

# PHYSICAL CHEMISTRY OF THE FISCHER-TROPSCH SYNTHESIS<sup>1</sup>

By

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## Summary

**T**HIS PAPER summarizes the results of physicochemical studies of the Fischer-Tropsch synthesis (the catalytic hydrogenation of carbon monoxide) undertaken by the Federal Bureau of Mines as part of its program on improving processes for producing liquid fuels from coal.

Criteria for activity in the Fischer-Tropsch synthesis are considered. For example, ferromagnetism is a satisfactory criterion of activity in elements of the iron group and their compounds.

The effectiveness of iron catalysts after different pretreatments is examined. A precipitated ferric oxide containing copper oxide and potassium carbonate showed virtually the same activity after a variety of pretreatments; its selectivity, however, varied widely. Catalysts treated directly with synthesis gas or carbon monoxide were reduced to magnetite and yielded a high-molecular-weight product, whereas catalysts reduced in hydrogen, as well as those reduced in hydrogen and subsequently converted to carbide, yielded products of lower molecular weight. Those reduced in hydrogen and nitrified yielded products having the lowest molecular weight and high concentrations of oxygenated chemicals.

The same general trends in selectivity were observed with fused iron oxide catalyst containing small amounts of magnesia and potassium oxide. However, catalysts converted to nitrides, carbonitrides, or carbides were more active than reduced catalysts. The reduced catalyst was more active than a re-oxidized catalyst. At pressures of 300 p.s.i.g. the activity of catalysts converted to carbides decreased rapidly, presumably because of the rapid oxidation rate of the carbide phases. On the other hand, nitrified catalysts oxidized slowly.

Detailed information is presented for changes in surface area, pore volume, and average pore radii of fused iron oxide catalyst during reduction, carburization, nitriding, and oxidation. The pore geometry of these catalysts can be varied over wide ranges by proper choice of reduction conditions.

With iron catalysts the synthesis rate increased linearly with operating pressure, and overall apparent activation energies of 18 to 21 kcal. per mole have been obtained. The variation of conversion with space velocity can be

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expressed by a simple first-order empirical equation. Apparently, the primary reaction produces water as its principal oxygenated product. This reaction is followed by the water-gas shift. Kinetic data on synthesis with cobalt and nickel catalysts are also summarized.

Information on the mechanism of chain growth was obtained from observed isomer and carbon-number distributions of the products from the Fischer-Tropsch synthesis. A simple growth scheme involving stepwise addition of carbon atoms to end or adjacent-to-end carbons at one end of the growing chain is described. This growth pattern led to the hypothesis of a more detailed mechanism for the synthesis involving oxygenated intermediates. For iron catalysts this hypothesis has been largely substantiated by experiments on incorporating alcohols tagged with carbon-14 into the synthesis products.