# PORE GEOMETRY OF A FUSED IRON OXIDE CATALYST

Fused-iron catalysts in the raw state have virtually no porosity or internal surface area, the pore structure being developed during reduction as shown in table 3 for our standard

TABLE 3.—*Changes in pore geometry of fused $Fe_3O_4$–$MgO$–$K_2O$, catalyst D3001, during reduction in hydrogen at 450° C.*

| Reduction, percent | Per gram of unreduced catalyst | | | Average pore diameter, A. |
|---|---|---|---|---|
| | Volume of mercury displaced, cc. | Pore volume, cc. | Surface area, m.² | |
| 0 | 0.203 | 0.002 | 0 | |
| 10 | .203 | .010 | 1.0 | 400 |
| 20 | .203 | .018 | 2.1 | 343 |
| 30 | .203 | .027 | 3.1 | 348 |
| 40 | .202 | .035 | 4.2 | 333 |
| 50 | .204 | .043 | 5.2 | 331 |
| 60 | .201 | .052 | 6.3 | 330 |
| 70 | .200 | .061 | 7.3 | 334 |
| 80 | .200 | .071 | 8.4 | 338 |
| 90 | .199 | .082 | 9.4 | 349 |
| 95 | .199 | .086 | 9.9 | 348 |
| 100 | .198 | .089 | 10.1 | 352 |

catalyst D3001.[25] The pore volume and total surface area of this catalyst increased linearly with extent of reduction, except in the interval from 95 to 100 percent, where the increase in area was less than linear. The average pore diameter, $\bar{d}$, calculated on the basis of long cylindrical pores ($\bar{d}=4V/A$, where V is pore volume and $A$ surface area), remained essentially constant and finally increased slightly near 100-percent reduction. The external volume of the catalyst granules, measured by displacement of mercury at atmospheric pressure, remained virtually constant throughout the reduction. The external volume also remained constant during reduction at temperatures other than 450° C., and the pore volumes for these essentially completely reduced samples were about the same. (See table 4.) Microscopic examination of partly reduced catalysts shows a zone of reduced metal that increases in width with increase in reduction. Table 4 shows that varying the reduction temperature is a method

TABLE 4.—*Changes in pore geometry during reduction at different temperatures*

[Catalyst D3006 almost identical in composition to D3001]

| Reduction temperature, °C. | Per gram of unreduced catalyst | | | Average pore diameter, A. |
|---|---|---|---|---|
| | Volume of mercury displaced, cc. | Pore volume, cc. | Surface area, m.² | |
| 450 | 0.194 | 0.086 | 9.4 | 366 |
| 500 | .198 | .091 | 5.3 | 687 |
| 550 | .195 | .090 | 4.5 | 800 |
| 600 | .193 | .092 | 2.0 | 1,840 |
| 650 | .199 | .097 | 1.6 | 2,420 |
| (¹) | .201 | .002 | .0 | |

¹ Raw catalyst.

of "tailormaking" catalysts to a desired average pore size. The following statements characterize the reduction of fused iron catalysts:

(a) The external volume of the particles remains virtually unchanged, the pore volume being generated by removal of oxygen.

(b) Once initiated in a portion of the catalyst, reduction proceeds very rapidly, almost but not quite, to completion. Magnetite is reduced directly to iron.

(c) At a given temperature, the reduced portion of the catalyst is rapidly converted to a relatively stable structure of constant average pore diameter.

(d) On a macroscopic scale, reduction begins at the external surface and moves uniformly inward.

Oxidation of a reduced specimen using steam at 250° to 450° C. was initially fast (up to 30 to 40 percent oxidation) but then became very slow.[26] The reoxidized catalyst at 300° C. was reduced more quickly than the raw catalyst at 450° C.

During oxidation the total surface area decreased more rapidly than would be expected for a system of long cylindrical pores where oxidation might result in (a) a decrease in length of the pores, with the average diameter remaining constant, or (b) a decrease in the diameter of the pores, with the length remaining constant. An explanation consistent with these observations is that the walls of the larger pores have a sizable roughness factor and that oxidation, which proceeds all along the pore walls but to a greater extent near the external surface, tends to smooth the pore walls.

Changes in pore volume and surface area for fused catalyst D3001 after reduction with

²⁵ Hall, W. K., Tarn, W. H., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. VIII. Surface Area and Pore Volume Studies of Iron Catalysts: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 5436–5443.

²⁶ Hall, W. K., Tarn., W. H., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. XIII. Structural Changes of a Reduced Iron Catalyst on Reoxidation and on Formation of Interstitial Phases: Jour. Phys. Chem., vol. 56, 1952, pp. 688–691.

hydrogen, oxidation with steam, carburization with carbon monoxide, and nitriding with ammonia are given in table 5.[26] During reoxidation the external volume of the particles was not changed, but their pore volume decreased. Conversion of metallic iron to carbide or nitride increased the external volume of the particles; the expansion was of the same magnitude as that occurring when massive iron is carbided or nitrided. This expansion also resulted in increasing the pore volume but had virtually no influence on the surface area or porosity.

Electron microscopic studies confirmed the pore structure suggested by the studies of surface area and pore volume.[27] Large pieces of raw catalyst were ground flat and polished by usual metallographic techniques. Replicas stripped from the flat surfaces of samples reduced in hydrogen at 450° or 550° C. showed a variety of ridges and peaks. The shortest dimensions of the structures that probably represent pores averaged 500 to 1,000 A. Replicas from polished surfaces of raw catalyst showed no fine structure.

[27] McCartney, J. T., and Anderson, R. B., Electron Microscopic Replica Studies of Porosity in Fused Iron Catalysts: Jour. Appl. Phys., vol. 22, 1951, pp. 1441-1443.

TABLE 5.—*Changes in pore geometry during oxidation, carbiding, or nitriding of catalyst D3001*

| Treatment | Iron phases present, X-ray analysis | Composition | Per gram of unreduced catalyst | | | Average pore diameter, A. | Porosity, percent |
|---|---|---|---|---|---|---|---|
| | | | Volume of mercury displaced, cc. | Pore volume, cc. | Surface area, m.² | | |
| (1) None (raw)_____ | Fe₃O₄ | ----------------- | 0.203 | 0.002 | 0 | -------- | 1 |
| (2) Hydrogen at 550° C. | α–Fe | Almost completely reduced. | .201 | .093 | 4.7 | 785 | 46 |
| (3) Treatment (2) plus steam at 250° C. | α–Fe, Fe₃O₄ | 68 percent reduced____ | .200 | .061 | 2.9 | 820 | 30 |
| (4) Treatment (2) plus carbon monoxide at 150°–350° C. | Fe₂C(Hägg), α–Fe(?) | Atom ratio C:Fe =0.494. | .225 | .096 | 4.7 | 820 | 43 |
| (5) Treatment (2) plus ammonia at 350° C. | ε–Fe₂N | Atom ratio N:Fe =0.482. | .237 | .107 | 4.8 | 898 | 45 |