

# KINETICS OF THE FISCHER-TROPSCH SYNTHESIS ON IRON CATALYSTS

by

R. B. Anderson,<sup>1</sup> F. S. Karm,<sup>1</sup> and J. F. Shultz<sup>1</sup>

## Abstract

As a part of a Bureau of Mines program on the conversion of coal to liquid and gaseous fuels, the kinetics of the Fischer-Tropsch synthesis on iron catalysts was investigated.

Nitrided catalysts were studied at 21.4 atmospheres using feed gases ranging from  $2\text{H}_2 + 1\text{CO}$  to  $0.25\text{H}_2 + 1\text{CO}$ , and at 7.8 to 21.4 atmospheres using  $1\text{H}_2 + 1\text{CO}$  gas. The overall apparent activation energy increased with increasing carbon monoxide content of the feed gas from 19.5 kcal/mole for  $2\text{H}_2 + 1\text{CO}$  to 23.7 for  $0.7\text{H}_2 + 1\text{CO}$ . The rate of synthesis with  $1\text{H}_2 + 1\text{CO}$  feed increased linearly with operating pressure from 7.8 to 21.4 atmospheres. A semifundamental rate equation of the form  $r = a' p_{\text{H}_2}^{0.6} p_{\text{CO}}^{0.4} - f' r^{0.5} p_{\text{H}_2\text{O}}^{0.5}$  was shown to fit the data satisfactorily. The relative usage of hydrogen to carbon monoxide decreased with increasing conversion, passed a minimum, and then increased. Apparently water is the principal primary product and carbon dioxide is produced by subsequent water-gas shift reaction.

In another group of experiments water, carbon dioxide, argon, and methane were added to  $1\text{H}_2 + 1\text{CO}$  feed to a nitrided iron catalyst. Argon and methane were only diluents. Carbon dioxide was a slight inhibitor and water vapor was a strong inhibitor to the rate of synthesis. Water accelerated the water-gas shift and usually increased methane production.

Important factors of catalyst geometry in determining rate were found to be particle size and extent of reduction. Apparently the active portion of the catalyst is confined to a layer of 0.01 to 0.02 cm from the external surface of particles. A special solution was made of differential equations relating reaction at the catalyst surface to diffusion in pores of the catalyst for spherical particles with an active layer surrounding an inert core. The equation derived expressed the experimental data reasonably well. Diffusivities determined by this equation varied from  $3$  to  $24 \times 10^{-6}$  cm<sup>2</sup>/sec; these values are of the same magnitude as observed for the diffusion of gases in liquid.

The appendix presents a group of synthesis experiments at pressures of 21.4 to 103 atmospheres. In this range the rate of synthesis on nitrided iron catalysts increased with pressure to the 0.74 to 0.84 power.

## Introduction

The kinetics of the Fischer-Tropsch synthesis has been investigated as a part of a Bureau of Mines program on the conversion of coal to liquid or gaseous fuels. In this process coal is gasified by reacting it with steam and oxygen at high temperatures to form a gaseous mixture of hydrogen and carbon monoxide called synthesis gas. The  $\text{H}_2 + \text{CO}$  mixture, after removal of extraneous components such as  $\text{CO}_2$  and sulfur compounds, is reacted at a lower temperature on a catalyst containing iron, cobalt, or nickel as an active component to produce hydrocarbons and oxygenated organic molecules. This step of the process is the Fischer-Tropsch synthesis. The net reaction is water plus coal

<sup>1</sup> Supervisory chemist, Pittsburgh Coal Research Center, Bureau of Mines, Pittsburgh, Penna.

to yield hydrocarbons and oxygenated organic compounds plus  $\text{CO}_2$ ; however, the direct reaction cannot be achieved, because the thermodynamics of this reaction is unfavorable. Kinetic studies, in addition to yielding basic information about the process, provide practical information needed for rational design of reactors.

The first part of this Bulletin describes rate studies on iron catalysts and the second part the influence of catalyst geometry on rate. The appendix describes special experiments at higher pressures than those usually employed in the synthesis on iron catalysts.

Kinetic data for the Fischer-Tropsch synthesis on iron catalysts are meager. Early German experiments (52, 60)<sup>2</sup> were usually not designed to permit a simple interpretation of kinetic aspects of the synthesis. Kinetic data for the Fischer-Tropsch synthesis on iron catalysts have been reviewed by Anderson (1) and Tramm (62), and Uchida (64) has proposed kinetic equations. Hall, Kokes, and Emmett (27) have interpreted a semiempirical equation of Anderson (1) in terms of more recent information on the mechanism of the synthesis. Recently, Frye, Pickering and Eckstrom (22) described the kinetics of the Fischer-Tropsch synthesis on iron catalysts at substantially higher temperatures ( $300^\circ\text{--}340^\circ\text{C}$ ) than had been used in most previous studies. In this temperature range, time-dependent changes of rate occurred after variations in operating conditions. Powers has proposed rate equations that approximate both steady-state and transient conditions (48).

Water has manifold roles in the Fischer-Tropsch synthesis, being a product under some conditions, a reactant under others, and usually an inhibitor. Soviet workers have shown that  $\text{CO}_2$  production increased when water was added to synthesis gas on iron Fischer-Tropsch catalysts at atmospheric pressure (11). With a feed of  $1\text{H}_2 + 1\text{CO} + 1\text{H}_2\text{O}$  at  $230^\circ\text{C}$  the water-gas shift was 13 times as fast as the synthesis. Kölbel and Engelhardt investigated the reactions of  $\text{H}_2\text{O} + \text{CO}$  mixtures over iron and cobalt catalysts (37-39). On iron catalysts with  $1\text{H}_2\text{O} + 1\text{CO}$  at atmospheric pressure the water-gas shift, the principal reaction, proceeded rapidly at  $240^\circ\text{C}$ . With  $1\text{H}_2\text{O} + 3\text{CO}$  feed, products typical of the Fischer-Tropsch synthesis were obtained, and hydrogen was produced. Recently Kölbel's group presented kinetic measurements on the water-carbon monoxide synthesis on iron, cobalt, and nickel catalysts (40).

Tramm has shown that water vapor strongly decreases the rate of synthesis and that  $\text{CO}_2$  has a much smaller inhibiting effect (63). Prolonged exposure to high concentrations of  $\text{CO}_2$  or  $\text{H}_2\text{O}$  leads to permanent loss of catalytic activity. As the water vapor is an important component in determining both rate and selectivity, experiments were arranged to demonstrate its influence more clearly.

Diffusion in the pores of catalysts is intimately related to the reactions at the surface, as the concentration gradients required for diffusion are produced by the catalytic reaction. Several investigators (19, 61, 65) have solved differential equations for simple hypothetical catalytic reactions in which diffusion in pores was coupled with reaction at the surface. Wheeler (68, 69) has summarized and extended this work to include consideration of selectivity and poisoning in porous catalysts and an appraisal of well-known catalytic reactions. Weiss and Prater (66) have treated dehydrogenation reactions on this basis, and Bokhoven and associates (16) have considered diffusion and reactions in iron catalysts. Kölbel, Ackermann, and Engelhardt (35) have considered mass transport in the Fischer-Tropsch synthesis with emphasis on liquid-cooled reactor synthesis.

Previous Bureau papers (28, 29) have shown that the pore geometry of fused-iron catalysts can be "tailor-made" within certain limits by varying the extent and temperature of reduction: (1) At all temperatures studied,  $400^\circ$  to  $625^\circ\text{C}$ , the pore volume and porosity increase linearly with extent of reduction; (2) the reduction, at least on a macroscopic scale, proceeds uniformly inward from the external surface; (3) the average pore diameter of the reduced portion of the catalyst increases with increasing temperature of reduction.

<sup>2</sup> Italic numbers in parentheses refer to items in the list of references at the end of this report.