

FIGURE 41.—Correlation of Activity of Cobalt-Thoria-Magnesia-Kieselguhr Catalysts With Volume of Chemisorbed Carbon Monoxide at -195°C .

All data per gram of unreduced catalyst.

types of iron catalysts the empirical equation⁸² satisfactorily fits the rate data,

$$-\log(1-x) = AS^{-1} \exp. (-E/RT), \quad (24)$$

where x , is the fraction of $\text{H}_2 + \text{CO}$ consumed, A is a constant, S is space velocity of $\text{H}_2 + \text{CO}$ feed, and E is the apparent activation energy, R is the gas constant, and T is the synthesis temperature, in degrees Kelvin. By assuming $E=19.0$ kcal./mole, the following equation for activity of the catalyst per cubic centimeter was derived

$$A_v = -1.241 \times 10^{-8} \times S \times 10^{130/T} \times \log_{10}(1-C), \quad (25)$$

where A_v is expressed as cubic centimeters (S. T. P.) of synthesis gas converted per cubic centimeter of catalyst per hour at 240°C . when the flow is varied to maintain a CO_2 -free con-

traction of 65 percent and C is CO_2 -free contraction observed. A corresponding activity per gram of iron, A_{Fe} , is obtained by dividing A_v by the weight of iron per cubic centimeter of catalyst.

In tests of iron catalysts described in this section the activity usually will be expressed per gram of iron, A_{Fe} , but in a few instances activity is also given per cubic centimeter of catalyst, A_v . Tabular data contain, in addition, average temperatures, flows, and conversions. The use of activities, A_{Fe} or A_v , permits simple comparison of the diverse data of a catalyst-evaluation program. Errors involved in computing activities are usually smaller than experimental uncertainties and reproducibility of tests. Frequently, activity data are present on a logarithmic scale so that relative changes can be easily discerned. Selectivity data cannot be corrected to a standard temperature, and considerations of selectivity must take into account the actual synthesis temperatures.

⁸² Anderson, R. B., Seligman, B., Shultz, J. F., Kelly, R. E., and Elliott, M. A., Fischer-Tropsch Synthesis. X. Some Important Variables of the Synthesis on Iron Catalysts: Ind. Eng. Chem., vol. 44, 1952, pp. 391-397.

CHEMICAL AND PHYSICAL NATURE OF CATALYSTS

METHOD OF PREPARATION

PRECIPITATED-IRON CATALYSTS

Iron catalysts for the Fischer-Tropsch synthesis can be prepared by a variety of methods and from several sources of iron. The mode of preparation and the iron source affect the activity of the catalyst in the synthesis. The methods of preparation have been described in a previous section, but their effect on the activity will be considered here.

The results of activity tests of several preparations of a precipitated catalyst with a composition of 100Fe : 10Cu : 0.5K₂CO₃ are summarized in table 42. These catalysts were all highly active, producing comparatively high yields of liquid and solid hydrocarbons and low fractions of methane. The reason for the comparatively low activity in test X-88 is not known. Test X-87 showed that pelleting caused a decrease in activity. Although granular and pelleted catalysts were strong in the raw state, both forms lost most of their mechanical strength in the pretreatment.

The observation had been made previously⁸³ that iron catalysts precipitated from ferric nitrate were active in the hydrocarbon synthesis, but those precipitated from ferric chloride were inactive. This observation by Fischer⁸⁴ and by Bureau of Mines investigators appeared to contradict the report that highly active ferrous-ferric catalysts were prepared from chlorides of iron by Pichler at Kaiser

Wilhelm Institut.⁸⁵ For example, in early Bureau of Mines tests a catalyst (10M) prepared from a solution of ferric nitrate and ferric chloride produced an average yield of C₅+ hydrocarbons of only 42 gm. per m.³ of 1H₂ : 1CO gas at 261° C. and 7.8 atmospheres. Even lower yields were obtained from catalysts precipitated from ferric chloride alone. These catalysts differed in appearance from those precipitated from ferric nitrate; and the difference was obvious, even during preparation. The precipitates from solutions containing chlorides were yellow-brown rather than red-brown; they were not voluminous; in the dry state they were less glossy.

To explain the anomalous results a series of catalysts prepared from solutions of chlorides was tested⁸⁶ at 7.8 atmospheres of 1H₂:1CO gas, as described in table 43. The catalysts were inducted in 1H₂:1CO gas at atmospheric pressure for 24 hours; the induction temperature was 225°-230° C. for preparations containing copper and 255°-260° C. for samples without copper.

Catalyst L3004 from ferrous and ferric chlorides was very active, as shown in table 43. As this catalyst was active despite the use of chloride salts in its preparation, tests were made to determine whether this activity was due to the presence of copper or ferrous iron. Tests were made with several preparations in which one or more of the constituents were omitted. The results show that these preparations from ferric chloride solution, like the earlier ones, were virtually inactive. Catalyst L3008 was prepared from ferrous chloride and,

⁸³ Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N., Synthetic Liquid Fuels From Hydrogenation of Carbon Monoxide, Part I: Bureau of Mines Tech. Paper 709, 1948, 213 pp.

⁸⁴ Fischer, F. and Tropsch, H. [The Hydrocarbon Synthesis. II]: Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 333-501.

⁸⁵ Pichler, H., Synthesis of Hydrocarbons From CO and H₂: Bureau of Mines Spec. Rept., June 1947, 159 pp.

⁸⁶ Hofer, L. J. E., Anderson, R. B., Peebles, W. C., and Stein, K. C., Chloride Poisoning of Iron-Copper Fischer-Tropsch Catalysts: Jour. Phys. and Colloid Chem., vol. 55, 1951, pp. 1201-1206.

TABLE 42.—*Synthesis tests of precipitated-iron catalysts, 100Fe : 10Cu : 0.5K₂CO₃*

6- to 8-mesh particles pretreated with 1H₂ : 1CO gas at atmospheric pressure and space velocity of about 100 hr.⁻¹ for 24 hr.; synthesis at 7.8 atm. of 1H₂ : 1CO gas

| Catalyst number | P3003.07 | P3003.03, P3003.042, P3003.05 | P3003.05 | Composite ¹ | P3003.07 | P3003.24 ² | P3003.24 ² |
|---|----------|-------------------------------------|----------|------------------------|----------|-----------------------|-----------------------|
| Color..... | Brown | Black | Black | Brown and black | Brown | Black | Black |
| Synthesis: | | | | | | | |
| Test number..... | X-82 | X-84 | X-86 | X-87 | X-88 | X-101 | X-149 |
| Duration, weeks..... | 7 | 10 | 9 | 10 | 9 | 6 | 6 |
| Space velocity..... hr. ⁻¹ | 118 | 100 | 92 | 134 | 127 | 132 | 100 |
| Average temperature..... ° C. | 231 | 236 | 236 | 250 | 255 | 232 | 221 |
| Contraction ³ percent | 72 | 74 | 69 | 71 | 68 | 64 | 65 |
| Activity, A..... | 126 | 94 | 75 | 71 | 52 | 110 | 128 |
| A _{Fe} | 155 | 148 | 138 | 79 | 59 | 121 | 136 |
| Products, gm./m. ³ feed gas: | | | | | | | |
| H ₂ O..... | 17 | 22 | 20 | 18 | 14 | 18 | 13 |
| CO ₂ | 404 | 351 | 410 | 447 | 349 | 311 | 358 |
| Hydrocarbons ⁴ | 135 | 131 | 146 | 122 | 108 | 123 | 122 |
| Distribution of products, weight-percent: | | | | | | | |
| CH ₄ | 7.9 | 10.8 | 14.0 | 11.5 | 8.4 | 5.1 | 4.3 |
| C ₂ | 5.9 | 6.4 | 9.6 | 11.2 | 7.0 | 4.4 | 3.9 |
| C ₃ +C ₄ | 15.6 | 15.3 | 12.8 | 12.3 | 16.4 | 9.3 | 7.0 |
| C ₅ + ⁴ | 70.6 | 67.5 | 63.6 | 65.0 | 68.2 | 81.2 | 84.8 |

¹ Pellets 3/8 by 1/16 inch.

² 6- to 14-mesh sample.

³ Apparent CO₂-free contraction.

⁴ Includes oxygenated molecules dissolved in oil phase.

TABLE 43.—*Synthesis tests of catalysts prepared from iron nitrate and chloride solutions*1H₂+1CO gas at 7.8 atm.; induction in 1H₂+1CO gas at atmospheric pressure for 24–25 hr.

| Catalyst number | 2001 | 2002 | 2003 | 3008 | 3008 | 3006 | 3004 | 3003.24 |
|--|------------------|---------|----------|------------------|------------------|----------|----------|---------|
| Catalyst composition: | | | | | | | | |
| Fe ²⁺ ----- | ¹ 100 | 0 | 0 | 100 | 100 | 0 | 75 | 0 |
| Fe ³⁺ ----- | 0 | 100 | 100 | 0 | 0 | 100 | 25 | 100 |
| Cu----- | 0 | 0 | 0 | 20 | 20 | 20 | 20 | 10 |
| K ₂ CO ₃ ----- | 0. 2 | 0. 2 | 0. 2 | 0. 2 | 0. 2 | 0. 2 | 0. 2 | 0. 5 |
| Source of iron----- | Nitrate | Nitrate | Chloride | Chloride | Chloride | Chloride | Chloride | Nitrate |
| Induction temp.-----° C----- | 260 | 260 | 260 | 224 | 225 | 227 | 226 | 230 |
| Synthesis temp.----- | 238 | 244 | 263 | ² 222 | ² 227 | 282 | 229 | 221 |
| Contraction-----percent ³ ----- | 64 | 63 | 28 | 65 | 66 | 37 | 66 | 65 |
| Space velocity-----hr. ⁻¹ ----- | 91 | 103 | 97 | 86 | 74 | 100 | 100 | 100 |
| Usage ratio, H ₂ :CO----- | 0. 74 | 0. 75 | 1. 44 | 0. 63 | 0. 68 | 1. 51 | 0. 65 | 0. 57 |
| Activity, A _{Fe} ----- | 100 | 69 | 15 | 243 | 181 | 11 | 159 | 131 |
| Products, gm./m. ³ : | | | | | | | | |
| CH ₄ ----- | 13 | 11 | 8 | 8 | ----- | 9 | 8 | 5 |
| C ₂ ----- | 11 | 9 | 3 | 5 | ----- | 13 | 7 | 5 |
| C ₃ +C ₄ ----- | 28 | 24 | 22 | 12 | ----- | 16 | 33 | 9 |
| Liquids+solids----- | 74 | 55 | 16 | 76 | 67 | 13 | 88 | 103 |

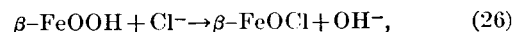
¹ Prepared by dissolving iron in dilute nitric acid at low temperatures.² These tests terminated after about 7 days owing to catalyst disintegration resulting in plugging of the reactor.³ CO₂-free apparent contraction.

after induction at 256° C. with water gas at 1 atmosphere for 25 hours, exhibited moderate activity in a 3-week test. This catalyst, however, disintegrated seriously in the reactor. It was evident that the presence or absence of ferrous iron was the significant factor that determined the activity of catalysts precipitated from chloride solutions. The explanation for this phenomenon was sought in X-ray studies and chemical analyses of these catalysts.

X-ray diffraction data (table 44) showed that the inactive catalysts prepared from ferric chloride contained a large proportion of β -Fe₂O₃·H₂O (or β -FeOOH) in the freshly precipitated, unreduced state; all of the catalysts prepared from ferric nitrate consisted chiefly of goethite, α -Fe₂O₃·H₂O (or α -FeOOH), and hematite, α -Fe₂O₃.⁸⁷ Catalysts precipitated from ferric and ferrous salts or only ferrous salts contained magnetite (Fe₃O₄). Because

these iron oxide phases usually are reduced or converted to carbides in the induction, the deactivating effect of precipitation from ferric chloride may result, not from the presence of β -Fe₂O₃·H₂O, but rather from some characteristic that this compound imparts to the final catalyst.

Data of Kolthoff and Moskovitz⁸⁸ indicated that chloride ion did not simply adsorb on β -Fe₂O₃·H₂O but instead exchanged slowly with the OH groups present both on the surface and in the interior of the crystallite, according to the equation,



and became a part of the crystal structure. A more descriptive formula was thus, $\beta\text{-FeO[OH, Cl]}$. This observation explained the difficulty in washing β -Fe₂O₃·H₂O free of

⁸⁷ Work cited in footnote 86, p. 74.⁸⁸ Kolthoff, I. M., and Moskovitz, B., The Constitution of Beta-Iron-Monohydrate: Jour. Am. Chem. Soc., vol. 58, 1936, pp. 777-779.TABLE 44.—*Physical properties and chemical analyses of precipitated-iron catalysts*

| State | | Catalyst | | | |
|------------|---|---|---|-------------------------------------|--|
| | | L2003 | L3006 | L3004 | L3008 |
| Raw----- | { Diffraction analysis----- | β -Fe ₂ O ₃ ·H ₂ O | β -Fe ₂ O ₃ ·H ₂ O | Fe ₃ O ₄ | Fe ₃ O ₄ |
| | { Chloride content-----percent----- | 0. 56 | 0. 92 | 0. 04 | 0. 02 |
| | { Potassium content-----do----- | . 12 | 1. 10 | . 07 | . 09 |
| Used----- | { Diffraction analysis----- | Fe ₃ O ₄ | Fe ₃ O ₄ : Cu | Fe ₃ O ₄ : Cu | Fe ₃ O ₄ : (h.c.p.) Fe ₂ C: Cu |
| Inducted-- | { Chloride content-----percent----- | ----- | 1. 08 | . 03 | ----- |
| | { Carbon content-----do----- | ----- | . 97 | 1. 85 | ----- |
| | { Surface area-----m. ² /gm----- | ----- | 21. 0 | 23. 8 | ----- |

¹ Sodium content was less than 0.001 percent.

chloride, as reported by Weiser and Milligan and also encountered in the preparation of Bureau of Mines catalysts precipitated from ferric chloride. Chemical analysis showed that the chloride content of the latter catalyst was at least 20 times greater than that of the more active catalysts that contained ferrous iron.

The explanation of the deactivating effect of chloride appears, therefore, to be the following:

1. In the presence of chloride and ferric ions alone, $\beta\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ was produced, which retained chloride in the crystal structure. During synthesis, the chloride ions poisoned the catalyst.

2. In the presence of chloride and ferrous and ferric ions (at least 35 percent Fe^{+2}) or chloride and ferrous ions alone, the $\beta\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ was not formed. Instead, magnetite (Fe_3O_4) was formed, and the chloride was easily removed from these precipitates by washing.

In contrast to its desirable effect as a support in cobalt catalysts, kieselguhr (or other supports) in precipitated-iron catalyst usually produces no major improvement in either activity or selectivity. German workers⁸⁹ reported some secondary advantages of utilizing small amounts of kieselguhr in iron catalysts, such as easier filtration in preparation and

⁸⁹ Work cited in footnote 81, p. 71.

TABLE 45.—*Effect of kieselguhr in precipitated-iron catalysts upon their activity and product distribution*

Pretreatment conditions: $1\text{H}_2 : 1\text{CO}$ gas at atmospheric pressure and space velocity of 100 hr.^{-1} at 230°C. for 24 hr.; synthesis at 7.8 atm. of $1\text{H}_2 : 1\text{CO}$ gas

| Catalyst number | P3003.24 | L6005 | L6006 | L6006.2 | German 234 ¹ |
|--|--|---|--|--|--|
| Composition gm./100 gm. Fe | 10Cu : 0.5K ₂ CO ₃ | 10Cu : 0.5K ₂ CO ₃ : 100KG (Filter-Cel) | 10Cu : 0.5K ₂ CO ₃ : 100KG (Hyflo-Super-Cel) | 10Cu : 2K ₂ CO ₃ : 100KG (Hyflo-Super-Cel) | 5.1Cu : 8.7CaO : 10.5K ₂ CO ₃ : 0.5Na ₂ O on KG |
| Test number | X-101 | X-122 | X-106 | X-239 | X-203 |
| Catalyst weight, gm. | 79.2 | 22.0 | 21.8 | 25.0 | 48.2 |
| Granules, mesh size | 6-8 | 7-10 | 7-10 | 6-8 | 6-8 |
| Weeks averaged | 5 | 5 | 5 | 5 | 5 |
| Temperature, °C. | 229 | 261 | 261 | 230 | 241 |
| Contraction, percent ² | 65 | 64 | 65 | 64 | 64 |
| Space velocity, hr. ⁻¹ | 133 | 100 | 102 | 100 | 100 |
| Activity: | | | | | |
| A_{Fe} | 141 | 191 | 209 | 503 | 153 |
| A_{p} | 135 | 30 | 34 | 92 | 60 |
| Hydrocarbon products, ³ weight-percent: | | | | | |
| C ₁ | 5.0 | 19.1 | 16.9 | 9.3 | 11.4 |
| C ₂ | 4.2 | 11.7 | 12.0 | 5.5 | 5.7 |
| C ₃ + C ₄ | 9.2 | 26.1 | 21.6 | 14.5 | 14.2 |
| C ₅ + | 81.6 | 43.1 | 49.5 | 70.7 | 68.7 |
| Distillation of liquids + solids, ³ weight-percent: | | | | | |
| < 185° C. | 2.6 | 65.8 | 34.8 | 22.0 | 21.5 |
| 185°-352° C. | 19.6 | 27.5 | 61.0 | 32.4 | 28.1 |
| 352°-464° C. | 17.5 | 3.8 | 3.9 | 16.5 | 16.9 |
| > 464° C. | 60.3 | 2.9 | .3 | 29.1 | 33.5 |
| Infrared analysis, weight-percent of functional group: | | | | | |
| < 185° C.: | | | | | |
| OH | 3.1 | .2 | .2 | 2.9 | 2.1 |
| CO + COOH | 1.7 | .0 | .4 | .8 | .6 |
| α -olefins (C=C) | 2.8 | .6 | .4 | 5.0 | 5.0 |
| Other olefins (C=C) | 1.0 | 5.8 | 6.4 | 2.6 | 2.9 |
| 185°-352° C.: | | | | | |
| OH | .7 | .0 | .0 | .5 | .1 |
| CO + COOH | 1.0 | .1 | .1 | .3 | .3 |
| α -olefins (C=C) | 1.9 | .0 | .0 | 1.3 | .9 |
| Other olefins (C=C) | 1.4 | 2.4 | 2.2 | 2.6 | 3.1 |

¹ Pretreatment of this catalyst was reduction in $3\text{H}_2 : 1\text{N}_2$ gas at 300°C. for 1 hour.

² CO₂-free apparent contraction.

³ "Hydrocarbons" includes oxygenated molecules dissolved in oil phase.

improved mechanical stability during synthesis.

Precipitated-iron catalysts supported on kieselguhr showed no lower activity per gram of iron than unsupported preparations; however, since the bulk density of supported catalysts was considerably lower, the activity per cubic centimeter, A_v , was lower than corresponding activities for unsupported catalysts. Data obtained in tests X-122 and X-106 with iron catalysts containing kieselguhr are compared in table 45 with those obtained from the corresponding unsupported catalyst P3003.24 ($100\text{Fe} : 10\text{CuO} : 0.5\text{K}_2\text{CO}_3$). Catalysts L6005 (test X-122) and L6006 (test X-106) contained the same constituents in the same proportions and, in addition, 100 parts, per weight of iron, of Filter-Cel and Hyflo-Super-Cel kieselguhr, respectively. In preparing these catalysts kieselguhr was added to the solution of metal nitrates immediately before the precipitant was introduced. Large yields of gaseous hydrocarbons and small oil yields were obtained with catalysts L6005 and L6006. Somewhat higher oil yields and slightly lower gas yields were produced by catalyst L6006. The products of these supported catalysts are typical of catalysts containing a very low content of alkali, and it was inferred that alkali was removed by reaction or adsorption on the kieselguhr. In removing alkali the natural Filter-Cel should be more effective than the flux-calcined Hyflo-Super-Cel, and the preparation containing the natural kieselguhr appeared more alkali deficient. On the assumption that the shift in product distribution resulted from removal of alkali by interaction with kieselguhr, catalyst L6006.2, containing 2 percent of added K_2CO_3 , was tested in test X-239. This addition improved the product distribution, but the oil fraction was still not as large as in test X-101 (catalyst without kieselguhr).

In the last column of table 45 test data for a sample of a Ruhrchemie catalyst (No. 234) are shown. This catalyst was precipitated on kieselguhr and, according to analysis by the Bureau of Mines laboratory, contained 5.1 parts Cu, 8.7 CaO, 10.5 K_2O , 0.5 Na_2O , and 15 kieselguhr (estimated from German data) per 100 parts of iron. This catalyst required a higher operating temperature than that in test X-239, but the selectivity was about the same.

FUSED-IRON CATALYSTS

The first tests of fused-iron catalysts in the current program were made on a series of 6- to 8-mesh American commercial ammonia-synthesis catalysts (table 46, part A). The activities were relatively low and decreased with time, as shown in figure 42. Three early Bureau of Mines preparations in tests X-129, X-148,

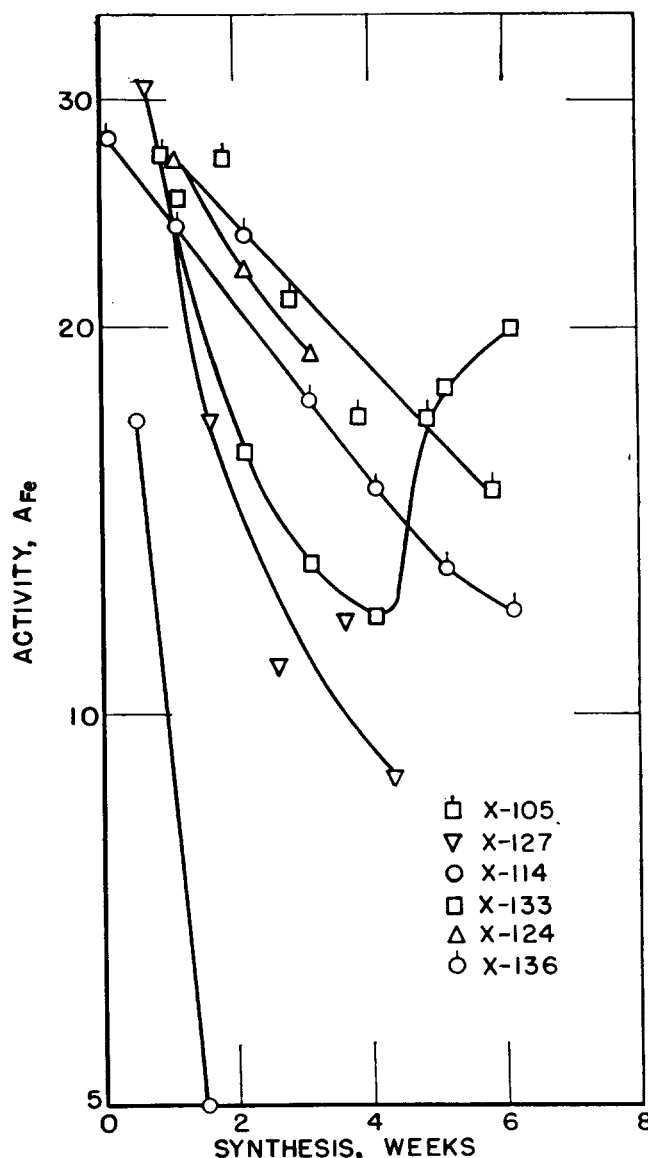


FIGURE 42.—Activity of Commercial Synthetic-Ammonia Catalysts in Fischer-Tropsch Synthesis With $1\text{H}_2 : 1\text{CO}$ Gas at 7.8 Atmospheres.

and X-171 had similar activities (table 46-part B). On the assumption that the low activity of catalyst D3004 (test X-114) was caused by the high alkali content, this catalyst was extracted with water to decrease the content of potassium oxide. The resulting catalyst (D3004.1 in test X-182) was more active than D3004. However, a similar extraction of catalyst D3001 with water caused a marked decrease in activity; the extracted catalyst D3004.1 in test X-195 was less active than D3001 in X-105.

In test X-113 a captured sample of German synol catalyst received as 20- to 50-mesh particles had high initial activity, and its activity increased with time. The factors leading to the high activity and the desirable

TABLE 46.—*Part A: Tests of American ammonia-synthesis catalysts*6- to 8-mesh particles reduced in dry H₂ at space velocity of 2,500–5,000 hr.⁻¹ and 450° C. for 40–50 hr.; synthesis with 1H₂:1CO gas at 7.8 atm. and space velocity of 100 hr.⁻¹

| Catalyst number..... | D3005 | D3007 | D3008 | D3004 | D3004.1 ¹ | D3006 | D3001 | D3001.1 ¹ |
|---|---------------------|-----------------------------|---------------------|---------------------|----------------------|--|--|--|
| Composition, gm./100 gm. Fe: | | | | | | | | |
| Al ₂ O ₃ | 4.0 | 4.1 | 2.8 | 3.7 | 3.6 | None | None | None |
| MgO..... | None | None | None | None | None | 6.9 | 6.9 | 6.7 |
| K ₂ O..... | 2.1 | 1.9 | 1.4 | 2.5 | 1.1 | 7 | 9 | 6 |
| Other..... | 0.2SiO ₂ | 2.8SiO ₂ -0.3CaO | 0.3SiO ₂ | 0.6SiO ₂ | 0.4SiO ₂ | 0.8Cr ₂ O ₃ -1.6SiO ₂ | 1.1Cr ₂ O ₃ -0.9SiO ₂ | 0.8Cr ₂ O ₃ -1.3SiO ₂ |
| Synthesis: | | | | | | | | |
| Test number..... | X-136 | X-133 | X-127 | X-114 | X-182 | X-124 | X-105 | X-195 |
| Weight loss on reduction, percent..... | 23.8 | 16.1 | 18.5 | 16.1 | 20.6 | 25.8 | 25.1 | 24.1 |
| Duration..... weeks..... | 5 | 5 | 4 | 1 | 6 | 2 | 4 | 5 |
| Average temperature..... °C..... | 262 | 265 | 271 | 298 | 263 | 252 | 256 | 277 |
| Contraction ² percent..... | 65 | 65 | 64 | 65 | 63 | 62 | 63 | 65 |
| Activity, A _{Fe} | 17 | 16 | 12 | 5 | 17 | 21 | 20 | 11 |
| Products, gm./m. ³ feed gas: | | | | | | | | |
| H ₂ O..... | 26 | 18 | 27 | 21 | 18 | 29 | 26 | 23 |
| CO ₂ | 329 | 383 | 347 | 304 | 307 | 333 | 324 | 326 |
| Hydrocarbons ³ | 116 | 123 | 115 | 100 | 97 | 113 | 119 | 120 |
| Distribution of products, weight-percent: | | | | | | | | |
| CH ₄ | 15.6 | 14.4 | 14.9 | 26.1 | 19.2 | 13.7 | 12.0 | 19.3 |
| C ₂ | 9.4 | 9.8 | 10.0 | 8.9 | 9.6 | 9.2 | 8.6 | 9.6 |
| C ₃ +C ₄ | 21.2 | 16.6 | 20.7 | 19.3 | 20.7 | 18.9 | 19.4 | 18.7 |
| C ₅ + ³ | 53.8 | 59.2 | 54.4 | 45.7 | 50.5 | 58.3 | 60.0 | 52.5 |

¹ Catalysts D3004 and D3001, respectively, extracted with water to decrease alkali content.² CO₂-free apparent contraction.³ Hydrocarbons include oxygenated molecules dissolved in the oil phase.TABLE 46.—*Part B: Comparison of synol and ammonia-synthesis catalysts*Catalyst reduced in dry H₂ at space velocity of 2,500–5,000 hr.⁻¹ at 450° C. for 40–50 hr.; synthesis with 1H₂:1CO gas at 7.8 atm. and space velocity of 86–100 hr.⁻¹

| Catalyst number..... | German synol | D3001 | L3011 ^{1,2} | A3212 ² | A3217 ² | A4900 ² |
|---|--------------|--|--|--------------------|--------------------|--------------------|
| Composition, gm./100 gm. Fe: | | | | | | |
| Al ₂ O ₃ | 4.9 | None | None | 8.0 | 5.2 | 4.1 |
| MgO..... | None | 6.8 | 3.2 | None | None | None |
| K ₂ O..... | 9 | 9 | 3 | 9 | 5 | 9 |
| Other..... | 2.9CaO | 0.96Cr ₂ O ₃ -1.05SiO ₂ | 0.7Cr ₂ O ₃ -0.7SiO ₂ | | | 2.3CaO |
| Particle size, mesh..... | 20–50 | 6–8 | 40–60 | 6–8 | 6–8 | 6–8 |
| Synthesis: | | | | | | |
| Test number..... | X-113 | X-105 | X-201 | X-208 | X-129 | X-148 |
| Weight loss or reduction, percent..... | 14.8 | 25.1 | 26.5 | 18.8 | 16.7 | 15.7 |
| Duration..... weeks..... | 8 | 4 | 7 | 4 | 3 | 4 |
| Average temperature..... °C..... | 219 | 256 | 227 | 247 | 281 | 266 |
| Contraction ³ percent..... | 66 | 63 | 65 | 65 | 66 | 64 |
| Activity, A _{Fe} | 76 | 20 | 57 | 30 | 9 | 14 |
| Products, gm./m. ³ feed gas: | | | | | | |
| H ₂ O..... | 18 | 26 | 23 | 29 | 22 | 18 |
| CO ₂ | 330 | 324 | 279 | 291 | 315 | 347 |
| Hydrocarbons ⁴ | 123 | 119 | 113 | 105 | 109 | 116 |
| Distribution of products, weight-percent: | | | | | | |
| CH ₄ | 6.0 | 12.0 | 7.1 | 12.3 | 16.1 | 16.6 |
| C ₂ | 4.9 | 8.6 | 5.8 | 6.5 | 8.0 | 10.4 |
| C ₃ +C ₄ | 10.5 | 19.4 | 14.0 | 19.4 | 21.8 | 18.7 |
| C ₅ + ⁴ | 78.6 | 60.0 | 73.1 | 61.8 | 54.1 | 54.3 |

¹ D3001 fused with 30-percent carbonyl iron.² Bureau of Mines preparations.³ Apparent CO₂-free contraction.⁴ Includes oxygenated molecules in oil phase.

operating characteristics of the synol catalysts were studied. Two major differences between conventional fused catalysts and the synol preparation were known: (a) Captured documents from Leuna^{90,91} indicated that the synol catalyst was made by remelting a conventional catalyst with carbonyl iron, and (2) the particle size of the synol catalyst was 20- to 50-mesh compared with 6- to 8-mesh samples in the original experiments. A test of 40- to 60-mesh particles of catalyst D3001 in test X-201 showed that activity varied approximately inversely

with average particle size, and the small particle size of the synol catalyst could account for most of its high activity. Catalyst L3011 was prepared by fusing finely pulverized unreduced catalyst D3001 with 30-percent carbonyl iron. This catalyst was significantly more active in test X-208 than D3001 in X-105. The effects of these two variables are compared in figure 43. Compared with other Fischer-Tropsch iron catalysts, the fine-mesh synol catalyst approximately equaled the precipitated- and alumina-cemented-iron catalysts in activity but considerably surpassed the 6- to 8-mesh commercial synthetic-ammonia catalysts.

The results of tests of fused catalysts other

⁹⁰ Reisinger, —, Report on the Synol Synthesis: TOM Reel 134, Rept. 283, May 2, 1941, 19 pp.

⁹¹ Wenzel, —, State of the Synol Problem: TOM Reel 134, Sec. II, No. 10, Rept. 326, Apr. 10, 1942, 33 pp.

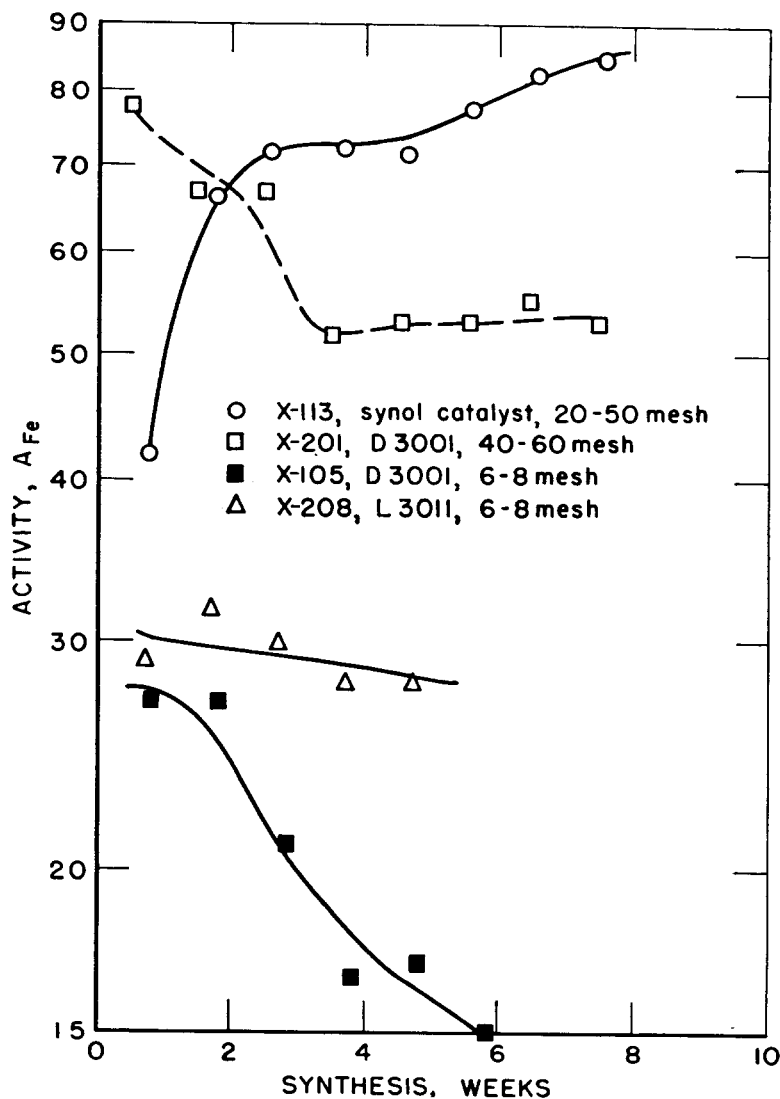


FIGURE 43.—Comparison of Activity of Synol and Other Fused Iron Oxide Catalysts in $1\text{H}_2 : 1\text{CO}$ Gas at 7.8 Atmospheres.

than the usual synthetic-ammonia type are presented in table 47. Catalyst P3003.232, prepared by fusing a precipitated $\text{Fe}_2\text{O}_3\text{-CuO-K}_2\text{CO}_3$ catalyst at $1,500^\circ\text{C}$., was somewhat more active in test X-132 than catalyst D3001 in test X-105. Pure fused magnetite, prepared by oxidizing and fusing electrolytic iron, was a poor catalyst, which did not show improved activity on addition of alkali (tests X-147 and X-158, respectively). Catalysts A3209 and A3208.1, in tests X-184 and X-197, respectively, which were prepared by the thermite process, had only moderate to low activity. Catalyst P2007 ($\text{Fe}_3\text{O}_4\text{-Al}_2\text{O}_3$) showed low activity in test X-222, but the activity was improved by alkali addition (test X-210). Catalyst L3012 was a reproduction of the Duftschmid catalyst, which had been reported to produce very low yields of methane. This catalyst,

tested at 21.4 atmospheres of $1\text{H}_2 : 1\text{CO}$ gas in test X-234, was somewhat more active than reference catalyst D3001 in test X200A; but the yields of methane and other products were not significantly different. Another fused preparation containing manganese and potassium, catalyst L3016 in test X-247, had low activity.

CEMENTED- AND SINTERED-IRON CATALYSTS

Methods for preparing catalysts in the form of mechanically stable granules by thermal treatment of various iron oxide powders, in some instances in the presence of bonding agents and in others without bonding agents, are given in the catalyst-preparation section. Preparations containing bonding agents are termed "cemented" catalysts and the others

TABLE 47.—*Synthesis tests of other fused-iron catalysts*6- to 8-mesh particles reduced in dry H₂ at space velocity of 1,000 hr.⁻¹; synthesis with 1H₂ : 1CO gas at 7.8 atm., except as indicated

| Catalyst number..... | P3003.232 ¹ | A1000 | A2100 | A3209 | A3208.1 | P2007 | A3207 | L3012 ^{2,3} | D3001 ³ | L3016 |
|---|------------------------|-------|-------|-----------------------|---------|-------|-------|---|--|------------------------------------|
| Composition, gm./100 gm. Fe: | | | | | | | | | | |
| K ₂ O..... | 0.18 | None | 0.50 | 1.1 | 0.8 | None | 0.5 | | 0.9 | 0.4 |
| Al ₂ O ₃ | | None | None | 22.4 | 17.5 | 4.7 | 4.5 | | | |
| Other..... | 9.1 Cu | None | None | 1.08 SiO ₂ | | | | 4.2 SiO ₂ 2.6 TiO ₂ 5 KMnO ₄ | 6.9 MgO 1.1 Cr ₂ O ₃ .9 SiO ₂ | 31. Mn ₂ O ₄ |
| Synthesis: | | | | | | | | | | |
| Test number..... | X-132 | X-147 | X-158 | X-184 | X-197 | X-222 | X-210 | X-234 | X-200A | X-247 |
| Reduction: | | | | | | | | | | |
| Temperature.....° C. | 450 | 375 | 400 | 450 | 550 | 450 | 450 | 500 | 450 | 450 |
| Time.....hours | 40 | 40 | 40 | 40 | 24 | 60 | 60 | 40 | 40 | 40 |
| Weight loss.....percent | 27.4 | 23.8 | 25.6 | 14.7 | 12.7 | 21.8 | 20.4 | 25.4 | 23.7 | 23.3 |
| Duration of synthesis.....weeks | 3 | 6 | 1 | 4 | 2 | 4 | 5 | 4 | 7 | 1 |
| Space velocity.....hr. ⁻¹ | 102 | 107 | 106 | 100 | 101 | 95 | 98 | 295 | 306 | 98 |
| Average temperature.....° C. | 250 | 285 | 306 | 278 | 288 | 272 | 254 | 247 | 258 | 274 |
| Contraction ⁴percent | 65 | 65 | 39 | 66 | 9 | 65 | 63 | 65 | 66 | 64 |
| Activity, A _{Fe} | 30 | 8 | 3 | 20 | 1 | 13 | 20 | 108 | 60 | 13 |
| Products, gm./m. ³ feed gas: | | | | | | | | | | |
| H ₂ O..... | 19 | 19 | 34 | 16 | 1 | 38 | 15 | 32 | 23 | 18 |
| CO ₂ | 300 | 329 | 180 | 321 | 23 | 280 | 306 | 277 | 327 | 308 |
| Hydrocarbons ⁵ | 114 | 113 | 75 | 105 | | 99 | 104 | 117 | 118 | 109 |
| Distribution of products, weight-percent: | | | | | | | | | | |
| CH ₄ | 9.0 | 21.7 | 23.6 | 24.5 | | 19.3 | 13.8 | 11.8 | 12.3 | 39.9 |
| C ₂ | 6.6 | 11.3 | 22.4 | 11.9 | | 11.1 | 7.5 | 9.7 | 8.2 | 10.2 |
| C ₃ +C ₄ | 19.4 | 22.5 | 9.9 | 25.7 | | 26.8 | 18.8 | 17.7 | 13.6 | 12.8 |
| C ₅ + ⁵ | 65.0 | 44.5 | 44.0 | 37.9 | | 42.8 | 59.9 | 60.8 | 65.9 | 37.1 |

¹ Fused precipitated catalyst, 7- to 16-mesh.² Duplicate of Duftscheidt catalyst.³ Synthesis pressure 21.4 atm.⁴ Apparent CO₂-free contraction.⁵ Includes oxygenated molecules dissolved in oil phase.

"sintered." Cemented catalysts will be discussed first.

The activity data for tests of catalysts cemented with alumina, A3218.087, A3213.24, and A3211 (tests X-196, X-131, and X-123), summarized in table 48, show that heating the mixture of constituents at 500° to 900° C. during preparation produced active catalysts. The catalyst was slightly less active when heated at only 150° C. (catalyst A3215 in X-138). The activity and productivity per unit volume of catalysts A3218.087, A3213.24, and A3211 were of the same order of magnitude as those of the best precipitated catalyst (for example, L3004 in test X-115) and the synol catalyst (test X-113). Like these catalysts, this cemented catalyst showed nearly constant activity during the entire test.

A catalyst bonded with sodium tetraborate (test X-165) was less active than alumina-bonded preparations but more active than fused catalyst D3001, as shown in figure 44. On the other hand, the material cemented with potassium tetraborate (test X-175) was relatively inactive. Granules cemented with alumina or borax were hard in the unreduced state but after reduction retained only about 10 percent of their mechanical strength. A small amount (about 3 percent) of sodium silicate produced a fair catalyst (test X-185), but its mechanical strength was low; when the amount of binding agent was increased, the resulting catalyst was inactive (test X-187). A catalyst bonded with potassium silicate in test X-146 had low activity.

In an attempt to avoid loss of mechanical strength during reduction the bonding agents were added to reduced magnetite ore; however, these preparations were poor with respect to both mechanical strength and activity.

Another form of starting material for preparing cemented-iron catalysts was magnetite glomerules prepared by sintering a powdered, highly concentrated magnetite ore into rough spheres and subsequently crushing them to the desired particle size. The glomerules were originally prepared to form sizable aggregates of finely divided iron oxide for use in conventional blast furnaces. Additional preparations were made in the Bruceton laboratory, as described in the catalyst-preparation section. All of the glomerules described in table 49 were made from Alan Wood magnetite and had essentially the same initial composition. Samples of glomerules crushed to 6- to 10-mesh particles were impregnated with solutions of bonding agents and/or alkali promoters. Testing data in table 49 demonstrate the influence of additives on activity and selectivity. Potassium oxide (as K₂CO₃) was effective in increasing activity and average molecular weight of the product. Alumina plus K₂CO₃ gave essentially the same results as K₂CO₃ alone. Catalysts bonded with borax were less active and produced lower molecular weight hydrocarbons. The addition of a small amount of K₂CO₃ did not improve the activity or selectivity of catalysts cemented with borax. A catalyst bonded with dextrin was less active than the similar preparation without this component. Table

TABLE 48.—*Synthesis with cemented catalysts prepared from Alan Wood magnetite*

| 6- to 8-mesh particles reduced in dry H ₂ at space velocity of 1,500-2,000 hr. ⁻¹ at 450° C. for 40-50 hr.; synthesis with 1H ₂ :1CO gas at 7.8 atmospheres and space velocity of 100 hr. ⁻¹ | | | | | | | | | | | | | | |
|--|-----------|----------|-------|-------|-------|---------|-------|-------|---------|--------------------|-----------------------|--------------------|--------------------|--------------------|
| Catalyst number | A3218.087 | A3213.24 | A3211 | A3215 | A3214 | L1002.2 | L1004 | A3310 | L1010.2 | L1016 ¹ | L1006.11 ¹ | L1017 ¹ | L2009 ¹ | L2012 ¹ |
| Composition, gm./100 gm. Fe: | | | | | | | | | | | | | | |
| Al ₂ O ₃ | | | | | | | | | | | | | | |
| K ₂ O | 3.0 | 5.9 | 3.7 | 3.6 | 2.6 | | | | | | | | | |
| Other | .39 | .76 | .79 | .86 | .75 | | | | | | | | | |
| Synthesis: | | | | | | | | | | | | | | |
| Test number | X-196 | X-131 | X-123 | X-138 | X-178 | X-165 | X-175 | X-146 | X-185 | X-187 | X-205 | X-199 | X-221 | X-231 |
| Weight loss on reduction, percent | 27.6 | 27.2 | 28.0 | 29.0 | 28.1 | 28.1 | 28.2 | 26.8 | 5 | 24.2 | 28.0 | 28.4 | 28.7 | 35.1 |
| Duration, weeks | 8 | 2 | 6 | 5 | 4 | 8 | 2 | 2 | 262 | 285 | 280 | 12 | 4 | 3 |
| Average temp., ° C | 228 | 233 | 233 | 242 | 253 | 249 | 283 | 297 | 64 | 59 | 64 | 63 | 61 | 236 |
| Contraction ³ , percent | 64 | 64 | 66 | 65 | 65 | 66 | 59 | 61 | 28 | 11 | 32 | 32 | 39 | 80 |
| Activity: A _{Fe} | 95 | 81 | 83 | 82 | 40 | 46 | 14 | 9 | 25 | 13 | 28 | 25 | 21 | 52 |
| Activity: A _{Fe} | 82 | 76 | 74 | 58 | 37 | 38 | 11 | 8 | 24 | 16 | 28 | 24 | 8 | 19 |
| Products, gm./m. ³ feed gas: | | | | | | | | | | | | | | |
| H ₂ O | 17 | 14 | 20 | 18 | 20 | 23 | 22 | 30 | 24 | 316 | 302 | 325 | 324 | 326 |
| CO | 229 | 342 | 369 | 353 | 323 | 286 | 314 | 278 | 334 | 98 | 107 | 118 | 102 | 96 |
| Hydrocarbons ⁴ | 87 | 121 | 127 | 124 | 121 | 107 | 95 | 94 | 116 | | | | | |
| Distribution of products, weight-percent: | | | | | | | | | | | | | | |
| CH ₄ | 8.0 | 6.6 | 12.9 | 8.6 | 10.3 | 14.4 | 21.3 | 27.6 | 13.8 | 34.5 | 21.0 | 21.0 | 9.3 | 10.0 |
| C ₂ | 4.9 | 6.4 | 8.8 | 7.6 | 7.0 | 7.8 | 10.8 | 12.7 | 9.7 | 9.6 | 11.8 | 16.8 | 7.1 | 8.0 |
| C ₃ +C ₄ | 10.4 | 13.8 | 20.4 | 18.5 | 14.7 | 19.2 | 11.2 | 21.8 | 20.1 | 18.0 | 24.9 | 18.2 | 13.6 | 19.7 |
| C ₅ + | 76.7 | 73.2 | 57.9 | 65.3 | 68.0 | 58.6 | 56.7 | 37.9 | 56.4 | 37.9 | 42.3 | 44.0 | 68.0 | 62.3 |

¹ Prepared asglomerules.² Reduced for 20 hr.³ Apparent CO₂-free contraction.⁴ Includes oxygenated molecules dissolved in oil phase.

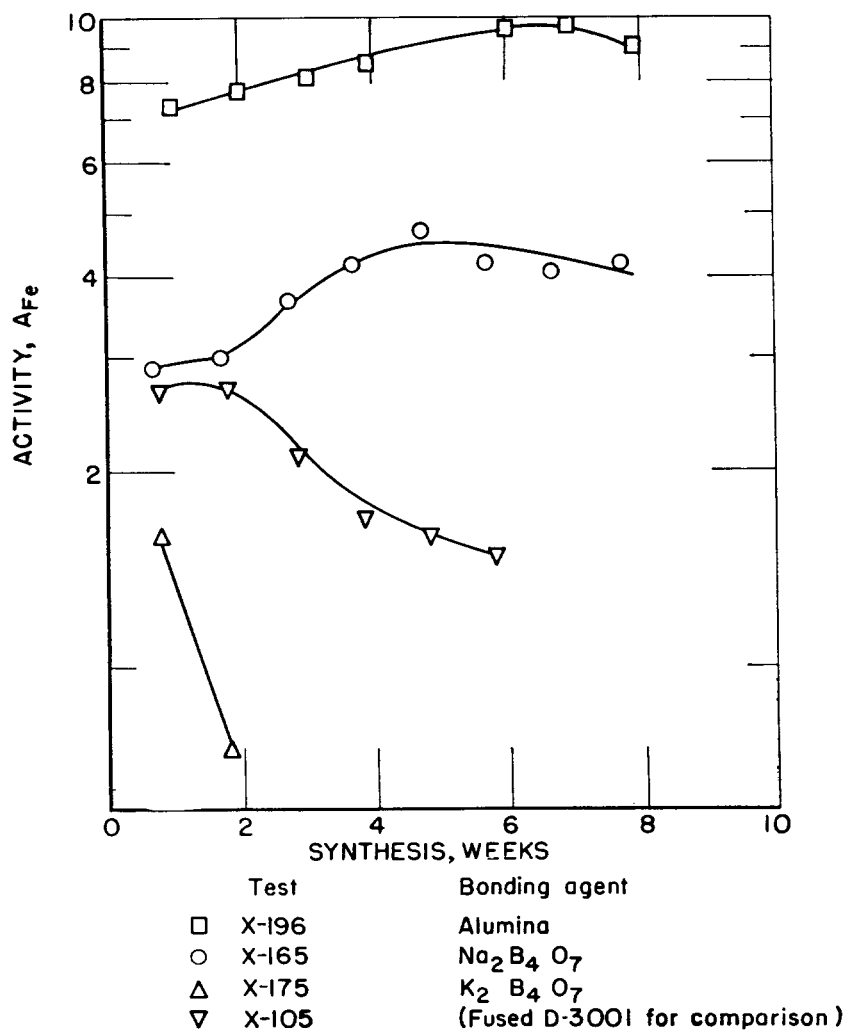


FIGURE 44.—Activities of Cemented Catalysts in Synthesis With $1\text{H}_2 : 1\text{CO}$ Gas at 7.8 Atmospheres.

49 also includes a test of catalyst P3003.2511, which was prepared by sintering a precipitated catalyst similar to P3003.24 at 600°C . This preparation was very inactive compared with similar unsintered preparations in table 42 (p. 74).

Life tests were made on two preparations bonded with borax. In test X-199 catalyst L1017 maintained a relatively constant activity at about 255°C . for 40 days. After 40 days it became necessary to increase the temperature steadily, whereupon the activity became constant again at 285° to 295°C . in the operating period from 60 to 80 days. After 50 days of testing the catalyst was removed for examination. It dropped freely from the reactor, and the particles apparently had not changed in size or in mechanical strength during this period. The catalyst was recharged into the reactor and the test continued to about 80 days. When the run was terminated, the

catalyst was caked in the reactor, although no excessive pressure drop through the catalyst bed had been observed. In test X-205, catalyst L1006.11, containing slightly more borax, required a temperature of 255° to 260°C . for 45 days; it was necessary to increase the temperature to 300°C . during the next 7 days. The test was terminated after several days at 300°C . The catalyst was badly disintegrated, presumably as a result of operation at this high temperature. Although the life of catalysts of this type might be extended appreciably by hydrogen treatment at elevated temperatures, when an increase in operating temperature becomes necessary, the present data indicate a life of 45 to 50 days for these catalysts.

To summarize the information in this section, sintered forms of iron oxide of relatively high purity when alkalinized with K_2CO_3 were very active in the synthesis but lacked mechanical strength after reduction. On this basis these

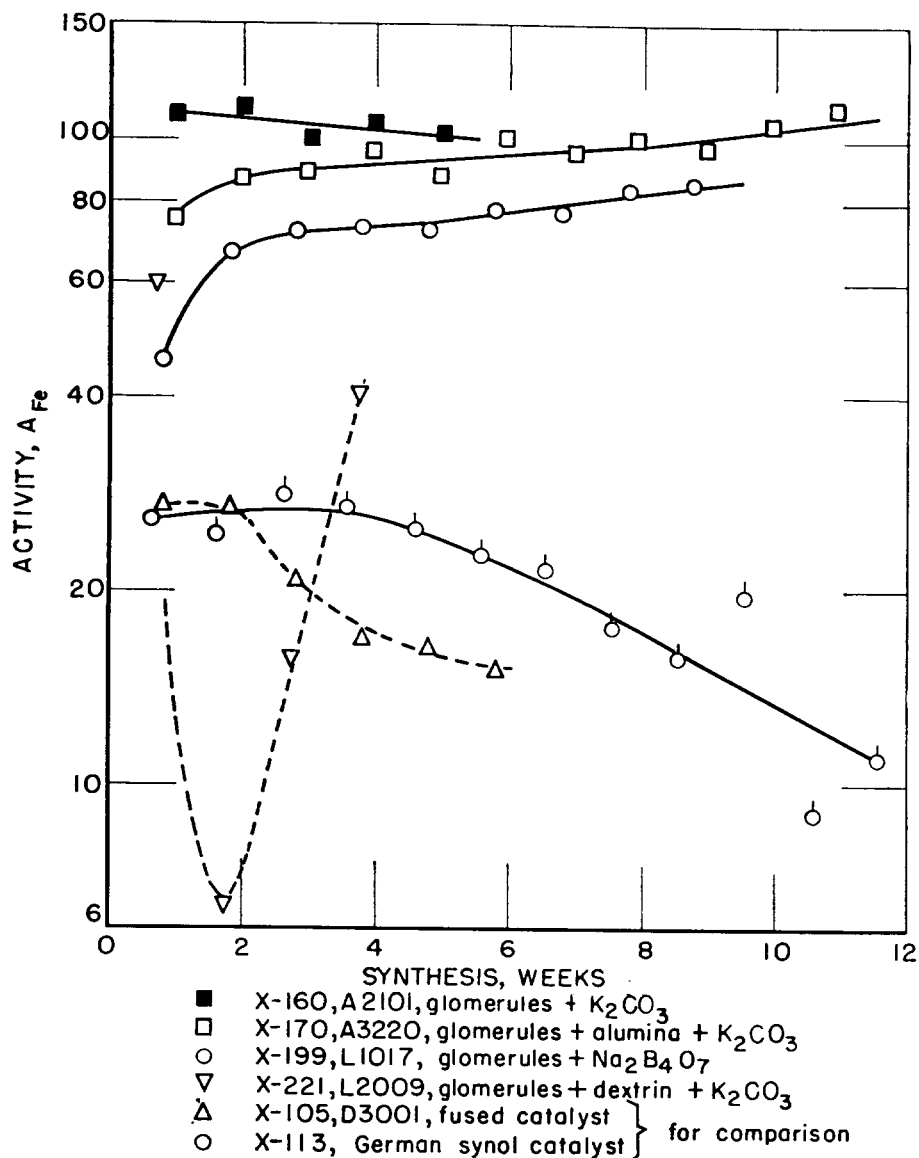


FIGURE 45.—Activities of Cemented-Magnetite Glomerules in Synthesis With $1H_2:1CO$ Gas at 7.8 Atmospheres.

catalysts may be suitable for use in slurry reactors, but not in fixed-bed or fluidized-bed systems. Some bonding agents such as alumina did not greatly influence activity or selectivity, but also did not greatly increase the mechanical strength after reduction. Other bonding agents, such as $K_2B_4O_7$, sodium waterglass, and dextrin, had an adverse effect on activity. Borax ($Na_2B_4O_7$) decreased the catalytic activity only moderately and gave moderately durable and long-lived catalysts; however, these preparations were at best only mediocre catalysts. Activity-time plots in figure 45 compare the sintered and cemented preparations with synthetic ammonia and synol catalysts.

CATALYSTS FROM COMMERCIALY AVAILABLE SOURCES OF IRON

A number of ores and byproducts containing iron were tested in the synthesis either in the form received with only alkali impregnation or after bonding plus alkali addition, as described in the previous section. The preparations shown in table 50 are listed in order of decreasing activity per gram of iron. Siderite ($FeCO_3$), catalyst L2104, was the most active of the group. Among the adequately active catalysts were the following:

1. Alkalized goethite ore ($\alpha-Fe_2O_3 \cdot H_2O$).
2. Alan Wood magnetite cemented with alumina and alkalyzed with potassium oxide, catalyst A3218.087.

TABLE 49.—*Synthesis tests of sintered- and cemented-iron catalysts*

| No. | Catalyst | | Synthesis data | | | | | | | | | | | | | |
|------------|-----------------------|--|----------------|-----------------------------------|------------|-------------|----------------------|----------------|-----------------|--|-----------------|--|-----------------|----------------|--------------------------------|-------------------------------|
| | Source of iron | Composition, gm./100 gm. Fe | Test No. | Weight loss on reduction, percent | Temp., °C. | Time, weeks | Contraction, percent | Activity | | Products, gm./m. ³ feed gas | | Distribution of hydrocarbons, weight-percent | | | | |
| | | | | | | | | A _r | A _{Fe} | H ₂ O | CO ₂ | Hydrocarbons ² | CH ₄ | C ₂ | C ₃ +C ₄ | C ₅ + ² |
| A1003 | Magnetite glomerules | 0.6K ₂ O | X-145 | 29.2 | 265 | 4 | 65 | 27 | 20 | 33 | 303 | 99 | 14.8 | 9.4 | 22.8 | 53.0 |
| A2101.1 | do. | 0.6K ₂ O-0.2Al ₂ O ₃ | X-160 | 29.5 | 220 | 11 | 64 | 132 | 98 | 16 | 332 | 126 | 6.0 | 4.6 | 10.9 | 78.5 |
| A3220 | do. | 0.6K ₂ O-0.2Al ₂ O ₃ | X-170 | 29.0 | 220 | 3 | 65 | 142 | 107 | 24 | 323 | 119 | 7.9 | 7.2 | 13.5 | 71.4 |
| A3811 | Reduced glomerules | 5N ₂ O ₂ B ₂ O ₃ | X-192 | 29.4 | 288 | 1 | 60 | 11 | 8 | 48 | 332 | 94 | 22.8 | 14.6 | 23.1 | 39.5 |
| P3003.2511 | Precipitated catalyst | 0.4K ₂ O-10Cu | X-112 | 29.4 | 300 | 1 | 18 | 2 | 2 | 0 | 59 | 26 | 6.0 | 4.2 | 13.9 | 2.3 |

¹ Apparent CO₂-free contraction.² Includes oxygenated molecules dissolved in oil phase.TABLE 50.—*Comparison of catalysts prepared from various iron materials commercially available*6- to 8-mesh particles reduced in dry H₂ at space velocity of 2,500 hr.⁻¹ at 400°-450° C. for 40 hr.; synthesis with 1H₂: 1CO gas at 7.8 atm.

| Catalyst | | Synthesis data | | | | | | | | | | | | | | | |
|-----------------------|--|---|-------------|--|---------------|----------------|---|-------------------------|----------------|-----------------|---|-----------------|---|-----------------|----------------|--------------------------------|------------------|
| No. | Source of iron | Composition gm./100 gm. Fe | Test No. | Weight loss on reduction, percent | Temp., °C. | Time, weeks | Space velocity, hr. ⁻¹ | Contraction, percent | Activity | | Products, gm./m. ³ feed gas | | Distribution of hydrocarbons, weight-percent | | | | |
| | | | | | | | | | A _r | A _{Fe} | H ₂ O | CO ₂ | Hydro- carbons | CH ₄ | C ₂ | C ₃ +C ₄ | C ₅ + |
| 2014 | Pa. Salt Co., siderite FeCO ₃ | 0.5K ₂ O | X-233 | 49.2 | 226 | 4 | 98 | 65.7 | 109 | 116 | 19.0 | 331.9 | 93.7 | 5.6 | 5.1 | 12.2 | 77.1 |
| 3210 | Pigment grade, Fe ₂ O ₃ | 4.5Al ₂ O ₃ -0.96K ₂ O | X-134 | 28.5 | 236 | 3 | 100 | 65.5 | 75 | 86 | 20.4 | 351.0 | 122.6 | 12.5 | 11.0 | 23.7 | 52.8 |
| 3003 ¹ | Mill scale | 3.5Al ₂ O ₃ -0.6K ₂ O | X-156 | 26.3 | 237 | 5 | 100 | 65.0 | 72 | 86 | 23.2 | 301.1 | 102.5 | 13.2 | 6.7 | 16.3 | 63.8 |
| 3218.087 ² | Alan Wood magnetite | 3.5Al ₂ O ₃ -0.54K ₂ O | X-196 | 27.6 | 228 | 8 | 101 | 64.3 | 95 | 82 | 17.4 | 229.0 | 86.8 | 8.0 | 4.9 | 10.4 | 76.7 |
| 2103 ³ | Goethite ore, α-Fe ₂ O ₃ ·H ₂ O | 0.5K ₂ O | X-181 | 35.6 | 230 | 4 | 100 | 65.5 | 60 | 75 | 37.4 | 238.4 | 102.3 | 8.3 | 7.8 | 17.1 | 66.8 |
| 2013 ¹ | Alabama ore | do. | X-232 | 32.8 | 256 | 3 | 99 | 66.5 | 38 | 39 | 46.4 | 234.3 | 126.5 | 10.0 | 6.2 | 17.6 | 66.2 |
| 3219 ² | U. S. Steel magnetite | do. | X-155 | 29.0 | 275 | 1 | 99 | 44.9 | 11 | 12 | 3.4 | 304.6 | 48.0 | 18.9 | 13.1 | 28.6 | 39.4 |
| 3312 ⁴ | St. Peter's sandstone | 62SiO ₂ -1K ₂ O | X-151 | 42.0 | 291 | 3 | 110 | 61.8 | 12 | 3 | 0 | 185.7 | 47.1 | 39.3 | 4.9 | 4.8 | 51.0 |
| 2104 ¹ | Wrought-iron drippings | 3SiO ₂ -1.6Al ₂ O ₃ -0.8K ₂ O | X-177 | 0.8 | 300 | 2 | 100 | 27.1 | 3 | 2 | 5.6 | 20.8 | 26.8 | 20.5 | 14.6 | 17.5 | 47.4 |
| 2300 ⁶ | Limonite ore | do. | X-202 | 36.2 | 284 | 1 | 93 | 9.3 | 1 | 2 | 2 | 300.1 | 57.3 | 34.4 | 19.9 | 32.3 | 13.4 |
| 2300 ⁶ | Commercial ferrosilicon | do. | X-117 | 11 | 331 | 1 | 99 | 48.4 | 2 | 2 | 17.3 | 300.1 | 57.3 | 34.4 | 19.9 | 32.3 | 13.4 |

¹ Reduction space velocity 1,500, 4- to 6-mesh.² Reduced 20 hours.³ Reduced 24 hours.⁴ Reduction space velocity, 4,000.⁵ Very small.⁶ No reduction; no pretreatment.

3. Pigment-grade iron oxide bonded with alumina and alkali.

4. Mill scale bonded with alumina and alkali.

Slightly less active, but of similar activity to the fused synthetic-ammonia-type catalysts, was a sample of Alabama iron ore impregnated with potassium carbonate. The following catalysts had low activity:

1. Magnetite (precipitated from iron sulfate solutions obtained in pickling processes) bonded with alumina and alkali.

2. St. Peter's sandstone, which contains only a small percentage of iron.

3. Alumina-cemented, alkaliized limonite ore, which had a high sulfur content (total S=1.2 percent).

4. Alkaliized wrought-iron drippings obtained from a process for making wrought iron; the extent of reduction was low, which may be ascribed to the high silica content (30 percent) of this material.

5. Commercial ferrosilicon, containing 47.3 percent silicon.

The following conclusion may be drawn:

1. Inexpensive iron ores or oxides may be used to prepare active Fischer-Tropsch catalysts.

2. These raw materials should not contain catalyst poisons, such as sulfur, or high concentrations of silica or other oxides that make reduction to iron difficult at temperatures below 550° or 600° C.

3. The active catalysts prepared from the inexpensive iron powders described above were usually not resistant to mechanical disintegration.

EFFECT OF ALKALI CONTENT

Of the promoters normally used in iron catalysts, alkali has the greatest effect on activity and product distribution. Earlier results concerning this effect, as reported in the literature, were frequently contradictory. For example, Fischer reported a maximum activity for catalysts containing 0.3 percent alkali, whereas Pichler stated that the activity of carefully induced catalysts was independent of alkali content. To clarify the picture, a study was made of cemented-, fused-, and precipitated-iron catalysts containing different amounts of potassium oxide; this study resulted in the data shown in table 51 and in figure 46. The data fall into

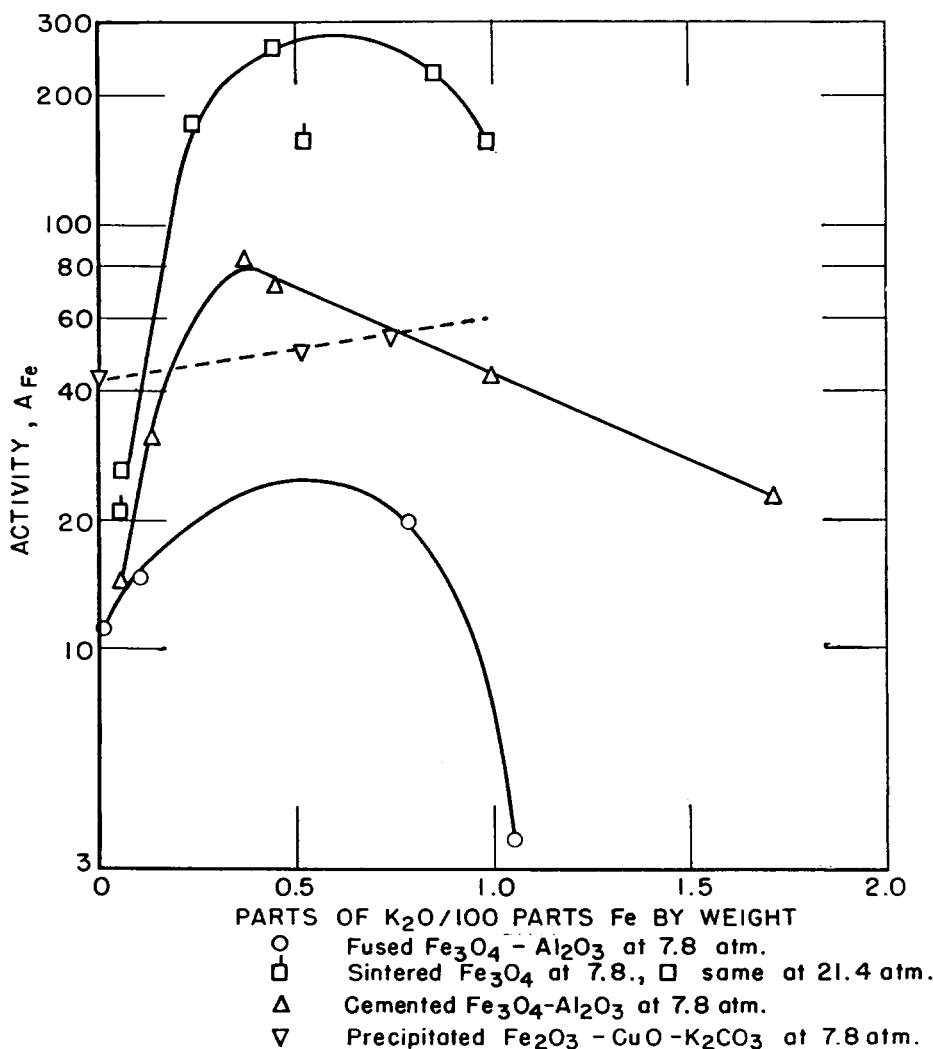


FIGURE 46.—Variation of Activity of Iron Catalysts With Alkali Content, Using $1H_2 : 1CO$ Gas.

two classes: (1) For cemented and fused catalysts the activity increased sharply to a maximum at about 0.4 part of K_2O to 100Fe (by weight); and (2) for precipitated catalysts the activity increased only gradually with alkali content. For all catalysts the rate of deposition of carbon in the catalysts increased with alkali content, as shown in table 51. The average molecular weight and the fraction of oxygenated molecules in the hydrocarbon fractions increased with increasing alkali content, at least to the concentration corresponding to the highest activity. The usage ratio, $H_2 : CO$, decreased with increasing alkali content in the range 0 to 0.8 K_2O per 100 Fe.

Synthetic-ammonia-type catalyst D3001 was

impregnated with potassium carbonate to increase its alkali content from 0.85 to 1.68 K_2O : 100Fe. This catalyst (L6011), after being nitrided to the ϵ -phase ($N : Fe = 0.48$), operated at 237° C. in the synthesis (test X-248). Figure 47 compares the activity of this catalyst with reduced and nitrided catalyst containing 0.85 K_2O : 100Fe (test X-214A), reduced and nitrided catalyst containing no alkali (test X-227), and reduced (unnitrided) catalyst containing no alkali (test X-222). These results, summarized in table 52, indicate that alkali is necessary for high activity of nitrided as well as reduced catalysts, but that large amounts of alkali are deleterious to the activity of the catalyst.

TABLE 51.—*Effect of alkali content on activity and selectivity of iron catalysts*

$1H_2 : 1CO$ gas

| Catalyst composition | $Fe_3O_4-K_2CO_3$ | | | | | $Fe_2O_3-CuO-K_2CO_3$ | | |
|--|--------------------|-------|-------|-------|-------|-----------------------|-------|------|
| Catalyst number | A2106 ¹ | | | | | P3003 ² | | |
| Test number | X-261 | X-322 | X-228 | X-288 | X-237 | X-130 | X-224 | 211 |
| Alkali content, K_2O : 100Fe | 0.06 | 0.23 | 0.45 | 0.85 | 0.94 | 0 | 0.52 | 0.76 |
| Testing data: | | | | | | | | |
| Temperature, °C | 228 | 229 | 226 | 227 | 228 | 265 | 261 | 254 |
| Space velocity ³ | 28 | 257 | 352 | 342 | 245 | 110 | 112 | 100 |
| Average activity, A_{Fe} ⁴ | 26 | 174 | 252 | 217 | 167 | 38.6 | 52.2 | 59.7 |
| Average usage ratio, $H_2 : CO$ | 1.40 | .74 | .74 | .67 | .67 | .89 | .68 | .62 |
| Atom ratio, C : Fe, in used catalyst ⁵ | .109 | | .393 | .455 | .418 | .049 | .237 | .289 |
| Composition of product: | | | | | | | | |
| Hydrocarbons, ⁶ weight-percent: | | | | | | | | |
| C_1 | 11.7 | 7.5 | 6.6 | 6.4 | 6.7 | 19.7 | 14.9 | 13.2 |
| C_2 | 8.4 | 6.9 | 6.4 | 6.9 | 5.1 | 12.2 | 16.0 | 7.6 |
| $C_3 + C_4$ | 30.3 | 15.7 | 14.6 | 15.7 | 10.9 | 32.7 | 27.6 | 19.0 |
| Liquids+solids | 49.6 | 69.9 | 72.4 | 71.0 | 76.3 | 35.4 | 41.5 | 60.2 |
| Acid number ⁷ | 5.1 | 4.4 | 3.1 | 10.4 | 12.2 | .3 | .7 | .9 |
| Distillation of liquids+solids, weight-percent: | | | | | | | | |
| <185° C. | 16.5 | 37.2 | 32.1 | 30.0 | 33.4 | 57.2 | 50.9 | 38.6 |
| 185°-352° C. | 42.0 | 23.0 | 33.8 | 30.3 | 30.1 | 36.6 | 32.2 | 35.2 |
| 352°-464° C. | 19.9 | 14.9 | 11.1 | 11.8 | 11.7 | 5.4 | 11.5 | 13.1 |
| >464° C. | 21.6 | 24.4 | 23.0 | 27.9 | 24.8 | .8 | 5.4 | 13.1 |
| Infrared analyses, weight-percent of functional group: | | | | | | | | |
| <185° C.: | | | | | | | | |
| CO+COOH | .9 | 2.4 | 4.0 | 3.0 | 4.1 | .6 | .7 | 1.3 |
| COO | .3 | .8 | 1.3 | 1.7 | 2.7 | .1 | .2 | .4 |
| OH | 3.5 | 5.5 | 7.5 | 5.4 | 6.3 | .2 | .6 | 1.9 |
| α -olefins ($C=C$) | 6.7 | 8.6 | 6.2 | 7.7 | 6.5 | .5 | .7 | 1.7 |
| Other olefins ($C=C$) | .5 | .7 | 0 | 0 | 0 | 7.5 | 6.1 | 7.2 |
| Bromine number | 48 | 62 | 41 | 51 | 43 | 53 | 45 | 59 |
| 185°-352° C.: | | | | | | | | |
| CO+COOH | .7 | 1.2 | 1.7 | 1.4 | 1.8 | .4 | .3 | .4 |
| COO | .7 | .7 | 2.8 | 3.9 | 4.1 | .1 | .1 | .3 |
| OH | 1.1 | 1.3 | 2.2 | 1.1 | 1.0 | 0 | .1 | .7 |
| α -olefins ($C=C$) | 2.5 | 5.0 | 4.2 | 4.6 | 4.1 | 0 | 0 | .2 |
| Other olefins ($C=C$) | 1.2 | .7 | .5 | .2 | .3 | 2.5 | 1.9 | 3.8 |
| Bromine number | 25 | 38 | 28 | 32 | 30 | 17 | 13 | 27 |

¹ 6- to 8-mesh granules.

² 6- to 10-mesh granules.

³ Volumes of synthesis gas (STP) per volume of catalyst space per hour.

⁴ Average activity, weeks 1 to 5.

⁵ Total carbon : iron ratios. Length of tests was as follows: X322, 4 weeks; X261, X228, X288, X224, and X211, 5 weeks; and X237 and X130, 7 weeks.

⁶ Total hydrocarbons and liquids+solids include oxygenated compounds dissolved in the hydrocarbon phases.

⁷ Acid number of liquids+solids.

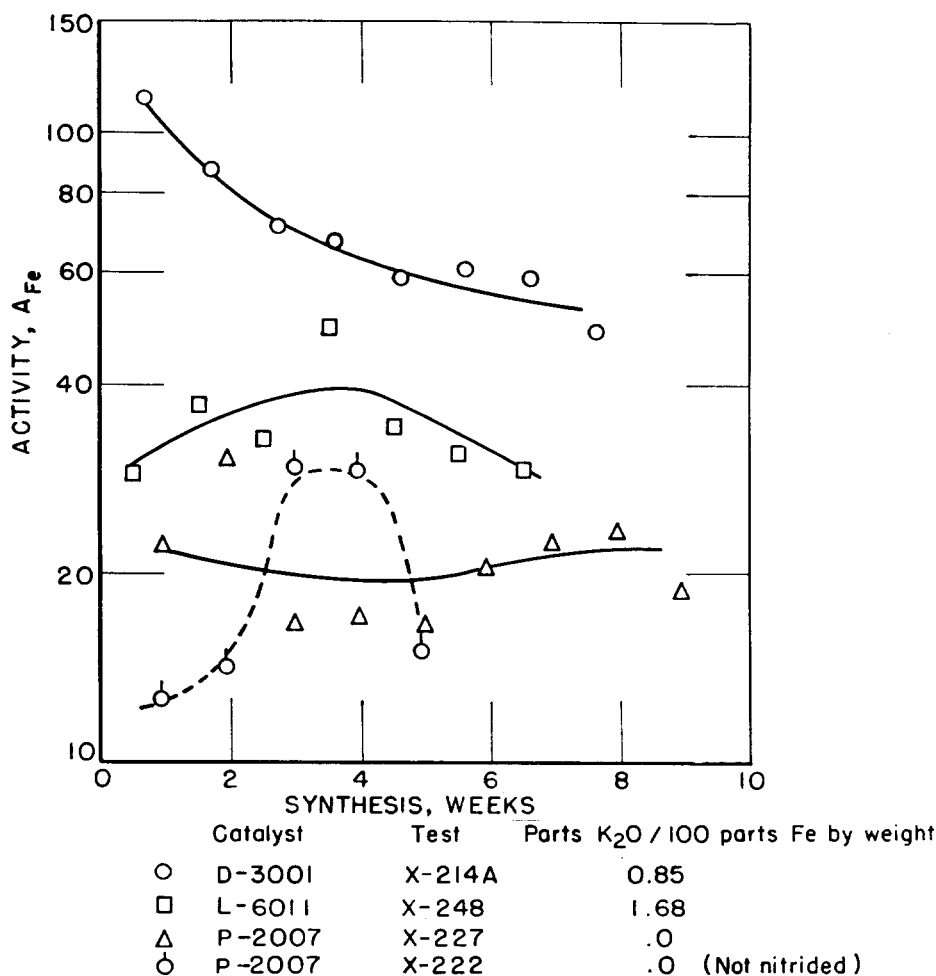


FIGURE 47.—Activity of Nitrided Fused Iron Oxide Catalysts as a Function of Alkali Content.

PARTICLE SIZE AND PELLETING

The effect of size of the catalyst particles on activity was illustrated by use of synthetic-ammonia-type catalyst D3001 of various particle sizes in the synthesis (100 p. s. i. g., 1H₂:1CO gas at a space velocity of 100 per hour).⁹² The temperature of the synthesis was adjusted to maintain an apparent contraction of 63 to 65 percent. The results of these tests are shown in table 53. As the particle size increased, the activity increased. The activity increased linearly with external (geometric) area to a particle size of 14- to 18-mesh. This result is of practical importance, because by using a catalyst of smaller particle size (1) the catalyst can be operated at a higher space-time-yield at the same temperature, or (2) the same space-time-yield may be obtained at a lower temperature with a lower production of light hydrocarbons and greater catalyst stability. These large variations of activity with particle size are not observed in many catalytic systems,

⁹² Work cited in footnote 82, p. 73.

especially those in which both products and reactants are gaseous. For example, data of Emmett⁹³ show that the rate of ammonia decomposition on fused-iron catalysts similar to the one used in these experiments is independent of particle size. In the Fischer-Tropsch synthesis, however, the catalyst pores are probably completely filled with hydrocarbons that are liquid at synthesis temperature, and this may account for the large dependence of rate on particle size. The product distribution (table 53) is probably not a function of particle size of the catalyst, except as it is affected by the operating temperature.

Although the following is an oversimplified picture, the assumptions will make possible the calculation of useful information: Assuming that (1) the catalyst particles were spheres and (2) a shell of constant thickness, Δr , is the portion of catalyst active in the synthesis, and (3) the activity per unit volume in this shell is constant, the following equation may

⁹³ Emmett, P. H., Twelfth Report of the Committee on Catalysis John Wiley & Sons, New York, N. Y., 1940, p. 64.

TABLE 52.—*Effect of alkali content on activity of nitriled synthetic-ammonia-type catalyst*
6- to 8-mesh; synthesis at 100 atmospheres of H_2 ; CO gas

| Test No. | Catalyst | Alkali content, K ₂ O : 100Fe | Pretreatment data | | | | | | | Initial iron phases | Testing data | | | Activity | | Selectivity, (weight-percent total hydrocarbons) | | | | | | | |
|----------|----------|--|-------------------|-------|------------------|-----------|-------------|-------|------------------|----------------------------------|------------------|-------------|----------------------|----------------|-----------------|--|----------------|--------------------------------|-------|---------|---------|------|------|
| | | | Reduction | | | Nitriling | | | | | SVH ¹ | Temp., ° C. | Contraction, percent | A _s | A _{Fe} | C ₁ | C ₂ | C ₃ +C ₄ | <185 | 185-352 | 352-404 | >404 | |
| | | | Temp., ° C. | Hours | SVH ¹ | Per-cent | Temp., ° C. | Hours | SVH ¹ | | | | | | | | | | | | | | N:Fe |
| N-222 | P2007 | 0.0 | 450 | 60 | 1,000 | 84 | | | | α-Fe ₂ N ₃ | 95 | 272 | 65 | 20 | 12 | 20.9 | 11.9 | 28.9 | 238.3 | | | | |
| N-227 | do | 0 | 450 | 40 | 1,000 | 91 | 350 | 12 | 1,000 | α-Fe ₂ N ₃ | 98 | 258 | 63 | 32 | 19 | 31.3 | 16.1 | 35.2 | 10.1 | 6.3 | 0.7 | 0.3 | |
| N-214A | D3001 | .85 | 450 | 40 | 2,500 | 100 | 385 | 4 | 5,000 | γ-Fe ₃ N | 98 | 225 | 64 | 105 | 62 | 20.5 | 10.3 | 25.3 | 25.6 | 14.7 | 3.0 | .6 | |
| N-248 | L6011 | 1.68 | 550 | 20 | 1,000 | 98 | 350 | 6 | 1,000 | ε-Fe ₂ N | 102 | 237 | 65 | 73 | 36 | 18.4 | 10.9 | 24.9 | 27.6 | 15.3 | 2.7 | .2 | |

¹ SVH = volumes of feed gas per volume of catalyst per hour.
: Total liquids + solids. Sample not separated.

TABLE 53.—*Effect of particle size on activity and selectivity of fused catalyst D3001*H₂ : CO gas at 7.8 atmospheres

| Test number | X-201 | X-118 | X-121 | X-105 | X-152 | X-212 |
|--|-------|-------|-------|-------|-------|-------|
| Mesh size | 40-60 | 14-18 | 14-18 | 6-8 | 6-8 | 4-6 |
| Testing data: ¹ | | | | | | |
| Average temperature °C | 226 | 238 | 238 | 253 | 260 | 255 |
| Space velocity ² | 99 | 99 | 97 | 100 | 97 | 98 |
| Average activity A_{Fe} ³ | 61.8 | 38.5 | 39.7 | 20.6 | 16.9 | 19.3 |
| Average usage ratio, H ₂ : CO | .78 | .79 | .71 | .79 | .72 | .76 |
| Composition of product: | | | | | | |
| Hydrocarbons, weight-percent: ⁴ | | | | | | |
| C ₁ | 5.0 | 10.2 | 10.2 | 11.2 | 13.2 | 14.6 |
| C ₂ | 4.5 | 7.4 | 7.7 | 8.0 | 8.8 | 9.7 |
| C ₃ +C ₄ | 13.6 | 15.3 | 17.1 | 19.4 | 20.6 | 15.9 |
| C ₁ -C ₄ | 23.1 | 33.0 | 35.0 | 38.6 | 42.6 | 40.2 |
| Liquids+solids ⁴ | 76.9 | 67.0 | 65.0 | 61.4 | 57.4 | 59.8 |
| Acid number ⁵ | 2.1 | 1.1 | | | .8 | .4 |
| Distillation of liquids+solids, weight-percent: | | | | | | |
| >185 °C | 16.5 | 26.6 | | | 36.5 | 48.3 |
| 185°-352 °C | 25.3 | 35.5 | | | 36.5 | 34.4 |
| 352°-464 °C | 16.6 | 17.2 | | | 15.3 | 10.4 |
| <464 °C | 41.6 | 20.7 | | | 11.7 | 6.9 |
| Infrared analyses, weight-percent of functional group: | | | | | | |
| <185 °C | | | | | | |
| CO+COOH | 1.1 | .7 | | | .6 | .5 |
| COO | .2 | .2 | | | .1 | .1 |
| OH | 2.1 | .5 | | | .2 | .2 |
| α -olefins (C=C) | 7.4 | 5.4 | | | 4.9 | 4.2 |
| Other olefins (C=C) | 1.6 | 3.5 | | | 5.1 | 5.6 |
| Bromine number | 60 | 59 | | | 66 | 65 |
| 185°-352 °C | | | | | | |
| CO+COOH | .4 | .3 | | | .3 | .3 |
| COO | .3 | .1 | | | .1 | .1 |
| OH | .7 | .0 | | | .0 | .0 |
| α -olefins (C=C) | 3.4 | .21 | | | 1.1 | 1.1 |
| Other olefins (C=C) | 1.9 | 3.4 | | | 3.9 | 3.7 |
| Bromine number | 35 | 24 | | | 33 | 32 |

¹ Catalysts reduced in hydrogen at space velocity of 2,500 hr.⁻¹ and 450° C. for 40 hr.² Volumes of synthesis gas (STP) per volume of catalyst space per hour.³ Average activity of the first 5 weeks.⁴ Total hydrocarbons and liquids+solids include oxygenated compounds dissolved in hydrocarbon phases.⁵ Acid number of liquids+solid "hydrocarbons".

be used to compute the thickness of the active layer, Δr :

$$A_{Fe} = k(\Delta r/r)(3 - 3\Delta r/r + \Delta r^2/r^2); \quad (27)$$

where A_{Fe} is the activity per gram of iron, k a constant, and r the particle radius. Activities predicted by this equation agree satisfactorily with observed values when an active catalyst thickness of about 0.1 mm. is assumed. Thus, only a thin layer of active material at the catalyst surface is required. Preparative methods for iron catalysts should be designed to produce as large an external area as possible within the limits imposed by the requirements for mechanical strength, pressure drop, etc., in practical equipment. These results led to studies of catalysts with inert oxide or metal cores covered by only thin layers of active material, for example, partly oxidized and reduced lathe turnings and partly reduced fused catalysts. These catalysts have excellent

mechanical stability in synthesis. These results will be described in a subsequent bulletin, when studies in progress are completely appraised.

In tests X-75 and X-81, precipitated-iron catalyst LH3001.0 (100Fe : 10Cu : 0.5K₂CO₃), in granular and pelleted forms, respectively, was tested. The granular catalyst had an activity (A_{Fe}), of 135, while the activity of the pelleted catalyst was 109. The yield of liquid plus solid hydrocarbons was lower for the pelleted catalysts.

PRETREATMENT OF IRON CATALYSTS

Methods of pretreating in many instances produce as wide changes in activity and selectivity as do catalyst type and composition. The literature on pretreatment appears quite confusing; however, when these data are considered in the light of chemical and structural changes that occur, the problem becomes less complicated. Precipitated catalysts as prepared have a high-area, gel-type structure

similar to that of silica gel, but on treatment with reducing gases the surface area decreases sharply. When the pretreatment temperatures are less than about 325° C., moderately high ($\sim 10 \text{ m.}^2/\text{gm.}$) areas are retained. Pretreatment at higher temperatures will lead to considerably lower areas, and in the presence of gases containing carbon monoxide excessive elemental carbon deposition will occur. Data demonstrating some of these statements are given in tables 27 to 29 of a previous section (pp. 43 and 44).

Fused iron oxide catalysts, on the other hand, have virtually no internal area in the raw state. The area and pore volume are generated by removal of oxygen during reduction. In general, the external dimensions of the catalyst particle remain unchanged, and the pore volume equals the volume change in the transition from magnetite to iron. The surface area of the reduced catalyst decreases with increasing reduction temperature. These statements are illustrated by data in table 26.

Fused catalysts usually require reduction in hydrogen before synthesis or further pretreatment, whereas raw precipitated catalysts can be used directly in synthesis or pretreated with gases containing carbon monoxide at 230° to 250° C. Other iron oxide catalysts, such as ores, usually require reduction in hydrogen before use; however, some preparations contain active enough forms of iron oxide to permit pretreatment in synthesis gas at moderate temperatures.

FUSED-IRON CATALYSTS

Reduction Procedures

The rate of reduction of fused catalysts increases with temperature. The presence of oxides of carbon and water vapor decreases the rate. Since water vapor is produced in the process, the rate increases to a maximum constant value as the flow of hydrogen is increased. On this basis, pure hydrogen at a high space velocity (1,000–5,000 hr.^{-1}) is usually employed. The rate decreases with extent of reduction. The process can be approximated by a first order type equation with the rate proportional to the fraction of oxide remaining. However, a considerably better rate equation was developed on the following premises:

1. The reduction process ($\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$) proceeds uniformly inward from the external surface.
2. The rate is proportional to the area of the interface of the metal-oxide contact.
3. The particles can be regarded as spheres (see p. 46).

For commercial application it is important to know the requirements for purity of hydrogen. The effect on the catalyst activity of reducing fused-iron catalyst D3001 in hydrogen containing small amounts of carbon monoxide is shown in table 54. It is evident that the presence of carbon monoxide was not deleterious to the activity of the catalyst in the hydrocarbon synthesis. However, a reducing gas containing carbon monoxide did yield catalysts that were reduced to a lesser extent than those reduced in pure hydrogen. Most of the carbon monoxide

TABLE 54.—*Influence of carbon monoxide or water in hydrogen used for reduction*Synthesis with $1\text{H}_2 : 1\text{CO}$ gas at 7.8 atmospheres on fused catalyst D3001

| Test number | X-105 | X-152 | X-144 | X-162 | X-139 | X-126 | X-173 | X-174 |
|---|-------|-------|-------|-------|-------|-------|-------|-------|
| Reduction: | | | | | | | | |
| Impurities in H_2 : | | | | | | | | |
| CO, percent..... | 0 | 0 | 0.2 | 0.4 | 0.8 | 1.4 | 0 | 0 |
| H_2O , percent..... | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.1 |
| Temperature, °C..... | 450 | 450 | 450 | 450 | 450 | 450 | 550 | 550 |
| Duration, hours..... | 44 | 43 | 39 | 46 | 39 | 40 | 40 | 40 |
| Space velocity, hr.^{-1} | 2,500 | 2,500 | 2,500 | 2,500 | 2,500 | 2,500 | 2,500 | 2,500 |
| Weight loss, percent..... | 25.1 | 23.5 | 21.7 | 21.1 | 17.8 | 18.0 | 25.1 | 24.9 |
| Synthesis: | | | | | | | | |
| Weeks averaged..... | 2-5 | 2-7 | ----- | 2-5 | 2-6 | 2-7 | 2-8 | 2-7 |
| Average temperature, °C..... | 256 | 270 | 249 | 250 | 251 | 263 | 259 | 256 |
| Activity, A_{Fe} | 20 | 14 | 25 | 24 | 22 | 17 | 19 | 20 |
| Distribution of products, ¹ weight-percent: | | | | | | | | |
| C_1 | 12.0 | 17.8 | 12.8 | 12.8 | 12.3 | 14.5 | 16.0 | 15.1 |
| C_2 | 8.6 | 9.5 | 10.9 | 9.9 | 7.8 | 8.3 | 11.3 | 7.8 |
| $\text{C}_3 + \text{C}_4$ | 19.4 | 19.9 | 19.2 | 20.1 | 18.9 | 21.4 | 18.1 | 23.8 |
| $\text{C}_5 +$ | 60.0 | 52.8 | 57.1 | 57.2 | 61.0 | 55.8 | 54.6 | 53.3 |
| Distillation $\text{C}_5 +$, ¹ of weight-percent: | | | | | | | | |
| 30°–185° C..... | ----- | 36.4 | 16.7 | 23.0 | 39.6 | 38.5 | 31.2 | 16.3 |
| 185°–352° C..... | ----- | 36.5 | 41.5 | 40.9 | 36.8 | 37.6 | 38.4 | 41.9 |
| 352°–464° C..... | ----- | 15.4 | 19.4 | 17.2 | 12.6 | 12.7 | 14.4 | 18.1 |
| >464° C..... | ----- | 11.7 | 22.4 | 18.9 | 11.0 | 11.2 | 16.0 | 23.7 |

¹ Includes oxygenated molecules dissolved in oil phase.

was hydrogenated to methane and water, leaving only about 0.6 percent carbon deposited in the catalyst. Similar data for the presence of water vapor in the hydrogen (table 54) indicate that water vapor did not affect activity or selectivity adversely.

In a number of experiments a reduction procedure normally used in the ammonia synthesis process was employed. The space velocity of dry hydrogen was $8,000 \text{ hr.}^{-1}$ and the temperature was maintained at (1) 400°C. for 24 hours, (2) 450°C. for 24 hours, (3) 500°C. for 12 hours, and (4) 525°C. for 12 hours. Although this reduction gave catalysts of somewhat greater activity than the standard procedure (40 hours at 450°C. , with a space velocity of hydrogen of $2,500 \text{ hr.}^{-1}$), catalytic behavior probably will not improve enough to compensate for the longer reduction procedure.

After reduction the catalyst usually is cooled in hydrogen and then exposed to an atmosphere of carbon dioxide. At room temperature carbon dioxide is a good protective medium for iron catalysts and apparently will prevent oxidation in the presence of small concentrations of air. For this reason reduced and pretreated catalysts usually are handled in carbon dioxide. Catalysts stored in carbon dioxide for 6 months

were tested. The activity of these samples was significantly less than that of similar preparations stored in carbon dioxide for only a few days; however, chemical analyses indicated that the catalysts had not oxidized to an appreciable extent. Storage in synthesis oils for extended periods did not change the activity.

Tests were made to determine whether it would be advantageous to start a reduced fused catalyst in the synthesis at atmospheric pressure rather than at 7.8 atmospheres. Catalyst D3001 in test X-140 was operated at atmospheric pressure for 26 hours at 221° to 267°C. before the pressure was increased. A comparison with test X-105 inducted at 7.8 atmospheres in figure 48 shows that the atmospheric induction was of no advantage.

Nitrided Fused Catalysts

One of the most important results of the Bureau of Mines research on Fischer-Tropsch catalysts was the discovery that iron nitrides have unique properties—⁹⁴ ⁹⁵ high activity, long life, and a change in selectivity. Reduced

⁹⁴ Anderson, R. B., Shultz, J. F., Seligman, B., Hall, W. K., and Storch, H. H., Studies of the Fischer-Tropsch Synthesis. VIII. Nitrides of Iron as Catalysts; *Jour. Am. Chem. Soc.*, vol. 72, 1950, pp. 3502-3508.
⁹⁵ Anderson, R. B. and Shultz, J. F., Iron Nitride Catalyst in Carbon Oxide Hydrogenation; U. S. Patent 2,629,728, Feb. 24, 1953.

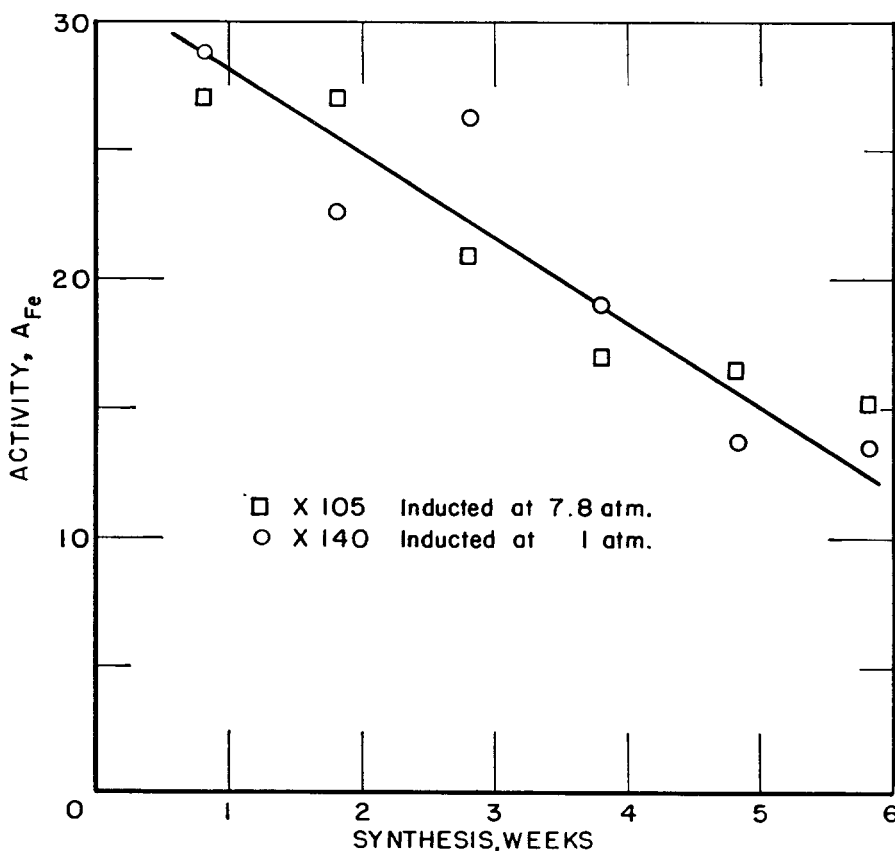


FIGURE 48.—Influence of Induction Pressure on Activity of Fused Catalyst D3001 with $1\text{H}_2 : 1\text{CO}$ Gas at 7.8 Atmospheres.

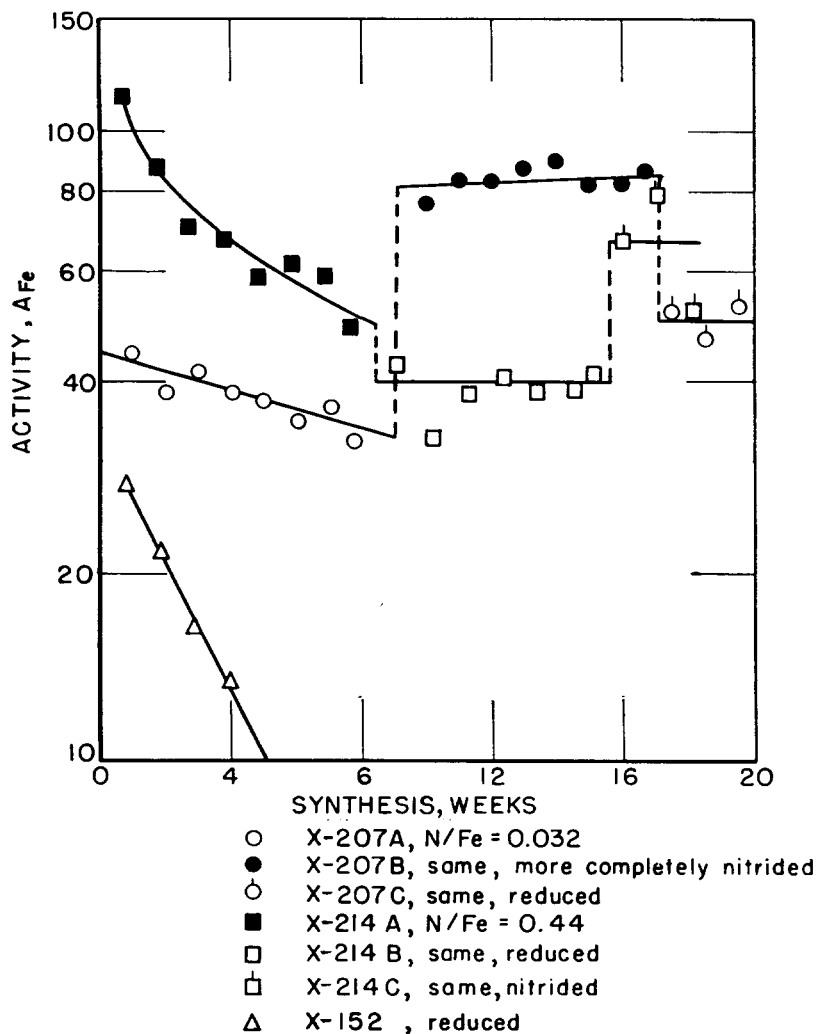


FIGURE 49.—Activities of Nitrided Fused Catalyst D3001 With $1\text{H}_2 : 1\text{CO}$ Gas at 7.8 Atmospheres.

catalysts can be readily converted to ϵ -nitride ($\sim\text{Fe}_2\text{N}$) by treatment with ammonia at $300^\circ\text{--}350^\circ\text{C}$. In reporting these results the nitrogen content is usually expressed as atom ratio of nitrogen to iron. Thus, for Fe_2N , $\text{N} : \text{Fe} = 0.50$.

Tests of reduced and nitrided catalyst D3001 at 7.8 atmospheres are compared with tests of similar reduced catalysts in table 55. The activity (A_{Fe}) for the catalyst in test X-152, which was reduced at 450°C . but not nitrided, is shown in figure 49 to have decreased steadily from 28 to 13 in about 28 days. Under similar conditions a catalyst that had been reduced at 450°C . and nitrided to the atom ratio, nitrogen:iron=0.032 ($\alpha\text{-Fe} + \gamma'\text{-Fe}_4\text{N}$), gave an activity of 44 to 33 in test X-207A. This catalyst, after 56 days operation in test X-207A, was treated further with ammonia under conditions which converted the metallic iron to ϵ -iron nitride. Upon reemployment in the synthesis (test X-207B), this catalyst increased in ac-

tivity to 76. Hydrogenation of the catalyst at 385°C . after 18 weeks of synthesis removed all of the nitrogen in the catalyst. When operated in the synthesis (test 207C), the activity A_{Fe} dropped to 51, which is still more active than the reduced (unnitrided) catalyst in test X-152 (compare also test X-105 in fig. 42, p. 77).

The effect of more extensive nitriding is exemplified by the catalyst in test X-214A (fig. 49, table 55). This catalyst was reduced at 450°C . and nitrided to the ϵ -phase (nitrogen:iron=0.44) and was operated initially at 210°C . The initial activity A_{Fe} was 113. In an operating period of 55 days the temperature had to be increased to 230°C ., corresponding to an A_{Fe} of 49, at which point the catalyst was hydrogenated. The temperature had to be increased to about 240°C . ($A_{\text{Fe}}=40$) (test X-214B). After 15 weeks of synthesis the catalyst was treated with ammonia under conditions