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SULFUR POISONING OF FIXED BEDS OF IRON CATALYSTS IN THE FISCHER-TROPSCH SYNTHESIS

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UNITED STATES DEPARTMENT OF THE INTERIOR

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SULFUR POISONING OF FIXED BEDS OF IRON CATALYSTS IN THE FISCHER-TROPSCH SYNTHESIS

by

R. B. Anderson,[1] F. S. Karn,[2] R. E. Kelly,[2] and J. F. Shultz[3]

Abstract

SULFUR poisoning of iron catalysts in the Fischer-Tropsch synthesis was investigated at the Bureau of Mines, because synthesis gas produced from coal contains sulfur compounds. Tests of two typical iron catalysts with synthesis gas containing known concentrations of H_2S were made to determine catalyst life as a function of sulfur concentration to ascertain the type of gas purification required. Fixed beds of activated steel turnings and a fused iron oxide catalyst were investigated in sulfur poisoning tests at 21.4 atmospheres with $1H_2+1CO$ gas containing 6.9, 23, or 69 mg S as H_2S per cubic meter (0.3, 1.0, and 3.0 gr per 100 cu. ft.). In tests of reduced catalysts at constant temperatures, more than 80 percent of the activity was lost when 0.5 mg S/g Fe was introduced. Poisoning of nitrided or carbided fused iron oxide catalysts to a given extent required more than twice as much sulfur than for the corresponding reduced catalyst. When the synthesis temperature was increased to compensate for loss in activity, tests of the fused iron oxide catalysts at constant productivity could be continued for 19 to 98 days. The tests were terminated by clogging of the reactor, presumably caused by carbon deposition.

One objective of the present work was to determine if synthesis gas, purified by the Bureau of Mines' hot-potassium carbonate process for removing H_2S, COS, and CO_2, is suitable for synthesis on iron catalysts. The sulfur content of the gas purified by this process is in the range of concentrations used in the present work. In constant-productivity tests of nitrided fused iron oxide catalysts with synthesis gas containing 6.9 mg S/m^3, catalyst lives are nearly long enough for serious consideration of this mode of operation. However, factors relating to selectivity and stability of the catalyst indicate that this type of operation is impractical for a commercial process. On this basis additional gas purification, such as iron oxide boxes following a hot potassium carbonate scrubber, is desirable.

Introduction

Sulfur poisoning of iron catalysts in the ammonia synthesis was observed about 60 years ago.[4] Fischer,[5][6] in 1935, cited a practical upper limit for sulfur concentration of 1 to 2 mg/m^3 for synthesis gas for the Fischer-Tropsch synthesis, and most commercial applications of this process have used synthesis gas containing sulfur concentrations below this limit.

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Work on manuscript completed April 1964.

[4] Titles enclosed in brackets are translations from the language in which the item was published.

[5] Mittasch, A. Early Studies of Multicomponent Catalysts. Ch. in Advances in Catalysis and Related Subjects, ed. by W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal. Academic Press, Inc., New York, v. 2, 1950, pp. 81-104.

[6] Fischer, F. Die Synthese der Treibstoffe (Kogasin) und Schmieröle aus Kohlenoxyd und Wasserstoff bei Gewöhnlichem Druck [Synthesis of Fuels (Kogasin) and Lubricants from Carbon Monoxide and Hydrogen at Ordinary Pressure.] Brennstoff-Chem., v. 16, No. 1, January 1935, pp. 1-11.

A survey of the literature to 1956 [7] showed only a few important contributions to the problem of sulfur poisoning of iron catalysts in either the Fischer-Tropsch or the ammonia synthesis. Brill [8] found that the resistance of fused catalysts to sulfur poisoning in the ammonia synthesis at atmospheric pressure increases in the following order:

pure iron	Fe
iron-potassium oxide	$Fe\text{-}K_2O$
iron-aluminum oxide-potassium oxide	$Fe\text{-}Al_2O_3\text{-}K_2O$
iron-aluminum oxide-calcium oxide-potassium oxide	$Fe\text{-}Al_2O_3\text{-}CaO\text{-}K_2O$

Frear, Shultz, and Elmore [9] found that about 20 mg of hydrogen sulfide per gram of catalyst were required to decrease the activity to very low values in the ammonia synthesis at 100 atmospheres on doubly promoted iron catalysts. Sulfur dioxide was found to be a temporary poison, similar to oxides of carbon and water vapor. More recently, Bulatnikova, Apel'baum, and Temkin [10] 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. Activity for ammonia synthesis decreased to zero when the concentration of sulfur per unit surface area was 0.4, 0.9, and 2.5 mg S/m² for $Fe\text{-}Al_2O_3$, $Fe\text{-}Al_2O_3\text{-}K_2O$, and $Fe\text{-}K_2O$ catalysts, respectively. The weights of sulfur per gram of catalysts were 3.2, 8.1, and 1.7 mg for $Fe\text{-}Al_2O_3$, $Fe\text{-}Al_2O_3\text{-}K_2O$, and $Fe\text{-}K_2O$, respectively.

Rapoport and Muzovskaya [11] investigated the poisoning of precipitated iron oxide-copper oxide catalysts by organic sulfur compounds in the Fischer-Tropsch synthesis. Catalysts that were reduced only to Fe_3O_4 or not at all were remarkably resistant to sulfur poisoning, and the synthesis could be continued at moderate to high yields until the sulfur content of the catalyst was increased to about 10 weight-percent. On the other hand, a similar catalyst completely reduced in hydrogen at 500° C. was reported to be inactive at a sulfur content of only 0.9 weight-percent.

British workers investigated the sulfur poisoning of reduced iron catalysts prepared from mill scale in the Fischer-Tropsch synthesis.[12] Prepoisoning by hydrogen sulfide introduced into an evacuated bulb containing the catalyst was more effective than poisoning by sulfur compounds in the synthesis gas. Methane production was increased by sulfur poisoning.

Research by the Pittsburgh Coal Research Center has examined the effect on activity of distribution of poison adsorbed on the catalyst as a function of length of a fixed bed of catalyst.[13] The conclusion drawn from this theoretical work is that accumulation of the poison near the inlet end of a fixed bed of catalyst decreases the effectiveness of a given amount of poison. Poisoning is most severe when the poison is uniformly distributed along the length of the catalyst bed. To investigate the poisoning of iron catalysts without a gradient of sulfur concentration as a function of bed length, pretreated fused iron oxide catalyst, D3001,[14] and activated steel turnings, L2201,[14] were prepoisoned by immersion in a solution of the sulfur compound in heptane prior to synthesis.[15] Sulfur dioxide was the most severe poison, and hydrogen sulfide and ethyl mercaptan were nearly as effective. Results of tests of reduced catalysts poisoned by carbonyl sulfide and carbon disulfide, as well

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[7] Anderson, R. B. Catalysts for the Fischer-Tropsch Synthesis. Ch. 2 in Catalysis, ed. by P. H. Emmett. Reinhold Pub. Corp., New York, v. 4, 1956, p. 242.

[8] Brill, R. Behavior of Calcium in the Ammonia Catalyst Toward Poisoning. FIAT Reel R-19, frames 7088-7104, 1941.

[9] Frear, G. L., J. F. Shultz, and K. Elmore. Poisoning and Reactivation of Ammonia Synthesis Catalysts. Tennessee Valley Authority Internal Rept. R545, 1950, 22 pp.

[10] Bulatnikova, Yu. I., L. O. Apel'baum, and M. I. Temkin. Izuchenie otravleniya katalizatora sinteza ammiaka serovodorodom s primeneniyem radiosery [The Use of Radioactive Sulfur to Study H_2S-Poisoning of Ammonia-Synthesis Catalyst]. Zhur. Fiz. Khim. [Jour. Phys. Chem.], v. 32, No. 12, 1958, pp. 2717-2724.

[11] Rapoport, I. B., and O. A. Muzovskaya. [Effect of Organic Sulfur Compounds on the Process of Synthesis Over Iron Catalysts. Pt. 1, 2.] Khim. i Tekhnol. Topliva i Masel, No. 2, 1957, pp. 18-24; pt. 2, No. 5, 1957, pp. 19-27.

[12] Fuel Research. Report of the Fuel Research Board, Greenwich, England, 1955, p. 20; 1956, p. 22.

[13] Anderson, R. B., and A. M. Whitehouse. Poisoning in Fixed Beds of Catalyst. Ind. and Eng. Chem., v. 53, No. 12, December 1961, pp. 1011-1014. Anderson, R. B. A Theorem Regarding the Poisoning of Fixed Catalyst Beds. J. Catalysis, v. 1, No. 4, August 1962, pp. 393-394.

[14] These catalysts are described in the section on experimental work, and poisoning of these catalysts with H_2S in synthesis gas is reported subsequently.

[15] Shultz, J. F., L. J. E. Hofer, F. S. Karn, and R. B. Anderson. Studies of the Fischer-Tropsch Synthesis. Prepoisoning of Iron Catalysts by Sulfur Compounds. J. Phys. Chem., v. 66, March 1962, pp. 501-505.

as a nitrided catalyst poisoned by hydrogen sulfide, were erratic. However, for all sulfur compounds tested, the activity of a reduced fused iron catalyst was decreased to less than 2 percent of the value for the fresh sample by the addition of 8 to 10 mg S/g Fe or 0.6 to 0.7 mg S/m^2 of surface. Activated steel turnings were more susceptible to sulfur poisoning than the reduced fused iron oxide catalyst, and about 0.7 mg S/g Fe or 1.4 mg S/m^2 was required to decrease the activity to less than 2 percent of its original value.

This bulletin describes the results of poisoning of fixed beds of reduced, carbided, and nitrided fused iron oxide catalysts and reduced steel turnings by H_2S in $1H_2+1CO$ synthesis gas in tests in which the temperature (1) was held constant and (2) was increased as required to maintain constant productivity. One objective of these experiments was to determine the suitability of using gas from a hot potassium carbonate gas purification process[16] without further sulfur removal. Carbonyl sulfide is hydrolyzed to H_2S in this process, and H_2S concentrations in the range 6.9 to 151 mg/m^3 (0.3 to 6.6 gr/100 ft^3) were obtained in the purified gas.[17] [18] Synthesis gas prepared from coal in high-temperature oxygen gasifiers contains only carbonyl sulfide and H_2S. Thus, in the present experiments synthesis gas containing concentrations of H_2S of 6.9, 23, and 69 mg S/m^3 (0.3, 1.0, and 3.0 gr/100 ft^3) were used. The selectivity of catalysts in constant-productivity tests is described.

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[16] Benson, H. E., J. H. Field, and W. P. Haynes. Improved Process for CO_2 Absorption Using Hot Carbonate Solutions. Chem. Eng. Prog., v. 52, No. 10, October 1956, pp. 433-438. Benson, H. E., J. H. Field, and R. M. Jimeson. CO_2 Absorption Process Employing Hot Carbonate Solutions. Chem. Eng. Prog., v. 50, No. 7, Oct. 1954, pp. 356-364.

[17] Benson, H. E., and Field, J. H. Method of Separating CO_2 and H_2S From Gas Mixtures. U.S. Pat. 2,886,405, May 12, 1959.

[18] 1 mg/m^3 is equivalent to 0.0437 gr/100 ft^3.

EXPERIMENTAL WORK

PREPARATION AND ANALYSIS OF SYNTHESIS GAS

Synthesis gas containing $1H_2+1CO$ and 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 were prepared in special cylinders, plastic-lined carbon steel, stainless steel, or aluminum.[19] Each cylinder type 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.

Analyses made by a modified Referee method[20] agreed with compositions computed from the preparation to within the following limits in terms of standard deviation: 1.8, 2.7, and 5.0 mg S/m³ for concentrations of 6.9, 23, and 69 mg S/m³.

SYNTHESIS TESTS

Catalysts used were (1) 6- to 8-mesh fused iron oxide catalyst D3001, containing in the raw state, in weight-percent, 67.4 Fe, 4.61 MgO, 0.65 Cr_2O_3, and 0.57 K_2O, and (2) activated SAE 1018 steel lathe turnings L2201, approximate dimensions 8 by 3 by 0.4 mm, oxidized 24.6 percent with steam at 700° C, and impregnated with K_2CO_3 to give a concentration of 0.13 weight-percent K_2O.

Catalyst D3001 was reduced in hydrogen at an hourly space velocity of 2,500 and 450° C for 40 hours to give a weight loss of about 24 percent, corresponding to 90 percent reduction of the oxides of iron. For some tests reduced catalyst D3001 was treated with ammonia at an hourly space velocity of 1,000 for 18 hours to convert the reduced iron to epsilon iron nitride.[21] In one test reduced catalyst D3001 was converted to Hägg iron carbide by treatment with carbon monoxide at an hourly space velocity of 100 for 38 hours. The temperature was increased from 170° to 350° C as required to maintain about 20 percent carbon dioxide in the exit gas.[22]

The surface area of the reduced catalyst D3001 was 14.8 m²/g Fe, and after 9 days of synthesis 1.1 to 0.8 m²/g Fe.[23] Before use in synthesis, nitrided and carbided samples had about the same area as reduced D3001. Presumably, the surface areas of carbided catalysts also decreased sharply during synthesis, because the catalyst was rapidly oxidized during synthesis. The surface area of a sample of nitrided D3001, which was initially reduced at 500° C, increased slightly during synthesis.[24]

Catalyst L2201 was reduced in hydrogen at an hourly space velocity of 1,000 and 450° C for 8 hours to give a loss in weight of 6.5 percent, corresponding to about 98 percent reduction of the oxidized zone. The surface areas of the reduced turnings from determinations on two separate samples were 0.4 and 0.8 m²/g Fe. After 9 days of synthesis the area of one sample increased from 0.4 to 0.5 m²/g Fe.[25]

Data for changes in composition and surface area for reduced catalysts D3001 and L2201 after 9 days of normal synthesis with $1H_2+1CO$ gas at 21.4 atmospheres and subsequent extraction of wax[26] are given in table 1. These data represent the condition of the catalyst at the start of poisoning after a stabilizing period on pure gas. The activated layer of turnings was largely converted to carbides, whereas the reduced fused catalyst was largely oxidized all along the length of the bed. The large decrease in surface area of catalyst D3001 is caused by filling of pores by oxidation. Carbided catalyst D3001 oxidized similarly to the reduced catalyst. However, nitrided D3001 was oxidized to a smaller extent and has a substantially larger surface area during use.

All tests were made at 21.4 atmospheres in stainless-steel reactors similar in design to the reactors that have been described previously.[27]

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[19] Shultz, J. F., F. S. Karn, and R. B. Anderson. Cylinders for Storing Sulfur-Containing Gases. Ind. and Eng. Chem., v. 54, No. 5, May 1962, pp. 44-45.

[20] Altieri, V. J. Gas Analysis and Testing of Gaseous Materials. The American Gas Association, Inc., N.Y. 1945, pp. 147-151.

[21] Anderson, R. B., J. F. Shultz, B. Seligman, W. K. Hall, and H. H. Storch. Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts. J. Am. Chem. Soc., v. 72, August 1950, pp. 3502-3508.

[22] Shultz, J. F., W. K. Hall, B. Seligman, and R. B. Anderson. Studies of the Fischer-Tropsch Synthesis, IV. Hägg Iron Carbide as Catalysts. J. Am. Chem. Soc., v. 77, January 1955, pp. 213-221.

[23] Shultz, J. F., F. S. Karn, J. Bayer, and R. B. Anderson. Composition Changes of Massive Iron and Fused Iron Oxide Catalysts in the Fischer-Tropsch Synthesis. J. Catalysis, v. 2, No. 3, June 1963, pp. 200-211.

[24] Stein, K. C., G. P. Thompson, and R. B. Anderson. Studies of the Fischer-Tropsch Synthesis. XVII. Changes of Iron Catalysts During Pretreatment and Synthesis. J. Phys. Chem., v. 61, July 1957, pp. 928-932.

[25] Work cited in footnote 23.

[26] Work cited in footnote 23.

[27] Shultz, J. F., L. J. E. Hofer, E. M. Cohn, K. C. Stein, and R. B. Anderson. Synthetic Liquid Fuels From Hydrogenation of Carbon Monoxide. Part 2. BuMines Bull. 578, 1959, 139 pp.

TABLE 1.—*Surface area and composition of catalysts*

Catalyst and state	Surface area, m²/g Fe	Composition, atom ratios		Phases from X-ray diffraction [1]
		C/Fe	O/Fe	
Turnings (L2201):				
Reduced	0.45	≈0	0	α
Used	.54	[2] .55	[2] .15	[3] x, C(?)
Fused iron oxide (D3001):				
Reduced particles	14.8	≈0	0	α
Used:				
Inlet portion	1.00	.31	.92	M, α
Middle portion	.77	.18	1.01	M, α
Outlet portion	.74	.15	1.06	M, α

[1] Phases listed in order of intensity of diffraction pattern. α=metallic iron, x=Hägg carbide, C=cementite, and M=magnetite. Phases with faint diffraction patterns are followed by (?).

[2] These analyses are given for activated layer. Composition can be expressed on the basis of entire turnings by dividing these values by 4.

[3] Diffraction analysis for activated layer.

Stainless-steel tubing and valves were used throughout the inlet system employed for sulfur-containing gas. The catalyst charge was 50 cm³ in all tests, and the inside diameter of the reactor was 1.58 cm. Testing procedures have been described previously.[28]

Tests were started on a sulfur-free $1H_2+1CO$ gas, total sulfur content less than 1 mg/m³, at an hourly space velocity of 300 and at 200° C, and the temperature was increased slowly so that about 48 hours were required for the apparent CO_2-free contraction to attain 65 percent. Usually a constant activity was reached at 260° C, and synthesis was continued for 9 to 20 days to establish a starting point for the poisoning tests.

Synthesis gas, $1H_2+1CO$, containing concentrations of H_2S of 6.9, 23, and 69 mg S/m³, was then introduced by a separate feed system without depressurizing the reactor.

Two modes of operation were followed after the change to feed gas containing sulfur:

1. Constant temperature, where the temperature was maintained constant at the temperature of the previous period of constant activity and the conversion was permitted to decrease with time.

2. Constant productivity, where the temperature was increased as required to maintain the CO_2-free contraction at about 60 percent.

Tests of the first type were usually terminated voluntarily after the conversion had decreased to a low constant value. Tests of the second type were usually terminated by clogging of the catalyst bed.

Weekly recoveries of products (gaseous, liquid, and solid) were made, and the product distribution was determined. The products were also analyzed for sulfur. At the end of the test the catalysts were analyzed and a sulfur balance was determined. Uncertainties in sulfur balances involve the accuracy of sulfur analyses of feed gas, used catalyst, and products as well as sampling of used catalyst. In early tests 55 to 90 percent of the sulfur introduced was found on the catalyst. However, in later tests with improved sampling and analytical methods, 80 to 100 percent of the sulfur introduced was found on the catalyst. The exit gas and synthesis products did not contain significant concentrations of sulfur.

For both types of experiments the activity of the catalyst, in terms of volume of H_2+CO reacted per gram of iron per hour at 240° C, was computed using an empirical rate equation,[29]

$$-ln(1-x)=(A/S)\ \exp-(E/RT),$$

where x is the fraction of H_2+CO reacted, A is a rate constant, S is hourly space velocity of H_2+CO, and E is the activation energy, and has a value of 19 kcal/mole. The following kinetic data on sulfur-poisoned catalysts indicate that activities computed by this equation are valid: (1) When hourly space velocities were decreased from 300 to 100, the same activities were obtained, and (2) activation energies of 20.9, 19.5, and 17.8 kcal/mole were obtained on a 6- to 8-mesh catalyst D3001 poisoned with H_2S to relative activities of 50, 25, and 8 percent, respectively.

Data from poisoning tests are given in terms of relative activity, defined as the activity of the poisoned catalyst divided by the activity of the unpoisoned catalyst at the start of the

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[28] Work previously cited on footnote 25.

[29] Anderson, R. B., B. Seligman, J. F. Shultz, R. Kelly, and M. A. Elliott. The Fischer-Tropsch Synthesis. Some Important Variables of the Synthesis Over Iron Catalysts. Ind. and Eng. Chem., v. 44, No. 2, February 1952, pp. 391–397.

poisoning. For catalysts described here, the activity in tests with sulfur-free gas remained essentially constant for 8 weeks or longer; therefore, the large decreases in activity in poisoning tests may be attributed to poisoning.

As the observed conversion data were averages for periods between flowmeter readings, the activities computed from these data were compared with the calculated amount of sulfur fed to the unit at a time halfway between the readings. A correction was made for the amount of gas containing H_2S required to flush the volume of the reactor ahead of the catalyst bed.

Space velocity is defined as STP (standard temperature and pressure) of synthesis gas fed to the reactor per unit volume of catalyst space per hour. All gas volumes reported have been corrected to STP conditions. The amount of sulfur introduced to the catalyst bed is given as milligrams of sulfur per gram of iron in the catalyst charge.

The product distributions are plotted as percent of the total hydrocarbons, the term "hydrocarbons" including oxygenated organic molecules dissolved in the condensed hydrocarbon phases. Total hydrocarbons are distributed into C_1, C_2, and C_3+C_4 gaseous hydrocarbons (by mass spectrometric analyses) and into the following distillation ranges of the condensed hydrocarbon phases: 30° to 185° C, 185° to 352° C, 352° to 464° C, and above 464° C. The percentages of olefins in the C_2 and C_3+C_4 fractions are indicated by a number following the double-bond symbol (=) in the block diagrams. Functional group analyses of the two lower distillation ranges by infrared methods[30] are indicated as follows: Br indicates the bromine number calculated from the amount of olefin, OH is the weight-percent of hydroxyl group, and CO indicates the weight-percent of carbonyl group present as aldehydes, ketones, and acids.

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[30] Anderson, J. A., and W. D. Seyfried. Determinations of Oxygenated and Olefin Compound Types by Infrared Spectroscopy. Anal. Chem., v. 20, No. 11, November 1948, pp. 998-1006.

EXPERIMENTAL RESULTS

CONSTANT-TEMPERATURE POISONING TESTS

Figure 1 presents data for the poisoning of reduced catalysts D3001 and L2201 with $1H_2+1CO$ gas containing 69 mg S/m^3 as H_2S. Similar data are presented in figure 2 for a sulfur concentration of 23 mg/m^3. For both carbided catalysts and reduced catalysts, following the initial short period of high activity, the relative activity decreased linearly with increasing sulfur fed to the catalyst until 50 to 75 percent of the activity was lost; subsequently the activity decreased less rapidly. For nitrided catalysts the linear portion of the poisoning curves did not extend beyond a relative activity of 0.7 for 69 mg S/m^3, and for 6.9 mg S/m^3 the linear portion was absent. These data are given in table 2 but are not shown on the poisoning curves. For catalyst L2201, the relative activity decreased steadily to zero when 1 to 2 mg S/g Fe had been introduced, but the relative activity of reduced and carbided catalyst D3001 decreased to a constant value of 0.03 to 0.10. For nitrided catalyst D3001 the relative activity decreased to a constant value of 0.1 to 0.2. Table 2 presents data for all tests read from experimental curves at equal intervals of relative activity.

Selectivity data obtained from constant-temperature tests are not very reliable, because the productivity decreases rapidly and small losses in recovery of liquid and solid hydrocarbons become significantly large compared with the quantity recovered. In special experiments with 28- to 32-mesh samples of reduced D3001, which poison more slowly than 6- to 8-mesh samples, the selectivity remained essentially constant until the relative activity decreased to at least less than 0.2. In tests of nitrided catalysts the fraction of C_5^+ hydrocarbons in the product remained constant or possibly increased during the initial stages of poisoning.

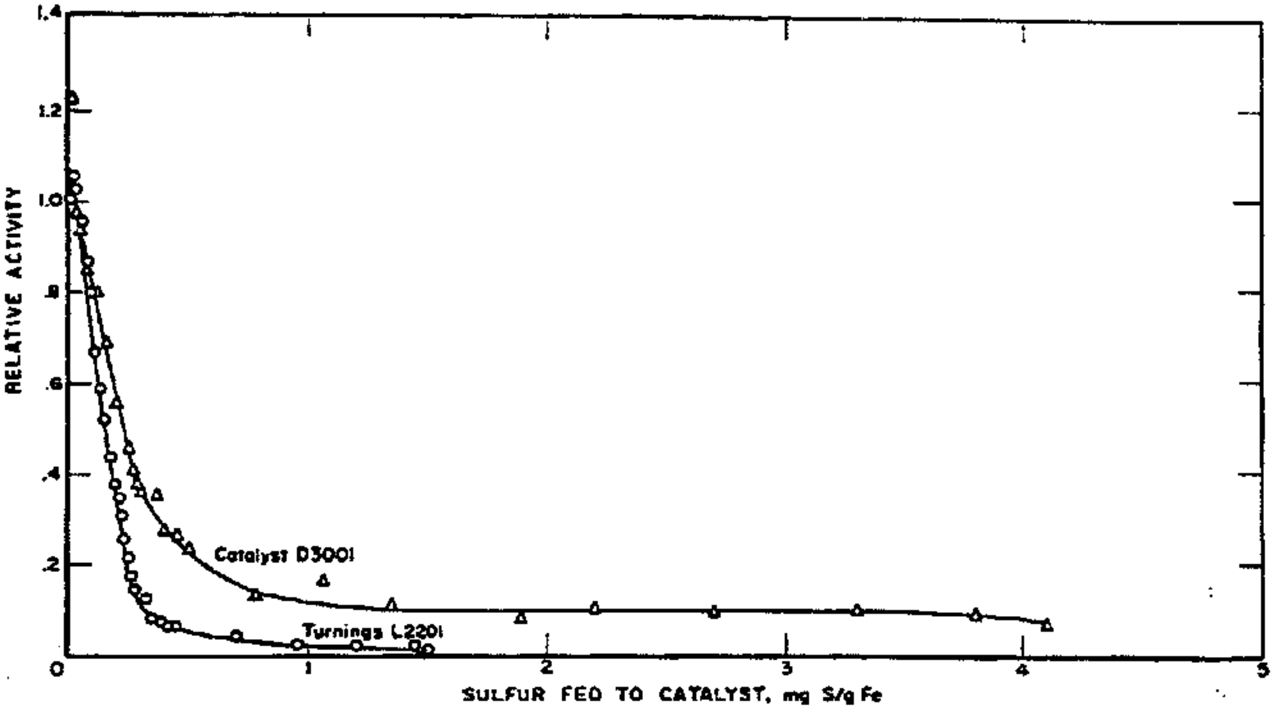

FIGURE 1.—Constant-Temperature Poisoning Tests of Reduced Iron Catalysts Using $1H_2+1CO$ Gas Containing 69 mg S/m^3 as H_2S.

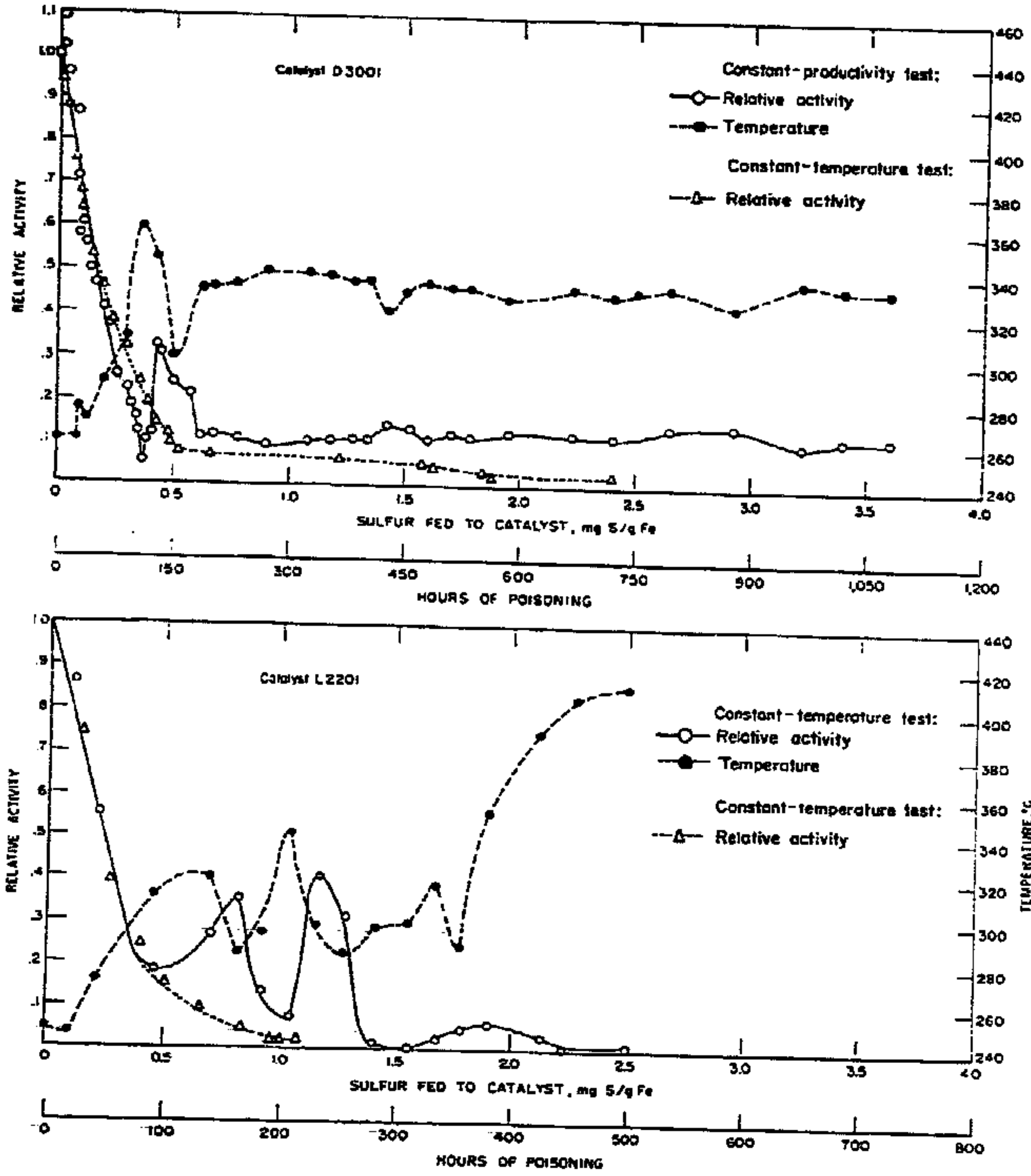

FIGURE 2.—Comparison of Constant-Productivity and Constant-Temperature Poisoning Tests of Catalysts D3001 and L2201 With $1H_2+1CO$ Gas Containing 23 mg S/m³ as H_2S.

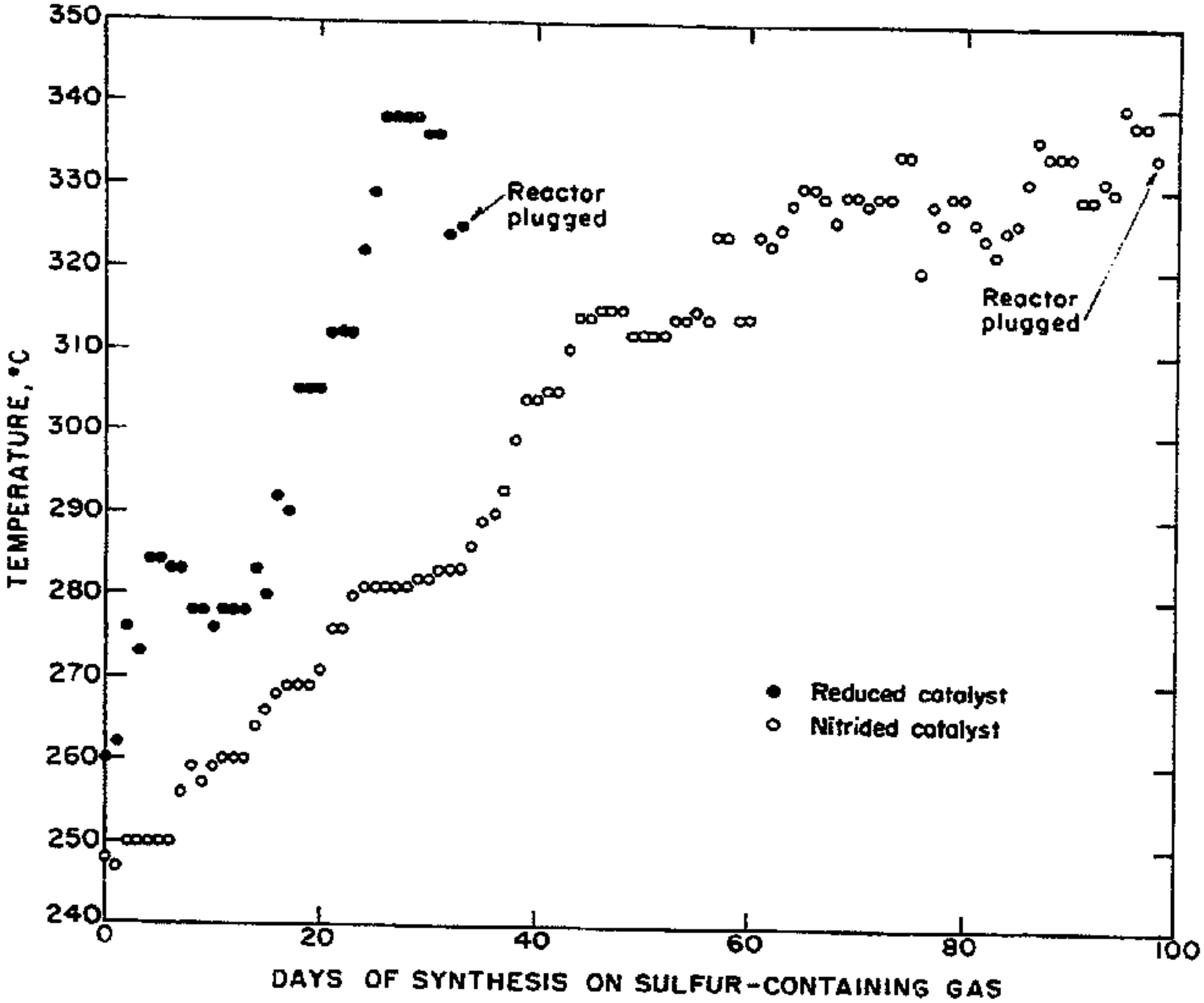

FIGURE 3.—Temperatures Required To Maintain Constant Productivity of Reduced and Nitrided Catalyst D3001 Using 1H_2+1CO Gas Containing 6.9 mg S/m³ as H_2S.

TABLE 3.—*Duration and maximum temperatures in constant-productivity tests*

Catalyst and pretreatment	Sulfur concentration, mg S/m³	Duration, days	Reason for terminating[1]	Temperature, °C		
				Start of poisoning	Maximum	End of test
Fused iron oxide (D3001):						
Reduced	6.9	33	C	260	338	325
	23	41	C	260	360	330
	69	18	C	256	355	355
Nitrided	6.9	98	C	248	338	338
	23	56	C	256	350	319
	69	28	C	249	349	346
Carbided	69	55	C	242	344	344
Turnings (L2201): Reduced	23	[2] 17.5	I	250	410	410
	69	[2] 11.7	I	260	396	396

[1] C=bed clogged, I=constant productivity could not be maintained.

[2] Time for which constant productivity was maintained. Test continued for 50 to 80 hours at low productivity before bed clogged.

TABLE 2.—*Summary of constant-temperature poisoning tests: Sulfur required to decrease relative activity to a given value, mg S/g Fe*

[All tests with $1H_2+1CO$ gas at 21.4 atm]

H_2S in feed gas mg S/m³	Catalyst D3001						Catalyst L2201, reduced	
	Reduced, synthesis at 260° C			Carbided, synthesis at 242° C	Nitrided, synthesis at 250° C		Synthesis at 260° C	Synthesis at 262° C
	6.9	23	69	69	6.9	69	23	60
Relative activity:								
0.9	0.031	0.031	0.046	0.092	0.015	0.090	0.082	0.062
0.8	.060	.056	.092	.180	.050	.180	.112	.086
0.7	.090	.090	.135	.242	.103	.260	.147	.112
0.6	.120	.125	.175	.352	.155	.410	.185	.137
0.5	.155	.165	.218	.455	.283	.740	.215	.160
0.4	.194	.216	.275	.552	.450	1.020	.250	.185
0.3	.242	.300	.353	.628	.600	1.460	.350	.220
0.2	.300	.379	.600	.980	.970	[1] >3.0	.400	.253
0.1	.950	.440	1.750	1.750	[1] >1.3	--------	.600	.340
0.05	[1] >1.5	1.600	[1] >4.2	(2)	--------	--------	.800	.700

[1] Tests were voluntarily terminated when this amount of sulfur had been introduced.
[2] Temperature was increased after 1.9 mg S/g Fe was fed to the catalyst.

CONSTANT-PRODUCTIVITY POISONING TESTS

Poisoning curves for constant productivity tests with 23 mg S/m³ as H_2S are shown in figure 2. The relative activity decreased initially in about the same manner as in the constant-temperature tests. However, after the temperature had been increased above 300° C, the activity often increased sharply and usually decreased again rapidly. These periods of sudden transient activation probably result from the generation of fresh active surface by processes related to carbon deposition which cause disintegration of the catalyst particles. The constant-productivity tests also exhibited periods of sustained higher activity, compared with the constant-temperature tests probably for the same reason. This type of activation of iron catalysts at moderately high temperatures has been described in a recent paper.[31] Carbon deposition was more rapid at the higher temperatures used in the constant-productivity tests, and the catalyst bed eventually clogged, presumably owing to carbon deposition. For tests with catalyst D3001, productivity could be maintained constant until the test was terminated by clogging of the reactor, but for catalyst L2201 the productivity decreased substantially before the reactor clogged. Figure 3 is a plot of temperatures of synthesis as a function of time for constant-productivity tests of reduced and nitrided catalyst D3001 using gas containing 6.9 mg S/m³ as H_2S. With the lower concentration of H_2S, the activity changes less rapidly and large fluctuations in activity usually were not observed.

Table 3 lists the life of catalysts in constant-productivity tests before clogging occurred for catalyst D3001 or before productivity decreased to a low value for catalyst L2201. Since conditions leading to clogging are diverse, the time before clogging occurs can be regarded as only an approximate value. Changes in reactor type or size may lead to widely differing values of time before clogging occurs.

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[31] Shultz, J. F., F. S. Karn, R. B. Anderson, and L. J. E. Hofer. A New Type of Catalyst—Carbon-Expanded Iron. Fuel, v. 40, No. 3, May 1961, pp. 181-192.

Table 4 gives product distribution data for constant-productivity experiments. As the temperature was increased substantially during poisoning, the selectivity data reflect, in addition to the effect of poisoning, the effects of high synthesis temperatures and of changes in the catalyst that occur at these temperatures.

For reduced catalyst L2201 and reduced or carbided, fused iron oxide catalyst D3001, yields of C_5^+ hydrocarbons decrease and yields of gaseous hydrocarbons increase during poisoning on constant-productivity tests. For nitrided catalyst D3001 the distribution of products into C_5^+ and C_1-C_4 fractions does not change significantly during poisoning.

Liquids plus solid products from the tests in table 4, which usually comprised 2 or more weeks operation, were combined and fractionated by a simple distillation. These data and infrared analyses of the two lower boiling fractions are presented in figures 4 to 6. Included in figures 5 and 6 are selectivity data for comparable tests of 6 weeks or longer on pure gas. These data are included because the products from the first week of synthesis usually have a lower molecular weight than observed in longer tests. During poisoning with reduced or carbided catalysts the yields of higher boiling fractions decreased substantially and the yields of gaseous hydrocarbons increased. The fraction of oxygenated molecules in distillation fractions decreased with poisoning, but the olefin content remained essentially constant.

For nitrided catalysts (fig. 6) in constant-productivity tests, the distribution into products of different boiling range did not change greatly during poisoning; however, the yields of C_1–C_4 hydrocarbons were large in all tests, 43 to 57 weight-percent of total hydrocarbons. In tests with pure gas nitrided catalysts, compared with reduced or carbided catalysts, produced larger yields of gaseous hydrocarbons and larger amounts of oxygenated organic compounds in the distillation fractions. Yields of oxygenated organics remained high during poisoning in test Z184, but decreased to low values in the latter part of test Z198. The decrease in oxygenated molecules during poisoning was accompanied by an increase in olefin content.

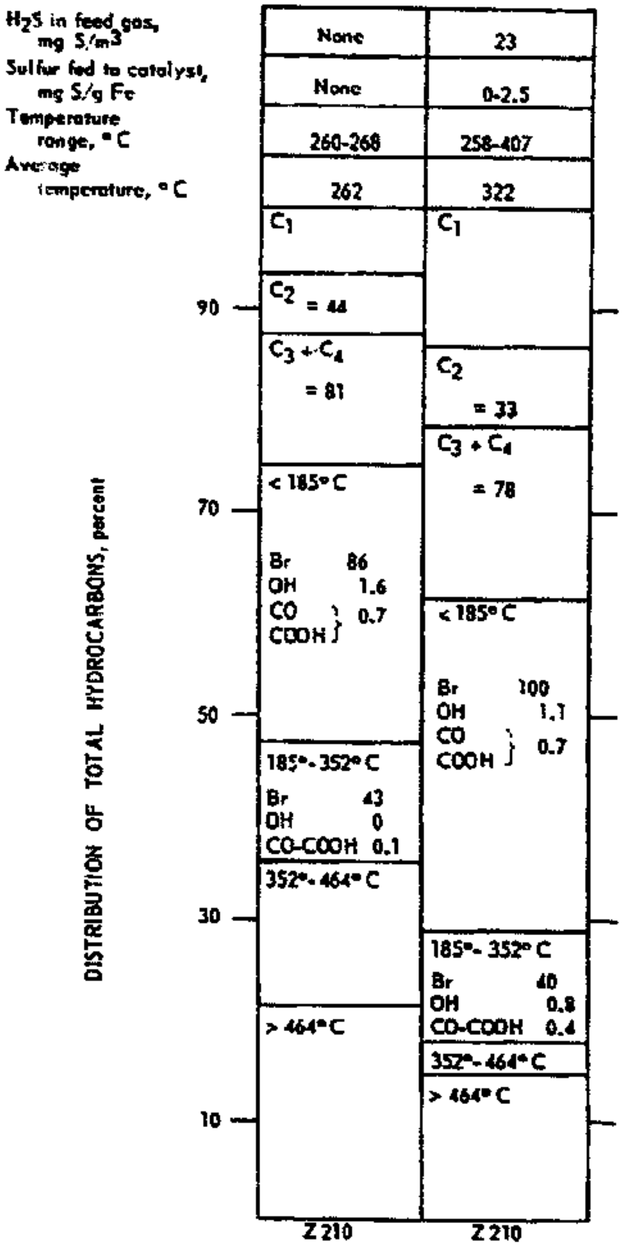

FIGURE 4.—Selectivity in Constant-Productivity Poisoning Tests of Steel Turnings L2201. Total hydrocarbons includes oxygenated material dissolved in liquid phase.

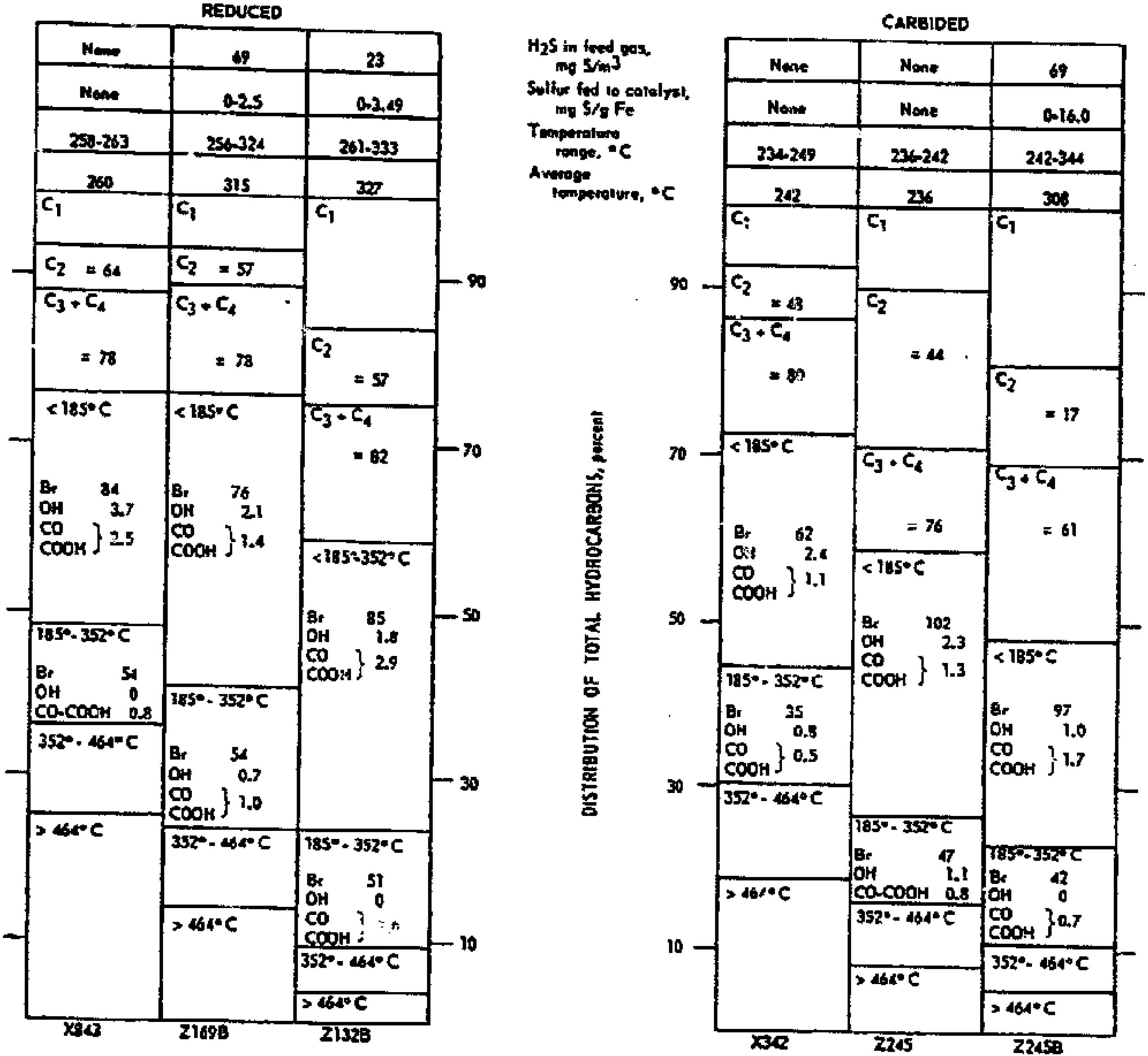

FIGURE 5.—Selectivity in Constant-Productivity Poisoning Tests of Reduced and Carbided Catalyst D3001. Total hydrocarbons includes oxygenated material dissolved in liquid phase.

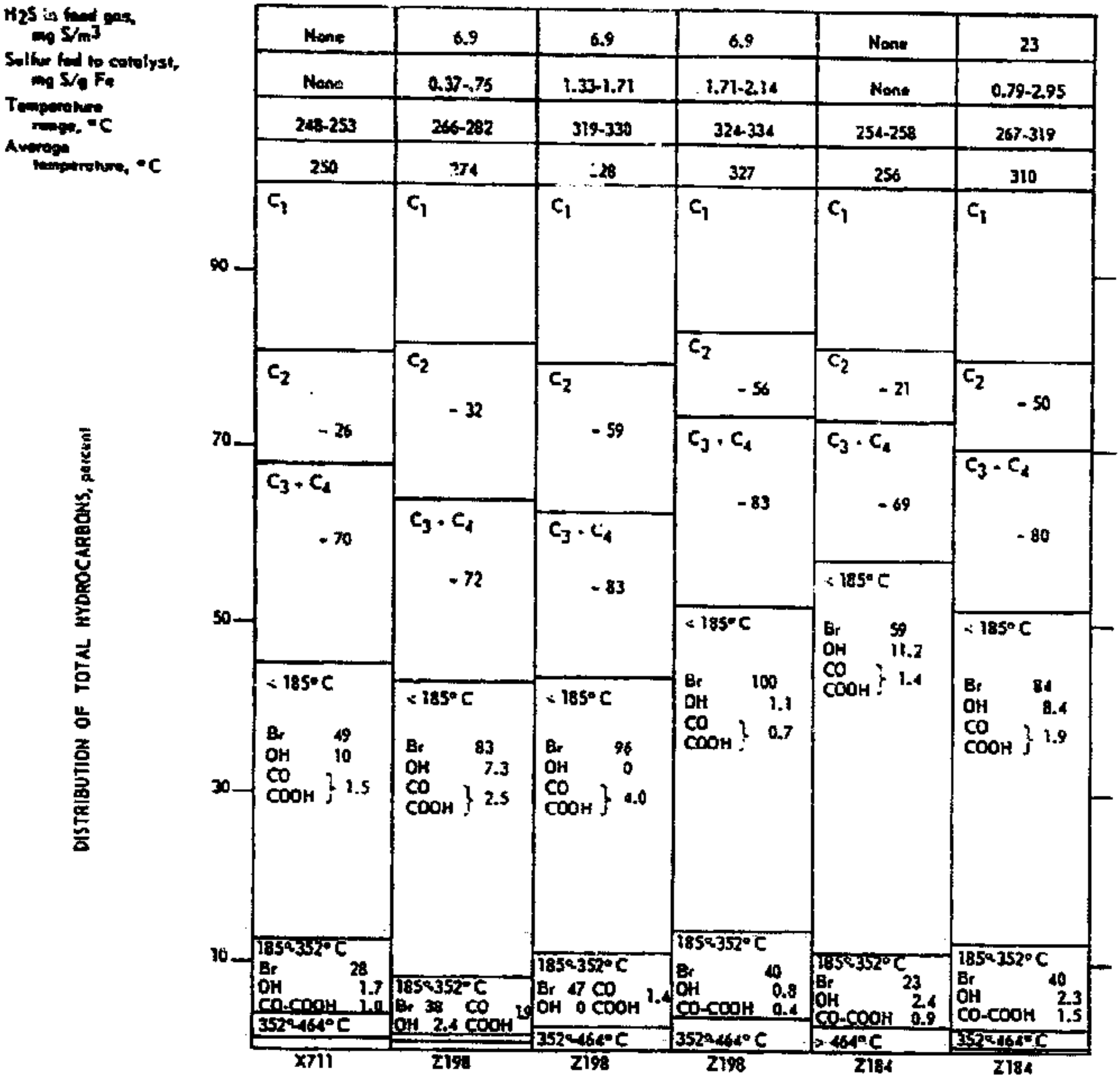

FIGURE 6.—Selectivity in Constant-Productivity Poisoning Tests of Nitrided Catalyst D3001. Total hydrocarbons includes oxygenated molecules dissolved in liquid phase.

TABLE 4.—*Product distribution in constant-productivity poisoning experiments*

Catalyst and test	Pretreatment	Sulfur concentration, mg S/m³	Sulfur fed to catalyst, mg S/g Fe	Temperature, °C	Distribution of hydrocarbons,[1] weight-percent			
					C_1	C_2	C_3+C_4	C_5+
Turnings(L2201) Z210	Reduced	0	[2] 0	262	6	6	13	75
		23	0 – .8	257–329	10	6	13	71
		23	.8– 1.7	288–350	17	10	24	49
		23	1.7– 2.5	322–357	26	12	23	39
Fused iron oxide (D3001):								
Z132	do	23	0 – 1.3	261–364	10	3	11	76
			1.3– 2.6	331	16	9	13	62
			2.6– 2.8	330–349	16	10	17	57
Z245	Carbided	69	[2] 0	236	10	19	12	59
			0 – 1.8	242	8	6	18	68
			3.6– 7.1	298	25	16	24	39
			8.9–10.6	303	17	11	25	47
			10.6–12.2	316	18	10	45	27
Z198	Nitrided	6.9	[2] 0	248	28	12	18	41
			0.2– .6	274	23	13	21	43
			2.2– 2.5	328	26	12	19	43
			2.5– 2.9	327	17	10	22	51
Z184	do	23	[2] 0	256	18	8	16	58
			1.3– 5.6	327	20	10	18	52

[1] Hydrocarbons include oxygenated molecules dissolved in liquid hydrocarbons.

[2] Products collected for 1st week of operation of fresh catalyst. Products from this period usually contain a greater fraction of gaseous hydrocarbons than products from subsequent weekly periods.

DISCUSSION OF RESULTS

Constant-productivity tests differ from constant-temperature tests, in that activation of the catalyst occurs in constant-productivity tests. These activations, which are presumably related to carbon deposition, usually occur above 290° C. In tests of activated steel turnings (catalyst L2201) the productivity decreased eventually to a low value, even though the temperature was increased to about 400° C. In tests of catalyst D3001, productivity could be maintained constant until the catalyst bed clogged. The behavior of these two types of catalysts in constant-productivity tests seems related, at least in part, to the results of constant-temperature tests; in these the activity of the turnings decreased steadily to zero, whereas for the fused catalyst the relative activity leveled out at a constant value in the range 0.03 to 0.10 for reduced and carbided catalysts and 0.1 to 0.2 for nitrided catalysts.

Sulfur poisoning of reduced and carbided catalysts in constant-productivity tests decreased the tendency of the catalyst to produce high-molecular-weight hydrocarbons and oxygenated organic molecules. In the long poisoning test of the carbided fused iron oxide catalyst, the average yield of C_4^+ decreased to less than 50 weight-percent of total hydrocarbons. For nitrided catalysts the yields of C_3^+ hydrocarbons remained nearly constant during poisoning; however, the C_4^+ fraction was only about 50 percent in tests with pure gas. In the poisoning of the nitrided catalyst in test Z184 over 56 days, the yield of oxyganated molecules in the distillation fractions remained high; in test Z198, of 102 days' duration, the yield of oxygenates decreased to low values in the latter part of the test. Analyses of the catalyst from Z198 revealed that the atom ratio of nitrogen to iron decreased from 0.45 to 0.03 during the test. X-ray diffraction lines for Hägg iron carbide, magnetite, and epsilon carbonitride were found in the nitrided catalysts used in constant-productivity poisoning tests. Possibly the shift in selectivity observed in test Z198 is related to conversion of part of the epsilon carbonitride to Hägg carbide.

CONCLUSIONS

For synthesis with gas containing 6.9 mg S/m^3, the lowest sulfur concentration that was reported for hot potassium carbonate scrubbing,[22] the following comments are made:

1. For the present catalysts operated at constant temperatures, or at increasing temperatures no higher than 290° C, catalyst life seems too short to be of practical interest.

2. For maximum temperatures of 350° to 400° C, lives of reduced, nitrided, or carbided D3001 at least approach those desired for practical synthesis processes. Because these tests are terminated by clogging, the length of time before the reactor becomes inoperable is probably strongly dependent on the configuration of the catalyst bed. Difficulties resulting from carbon deposition, particle disintegration, and other processes leading to clogging of the catalyst bed would probably become apparent earlier in life tests in large fixed-bed reactors than in the present laboratory units.

3. In constant-productivity operation the ability to control selectivity by adjusting temperature is lost. Gasoline production is not too seriously decreased by operation at higher temperatures. However, the yield of gaseous hydrocarbons increases substantially at the expense of fractions boiling above gasoline.

4. An increase in activity of the catalyst by a factor of 5 to 10, other characteristics in poisoning being the same, would probably permit practical operation in gas from the hot carbonate scrubber. Catalysts reported herein may be regarded as typical of robust iron catalysts in the form of lathe turnings or 6- to 8-mesh particles. Substantial increases in activity seem unlikely. A fivefold decrease in particle size will increase the activity about three times. However, the present catalysts represent about the smallest size that can be used conveniently in large fixed-bed reactors.

5. On the basis of the relatively short life of catalysts in tests with gas containing 6.9 mg S/m^3, and because of the possible operating difficulties and inferior selectivity, additional gas purification, such as by iron oxide boxes, following hot potassium carbonate scrubbing seems desirable. With this additional gas purification the content of H_2S could probably be decreased to less than 0.1 mg/m^3.

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[22] Third work cited in footnote 16.