	3.30	0.28	SiO_2
L3140[c]	0.51	—	3.52	~0.3	SiO_2
L3119[c]	0.37	—	3.22	~0.3	SiO_2
L3137[d]	0.79	—	3.52	~0.3	SiO_2
				0.92	MnO_2
L3122.1[e]	0.18	1.57	—	0.12	S
L3023[f]	0.42	1.57	—	—	

[a] D3001 extracted with hot water.

[b] Reduced D3001 impregnated with alcoholic KOH.

[c] P2007 impregnated with aqueous K_2CO_3.

[d] P2007 impregnated with aqueous $KMnO_4$.

[e] Fe_3O_4-MgO catalyst impregnated with aqueous K_2S.

[f] Fe_3O_4-MgO catalyst impregnated with aqueous K_2CO_3.

sulfur-containing gas. The catalyst charge was 50 cc in all tests, and the inside diameter of the reactor was 1.58 cm. Testing procedures have been described (10).

Tests were started on a sulfur-free 1 H_2 + 1 CO gas (total sulfur content less than 1 mg/m³) at an hourly space velocity of 300 and 200°C, and the temperature was increased slowly, so that about 48 hr were required for the apparent CO_2-free contraction to attain 65%. Usually the activity of the catalyst became constant in the first 3 days, and synthesis was continued for 4 to 30 days to establish a starting point for the poisoning tests. Synthesis gas, containing 69 mg S as H_2S/m³, was then introduced by a separate feed system without depressurizing the reactor. The reactor was maintained at the temperature of the previous period of constant activity on pure gas and the conversion decreased as poisoning proceeded. In test Z256 the synthesis test was started with gas containing H_2S, and temperature was increased as required to main-

tain the apparent CO_2-free contraction at about 65%. In test X999 synthesis gas containing 188 mg S as H_2S/m³ was used.

Data from poisoning tests are expressed in terms of relative activity, $\bar{F}$, defined as the activity of the poisoned catalyst divided by the activity of the unpoisoned catalyst at the start of the poisoning. Equations based on hypothetical poisoning and poison distribution equations in fixed beds generally reduce to the form $1 - \bar{F} = \alpha\bar{S}$, in the early part of the poisoning, where α is a constant and $\bar{S}$ the average concentration of poison on the catalyst (12, 13). For this reason poisoning data were plotted as $1 - \bar{F}$ against sulfur fed to the catalyst, on logarithmic scales. A straight line with a slope of one corresponds to the equation above. Table 2 summarizes pertinent data on catalyst tests including particle size, reduction conditions, and initial surface area and activity, temperature of poisoning tests, and the values of $1/\alpha$.

Surface area and chemisorption measure-

TABLE 2

TESTS OF CATALYSTS

Catalyst no.	Test no.	Mesh size	Reduction in H_2		Initial surface area (m²/g Fe)	Initial period on pure gas			Poisoning test	
			Temp (°C)	Time (hr)		Time (days)	Av temp (°C)	Activity, $A_{F\bullet}$	Temp (°C)	$1/\alpha$ (mg S/g Fe)
D3001	Z181	6–8	450	40	15.0	13	256	55	254	0.45
	Z256	6–8			15.0	0	—	—	261–326	0.64
	Z243	6–8	400	168	23.3	30	257	57	259	0.32
	Z295	28–32	450	48	15.0	9	226	177	228	1.50
	X920	6–8	450	40	15.0	12	264	41	267	0.22
	X999[a]	6–8	450	40	15.0	12	266	37	266	0.47
D3001X	Z262	6–8	450	41	—	22	255	62	248	0.35
D3001K	Z276	6–8	450	40	—	6	240	127	242	1.01
P2007	Z292	8–10	450	40	19.8	4	262	25	274	0.25
			499	25						
L3140	Z311	8–10	450	23	13.4	10	230	146	232	1.13
			500	43						
L3137	Z297	8–10	450	24	—	10	230	159	230	2.08
			500	24						
L3122.1[b]	Z47	6–8	450	40	—	50	255	65	—	—
L3023[b]	X638	6–8	450	40	—	50	228	163	—	—

[a] Test X999 was made with gas containing 188 mg S/m³.

[b] L3122.1 and L3023 containing K_2S and K_2CO_3, respectively, as alkali promoters. These catalysts were not tested with gas containing H_2S.

ments were made with a conventional gas adsorption apparatus. Surface areas were determined from nitrogen adsorption isotherms at $-195°C$ by the BET method. The effect of chemisorbed H_2S on the chemisorption of CO at $-195°C$ and CO_2 at $-78°C$ was determined on several reduced catalysts. H_2S was chemisorbed on the reduced catalyst at $30°C$, and the catalyst was then heated in hydrogen for 1 hr at $450°C$ and evacuated for 1 hr at $450°C$. A nitrogen isotherm was determined at $-195°C$, and the sample was evacuated at room temperature. Then a CO isotherm was determined at $-195°C$, and the difference between the CO and N_2 isotherms plotted on relative pressure basis was taken as the amount of CO chemisorbed. The sample was then heated in H_2 for 1 hr and evacuated for 1 hr at $450°C$. A CO_2 isotherm was determined at $-78°C$, the sample evacuated at $0°C$, and a second CO_2 isotherm determined at $-78°C$. The difference in the amounts of CO_2 adsorbed was taken as chemisorbed CO_2. The surface area of samples did not change during chemisorption experiments.

EXPERIMENTAL RESULTS

Poisoning tests reported in this paper are summarized in Table 2 and Figs. 1 and 2.

All poisoning tests except X999 were made with $1 H_2 + 1 CO$ gas containing 69 mg S as H_2S/m^3. Table 2 presents conditions for the initial reduction in hydrogen and the initial period of synthesis on sulfur-free gas and the surface area of the reduced catalyst. For most tests as shown in Figs. 1 and 2, the initial part of the poisoning curve was of the form $1 - \bar{F} = \alpha \bar{S}$, where $\bar{F}$ is the relative activity and $\bar{S}$ the sulfur introduced. The reciprocal of constant α (Table 2) represents the quantity of sulfur that would decrease $\bar{F}$ to zero if the linear trend held for the whole poisoning curve. Where the initial portion did not follow the equation above, α was evaluated from data at $\bar{F} = 0.7$. Figure 1 presents data for the effect of surface area and particle size on the poisoning of catalyst D3001. Figure 2 shows the effect of alkali content on magnesia-promoted catalysts (Part A) and on alumina-promoted catalysts (Part B). Table 3 compares selectivity of poisoned and unpoisoned catalysts. Table 4 presents data on the concentration of sulfur in the catalyst as a function of bed length for catalyst D3001 after poisoning to relative activities of 0.19 to 0.13. Table 5 presents the effect of chemisorbed H_2S on the chemisorption of carbon monoxide at $-195°C$, V_{CO}, and the chemisorption of carbon dioxide at $-78°C$, V_{CO_2}.
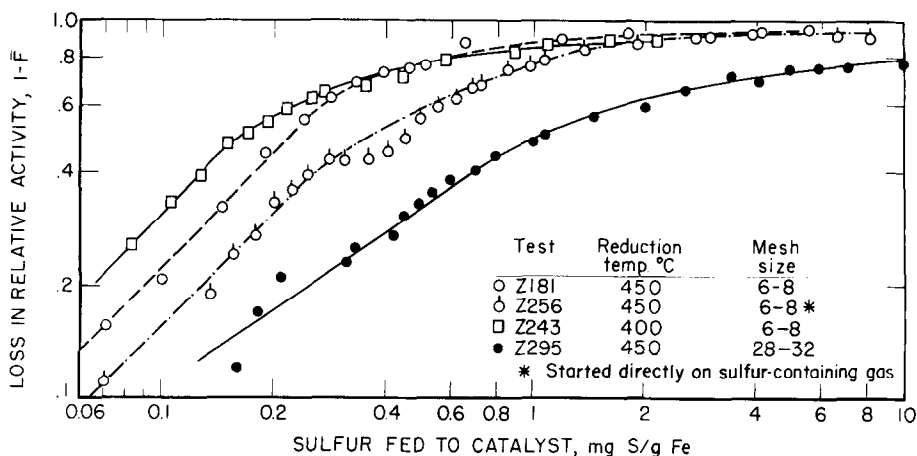

Test	Reduction temp °C	Mesh size
O Z181	450	6-8
◊ Z256	450	6-8 *
□ Z243	400	6-8
● Z295	450	28-32

* Started directly on sulfur-containing gas

FIG. 1. Effect of catalyst geometry on H₂S poisoning. Catalyst D3001 with $1H_2 + 1CO$ gas containing 69 mg S/m³.
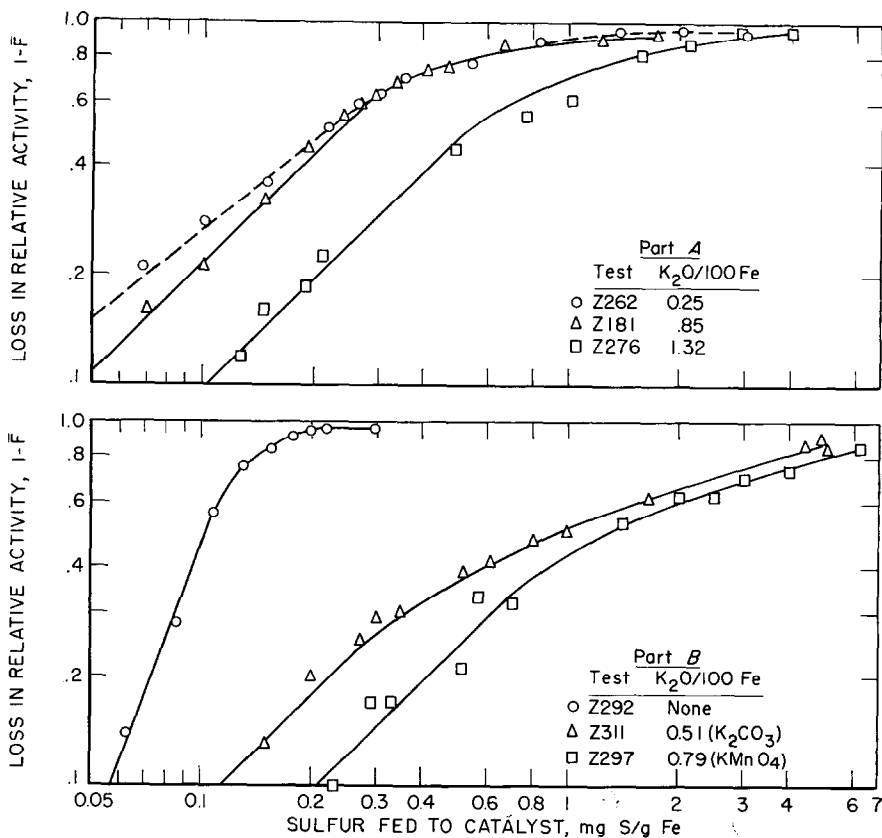
Fig. 2. Effect of alkali on H_2S poisoning. Part A, magnesia-promoted catalysts. Part B, alumina-promoted catalysts. $1H_2 + 1CO$ gas containing 69 mg S/m^3.

Discussion

Chemisorption of carbon monoxide at $-195°C$ and carbon dioxide at $-78°C$ provides at least qualitative measurements of the extents of iron and alkali surfaces in reduced fused iron oxide catalysts (14, 15). Data in Table 5 for L2021 indicate that magnesia also chemisorbed CO_2 under these conditions. Chemisorptions of CO and CO_2 are compared on reduced catalysts and on catalysts after chemisorption of 0.5 mg S/m^2 [$Vs/V_m = 1.53$, where Vs equals cc (STP) of H_2S adsorbed]. Chemisorbed hydrogen sulfide decreased the chemisorption of both CO and CO_2. Chemisorption of CO_2 was more drastically decreased on magnesia-promoted catalyst D3001 than on alumina-promoted L3119. On alumina-promoted catalysts the ratio of the decrease in the sum of chemisorptions of CO plus

CO_2 divided by Vs was 0.14–0.16, and for the magnesia-promoted catalysts it was 0.26–0.29. Thus, the decrease in chemisorbed CO plus CO_2 by chemisorbed H_2S was substantially less than mole for mole. Apparently H_2S reacts with the catalyst to form a thicker adsorbed phase than a monolayer.

In synthesis tests alumina-promoted catalysts have a larger initial activity and greater resistance to poisoning than catalysts promoted with magnesia, even when allowance is made for differences in particle size of the two catalysts. As shown in Fig. 2 and Table 2, addition of K_2CO_3 to base catalyst P2007 increases the activity of catalyst and the resistance to poisoning fourfold to sixfold. The catalyst promoted with $KMnO_4$ was more resistant to poisoning. Apparently the oxides of manganese contribute to increasing the resistance to poisoning; how-

TABLE 3

SELECTIVITY IN POISONING EXPERIMENTS AND TESTS ON
PURE GAS COMPARED FOR 28- TO 32-MESH D3001

Test no.	X527			Z295		
Sulfur introduced (mg S/g Fe)	0			1.1–19.4		
Temperature (°C)	226			230		
Hydrocarbons produced						
(wt % of total[a])						
Infrared analyses of fractions:						
C_1	9			9		
C_2	8			6		
$C_3 + C_4$	17			13		
Distillation fractions						
<185°C	27	Br no.	75	18	Br no.	68
		Wt % {OH	4.1		Wt % {OH	4.4
		CO	1.0		CO	1.7
		COOH	0.5		COOH	0.6
185–352°C[b]	17	Br no.	40	17	Br no.	48
		Wt % {OH	0.8		Wt % {OH	0.8
		CO	0.7		CO	0.8
		COOH	0.05		COOH	0.07
352–464°C[b]	9			11		
>464°C	13			26		

[a] Includes oxygenated molecules dissolved in liquid and solid hydrocarbons.

[b] Distillation performed at reduced pressure. Boiling ranges are calculated for atmospheric pressure.

TABLE 4

SULFUR CONCENTRATIONS IN BEDS OF CATALYST D3001 AS A FUNCTION OF BED LENGTH

Test no.	X920	X999	Z295	
Mesh size	6–8	6–8	28–32	
H_2S in feed gas (mg S/m³)	69	188	69	
Relative activity at end of test	0.19	0.15	0.13	

Position in bed from inlet (cm)	Sulfur concentration (mg S/g Fe)			Position in bed from inlet (cm)
0–10	2.3	6.1	31.6	0–14
10–20	0.6	0.9	0.9	14–21
20–30	0.6	0.2	0.6	21–30

TABLE 5

ADSORPTION DATA FOR CATALYSTS

Catalyst no.	Reduction temp (°C)	Surface area (m²/g Fe)	Chemisorption data				$\frac{(V_{CO} + V_{CO_2})H_2S}{(V_{CO} + V_{CO_2}) \text{ fresh}}$	$\frac{\Delta V_{CO} + \Delta V_{CO_2}}{\Delta V_S}$
			Fresh catalyst		After H₂S, 0.5 mg S/m²			
			V_{CO}/V_m	V_{CO_2}/V_m	V_{CO}/V_m	V_{CO_2}/V_m		
L2021	450	15.0	0.50	0.08	0.17	0.01	0.31	0.26
D3001	450	14.7	0.39	0.26	0.18	0.02	0.31	0.29
P2007.6	450 500	19.8	0.41	0.02	0.20	<.02	0.49	0.14
L3119	450	13.4	0.30	0.18	0.12	0.11	0.48	0.16

ever, the results are obscured by differences in alkali concentration.

In the present Fischer-Tropsch tests the relative activity of Fe-Al$_2$O$_3$ was decreased to 0.04 when 0.2 mg S/g Fe was introduced, and for Fe-Al$_2$O$_3$-K$_2$O the relative activity decreased to 0.12 at 4.4 mg S/g Fe. In ammonia synthesis tests of Temkin (8), 4.6 and 10.1 mg S/g Fe were required to decrease activity to zero for Fe-Al$_2$O$_3$ and Fe-Al$_2$O$_3$-K$_2$O, respectively, Alkali appears relatively more effective in increasing resistance to sulfur poisoning in the Fischer-Tropsch synthesis than in the ammonia synthesis.

Extraction of part of the alkali in catalyst D3001 with water, Fig. 2, had only a small effect on activity and resistance to poisoning; however, addition of KOH in alcoholic solution to the reduced catalyst appreciably increased activity and resistance to poisoning.

In test Z47, a Fe$_3$O$_4$-MgO catalyst was impregnated with an aqueous solution of K$_2$S before reduction, so that the reduced catalyst contained 1.2 mg S/g Fe. Tests Z47 and X638 were made with sulfur-free gas. The catalyst promoted with K$_2$S was remarkably active; however, its activity was only about one-third of the corresponding catalyst promoted by K$_2$CO$_3$ in test X638. The tests are difficult to compare as the potassium content of the catalyst impregnated with K$_2$S was significantly less than the optimum concentration, about 0.5 g K$_2$O/100 g Fe (6). In prepoisoning tests of reduced catalyst D3001 by H$_2$S in heptane, a concentration of sulfur of 1.2 mg S/g Fe decreased the relative activity to 0.75 (3). Thus, addition of sulfur as K$_2$S does not seem significantly more effective than prepoisoning by H$_2$S.

Selectivity during poisoning at constant temperatures remained essentially constant until the relative activity had been decreased to less than 0.2, as shown by data in Table 3. Test Z295 and X527 were the same except that Z295 was made with gas containing H$_2$S. The poisoned catalyst produced more wax and less gasoline than the unpoisoned catalyst. Poisoning to lower

relative activities increased the relative production of gaseous hydrocarbons, as has been reported previously. Comparison of relative usage of H$_2$ and CO were not made because the usage ratio varies widely as conversion is changed. The relative constancy of selectivity during early and intermediate stages of poisoning appears to preclude the possibility that H$_2$S is selectively chemisorbed to inactivate the alkali promoter.

Experiments showing the effect of pore geometry of catalyst D3001 are given in Fig. 1 and Table 2. For catalysts used in synthesis with pure gas before poisoning, tests Z181 and Z243, the surface area of the freshly reduced catalyst had little effect on initial activity or on resistance to poisoning; in fact, the sample with the larger initial surface area poisoned more readily. Previous work (16, 17) in this laboratory has shown that catalysts oxidize extensively during the early part of synthesis tests to leave only a thin layer of porous, active material near the outside of the particle. To explain the constant activity observed for catalysts reduced at different temperatures, the thickness of the active layer was postulated to increase with increasing pore diameter, i.e. with decreasing surface area (5). This postulate also explains the poisoning data.

In test Z256 synthesis gas containing H$_2$S was used from the beginning of the test, and poisoning and oxidation of the catalyst proceeded concurrently. Resistance to poisoning as judged from the initial linear portions of the poisoning curves was increased by about 40%.

Increasing the external surface area by decreasing particle size from 6–8 mesh to 28–32 mesh (increasing external area 5.16-fold) increased the activity by a factor of 3.22 (18) and the poisoning constant, 1/α, by 3.34. Thus, poisoning apparently occurs predominately on the active external portion of the catalyst and the thickness of the effective portion of the catalyst in synthesis and poisoning is about 0.1 mm.

In three tests the catalyst bed was divided into three sections which were removed separately and analyzed at the end of the test. The data in Table 4 indicate that the

sulfur accumulated largely in the initial portion of the bed, and the initial portion served to protect the remainder of the bed. For the same concentration of sulfur in the second portion from the inlet, the concentration in the inlet segment of 28- to 32-mesh particles was more than five times larger than for 6–8-mesh particles. Surface areas of 6–8 mesh and 28–32 mesh catalysts at the start of poisoning, i.e., after use in synthesis and extraction of adsorbed hydrocarbons, were about 0.75 and 3.9 m^2/g Fe, respectively. By making the favorable assumptions of sulfur chemisorbing in a covalent form on iron and reacting with alkali to form KHS, the maximum value for the sulfur monolayer is about 1.0 mg S/m^2 (3). Thus, the concentrations of sulfur in the inlet portions of the catalyst greatly exceed the formation of a monolayer.

Most of the sulfur introduced with synthesis gas was found in the inlet portion of the bed. The small concentrations of sulfur found in subsequent portions of the bed, 0.2–0.9 mg S/g Fe, were apparently sufficient to decrease the relative activity in the last two-thirds of the bed to 0.15 to 0.3. In previous tests (3) catalysts used in synthesis for 400–800 hr were removed from the reactor, extracted in heptane, and poisoned with a solution of H_2S in heptane. This procedure should distribute the poison reasonably uniformly on the individual particles. Under these conditions with 6–8-mesh samples of D3001, the relative activity was decreased to 0.28 and 0.12, when the sulfur concentration was 0.18 and 0.45 mg S/g Fe, respectively.

Pores in the catalyst may be regarded as long reactors, and sulfur concentration gradients, similar to those found along the length of a catalyst bed, should occur from the exterior to the interior of individual particles. In chemisorption experiments 1 mole of H_2S decreased the amount of chemisorbed CO plus CO_2 by only 0.14 to 0.29 mole. Formation of thick adsorbed layers of

sulfur near the external surface of the particle could explain these results.

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