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Composition Changes of Massive Iron and Fused Iron Oxide Catalysts in the Fischer-Tropsch Synthesis

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As a part of Bureau of Mines studies of the conversion of coal to gaseous and liquid hydrocarbons, changes in composition and surface area of massive iron and fused iron oxide catalysts in the Fischer-Tropsch synthesis were determined. The surface area of massive iron catalysts, after use in synthesis and extraction of adsorbed hydrocarbon, was slightly larger than the original reduced catalyst. Hägg carbide was the principal phase in the activated layer, and the catalyst was not extensively oxidized. Fused iron oxide catalysts were about 75% oxidized in the first 9 days of synthesis, and magnetite was the principal phase. The surface area, after extraction of adsorbed hydrocarbons, had decreased to about 7% of its original value.

INTRODUCTION

Papers from the Bureau of Mines Pittsburgh laboratory have described the influence of the geometry of reduced fused iron oxide on its behavior in the Fischer-Tropsch synthesis (*1*, *5*). Only the outer portions of the catalyst particles to a depth of about 0.1 mm were effective in the synthesis. This result suggested the use of massive iron catalysts prepared by oxidizing steel turnings or spheres to provide a thin activated layer. Effective catalysts of this type were prepared by Benson and co-workers (*3*).

The present studies were made to provide data on the composition and surface areas of fused iron oxide and massive iron catalysts at the start of sulfur-poisoning tests in which the catalysts were operated with sulfur-free synthesis gas for 9 to 14 days before introducing gas containing sulfur compounds (*4*). Results of longer tests of massive iron are also reported.

EXPERIMENTAL

Catalysts used were (a) 6- to 8-mesh fused iron oxide catalyst D3001 containing initially Fe 67.4 wt %, Mg 4.61, Cr_2O_3 0.65, and K_2O 0.57, and (b) activated SAE 1018 steel lathe turnings L2201, approximate dimensions 8 × 3 × 0.4 mm, oxidized with steam at 600°C to convert 24.6% of the iron to magnetite, and impregnated with an aqueous solution of K_2CO_3 to give a concentration of 0.13 wt % K_2O. Both catalysts were reduced in hydrogen at an hourly space velocity of 2,500, atmospheric pressure, and 450°C for 40 hr.

Both catalysts were tested in $1H_2 + 1CO$ gas at 21.4 atm and an hourly space velocity of 300 for 9 days. Temperature was changed as required to maintain the apparent CO_2-free gas contraction at 65%. Testing data were typical of other tests with these catalysts. With catalyst D3001, the standard testing condition was attained at 260°C and activity remained constant. For L2201 the activity was low at the beginning and the temperature was increased to 286°C. The activity then increased so that the temperature could be decreased to 268°C at the end of the test. The apparatus and procedures used in synthesis tests have been described previously (*6*).

The 50 cc bed of catalyst D3001 was separated into three equal portions by stainless steel screens. No attempt was made to segregate portions of the bed of turnings. After synthesis the catalysts were dropped from the reactor into heptane, the three sections of D3001 being collected separately. The catalysts were subsequently extracted with boiling heptane in a Soxhlet apparatus to remove wax. Portions of the extracted catalysts were taken for surface area measurements by the BET method using N_2 at $-195°C$, and for analysis by chemical methods for iron, carbon, and oxygen (by difference), and by X-ray diffraction. For analyses, entire particles of D3001 were used. For L2201 the surface layer was effectively removed by an extended, vigorous shaking of the turnings in a bottle partly filled with heptane, and this portion was analyzed.

In addition, two groups of experiments were made on massive iron catalysts. First, a series of activated and alkalized catalysts similar to L2201 was examined after 6 weeks of synthesis. Second, a series of synthesis tests of duration varying from 1 to 30 days was made on 1.6-mm steel spheres. The steel spheres were treated with steam at 600° to convert 15 wt % of the iron to the oxide and alkalized by impregnating with an aqueous solution of K_2CO_3 to give a concentration of 0.047 wt % K_2O. After drying, the catalyst was reduced at 450°C in hydrogen at an hourly space velocity of 1,000 for 8 hr.

RESULTS AND DISCUSSION

Surface areas and compositions of reduced and used catalysts are given in Table 1. Turnings L2201 were not oxidized severely during synthesis, but the carbon content of the activated layer exceeded that of Fe_2C. The surface area increased slightly during synthesis, possibly due to the deposition of finely divided elemental carbon. Hägg carbide and possibly traces of cementite were the only phases identified in the activated layer.

On the other hand, catalyst D3001 was about 75% oxidized to magnetite during 9 days of synthesis, and magnetite was the principal phase identified in all three sections of the bed. The amount of oxygen in each of the three sections increased only slightly with distance from the inlet, and the carbon content decreased in this order. Surface areas of sections decreased with distance from the inlet and with increasing oxygen content; however, the area of each section was less than 7% of the area of the reduced catalyst.

These phenomena have generally been observed in Fischer-Tropsch tests in fixed-bed reactors in this Bureau of Mines laboratory (see for example, results from an oil circulation pilot plant in ref. *3*). Composition changes during laboratory-scale

TABLE 1

SURFACE AREAS AND COMPOSITION OF CATALYSTS

Catalyst	State	Surface area (m^2/g Fe)	Composition, atom ratios		Phases from X-ray diffraction[a]
			C/Fe	O/Fe	
L2201	Reduced turnings	0.45	0	~0	α
	Used turnings	0.54	0.55[b]	0.15[b]	χ,C(?)[c]
D3001	Reduced particles	14.8	0	~0	α
	Used: Inlet portion	1.00	0.31	0.92	M,α
	Used: Middle portion	0.77	0.18	1.01	M,α
	Used: Outlet portion	0.74	0.15	1.06	M,α

[a] Phases listed in order of intensity of diffraction pattern. α = metallic iron, χ = Hägg carbide, C = cementite, and M = magnetite.

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

[c] Diffraction analysis for activated layer.

tests of fused iron oxide catalysts have been described previously (*7*). Two groups of experiments on massive iron catalysts demonstrate the course of composition changes during longer periods of synthesis. In the first group, 12 different turning catalysts were prepared from 1018 carbon steel. The turnings were oxidized, alkalized, reduced, and tested using procedures similar to those described for L2201. Analyses after 6 weeks of synthesis with $1H_2 + 1CO$ gas at 21.4 atm and 250° to 275°C were similar to those reported for L2201 in Table 1. Hägg carbide was the major phase in the activated layer, and magnetite, siderite, and metallic iron were present as minor phases in some of the samples.

A second series of laboratory-scale tests employing 1.6-mm steel spheres in the synthesis with $1H_2 + 1CO$ gas at 21.4 atm will be cited briefly. The spheres were oxidized with steam, impregnated with an aqueous solution of K_2CO_3, and reduced in hydrogen to provide a thin layer of activated iron on the surface of the spheres. Six identical tests except for duration were made with 50 cc aliquots of the original pretreated catalyst for periods from 1 to 30 days. In the first week of synthesis, temperatures of about 290°C were required, and subsequently the activity increased progressively so that the temperatures for constant conversion were decreased to 265°C at 30 days. The atom ratio O/Fe of the activated layer increased from 0.15 for the fresh catalyst to a constant value of 0.35 after 6 days. The atom ratio C/Fe of the activated layer increased from 0 to 0.39 in 1 day and subsequently to 0.60 in 30 days. X-ray diffraction patterns of the activated layers contained well-defined lines for α Fe and Hägg carbide. An indistinct pattern of magnetite was observed for all samples including the freshly reduced material.

The significant difference between the two types of catalysts is that the entire particles of fused iron oxide catalyst are activated by reduction, whereas massive iron catalysts have only a thin layer, about 0.1 mm, of active material on a core of massive iron. The pores of the catalysts are filled with wax which is liquid at synthesis temperature (*7*). As the rate of diffusion of $H_2 + CO$ in these liquid-filled pores is small with respect to the reaction rate at the catalyst surface, the reactants diffuse into the pores only a short distance before reacting. Thus the inner portion of particles of fused iron oxide catalysts are exposed to high ratios of H_2O/H_2 and CO_2/CO, and this part is largely converted to magnetite (*2*, *5*). Oxidation of the internal portion of fused iron oxide catalysts is accomplished mainly by H_2O and CO_2 formed within individual particles. This conclusion is based on the observation that position of catalyst in the bed and the corresponding increases in concentrations of H_2O and CO_2 from inlet to outlet of bed produce only minor changes in oxidation of the catalyst.

In poisoning by H_2S in synthesis gas after a period of 9–14 days on pure gas, plots of relative activities for catalysts D3001 and L2201 as a function of sulfur introduced per gram of iron were approximately the same until the relative activity had decreased to 20% (*4*). Surface areas for the two types of catalysts at the start of poisoning differed by less than a factor of 2.

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