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Report 8

Indirect Liquefaction Chemical Research

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INDIRECT LIQUEFACTION CHEMICAL RESEARCH

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This work is an experimental study of the action and behavior of typical catalysts used in the Fischer Tropsch (F-T) synthesis. We are attempting to characterize some of the many elementary reactions associated with the synthesis in an effort to better understand the dynamics of F-T synthesis. The work is focused on (1) the role and fate of gas-phase intermediates and by-products, such as 1-olefins and alcohols, in the mechanism and control of chain growth and product distribution and (2) the correlation of transient and steady state measurement techniques for the F-T synthesis.

The apparatus we have assembled for these studies employs a microreactor (1-5 cm³) which can operate in pulsed or steady state and either as a tubular reactor or a differential pumped loop reactor.

The catalyst emphasized so far is a hydrogen reduced commercial synthetic ammonia catalyst. Reduction conditions of the catalyst including pressure, temperature, and water vapor content can be controlled and monitored by means of a dedicated mass spectrometer system. The apparatus may be used at pressures to 200 psig (1.5 MPa) and varied compositions of gas mixtures of H₂, CO, and He. Some of the elementary reactions possibly associated with the F-T synthesis are indicated in Figures 1, 2, and 3. So far we have emphasized a consideration of the role of 1-olefins in the F-T synthesis.

We have found in this work that even in the absence of carbon monoxide, but in the presence of hydrogen, olefins such as butene-1 can homologate on "iron" forming hydrocarbons with carbon numbers of nine or more. This reaction we attribute to the reaction of olefin decomposition (Fig. 3, #1) which is then followed by homologation (Fig. 2, #3), forming the observed products.

The homologation of propylene, 1-butene, and 1-pentene occurs in competition with their hydrogenation to form propane, butane, and pentane. High hydrogen to olefin ratios favor hydrogenation and even at ratios of less than five (H₂/olefin) only a few percent of the olefin forms higher hydrocarbons. Of course, at very low hydrogen activities, aromatic compounds are produced. In two experiments the injection of 1-butene into a CO-H₂ mixture (1:3) produced only the amount of homologation found in the absence of CO. This finding is not yet adequate for drawing mechanistic conclusions, but is more consistent with a carbide intermediate mechanism than with a CO insertion mechanism.

Chain lengthening by carbidic species occurs irrespective of their source (in this case from an olefin). This conclusion was borne out by further studies using isobutylene, butene-1, and butene-2 which showed that carbon atom pairs (formed from some molecules of the butene) retain identity on the iron surface and react subsequently with an additional molecule of butene. These observations are shown in Table 1.

Table 1

GHSV = 340 hr⁻¹; 300°C; H₂ at 35 psia (0.25 MPa); olefin/H₂ ≥ 1/2; at iron

Injected Compound	Ratio C ₅ H ₁₂ /C ₄ H ₁₀ (one carbon atom lengthening)	Ratio C ₆ H ₁₄ /C ₅ H ₁₂ (two carbon atom lengthening)
$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \text{H}_3\text{C} \end{array}$ Isobutylene	0.025	0.078
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}=\text{CH}_2 \\ \\ \text{H} \end{array}$ 1-Butene	0.014	0.057
$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_3 \end{array}$ trans-2-butene	0.0069	0.13

In this example, the significant increase in two-carbon atom chain lengthening for the 2-butene compared with that for either of the terminally unsaturated compounds is the measurement of interest.

The effect of space velocity in the pulsed operation of the reactor was to increase the yield of chain lengthened product relative to hydrogenation. At 3500 hr⁻¹ a yield of 5% homologation to a five carbon species is obtained from 1-butene. The heat of activation of the chain lengthening reaction of 1-butene appeared to be about 10 kcal/mole (40 kJoules/mole) greater than the heat of activation for hydrogenation to butane.

This work has added support to the carbidic route for the FT synthesis. In particular, surface methyldene ($=CH_2$) groups can be formed from olefins and react subsequently with other olefin molecules to form a range of hydrocarbons with larger carbon numbers than the initial olefin. It appears from our observations to date that hydrogen activity is a critical parameter in determining the course of chain lengthening.

Because distribution data of hydrocarbons formed in a Fischer-Tropsch reaction do not distinguish between key elementary steps (1), these mechanistic studies are directed toward the determination of lability and reactivity of the various surface species. Although this type of homologation reaction has been reported on ruthenium, tungsten, and molybdenum, we have not found earlier references to the reaction occurring on iron catalysts such as are used in the Fischer-Tropsch synthesis.

(1) See for example, P. Biloen, J. N. Helle, and W. M. H. Sachtler, *J. Catalysis* 58, 95-107(1979).

F-T SYNTHESIS
ELEMENTARY REACTION TYPES

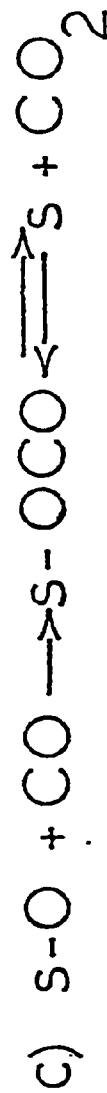
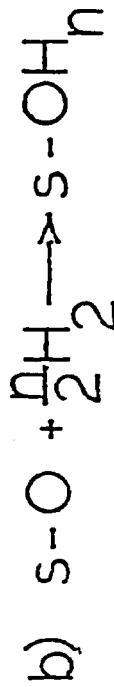
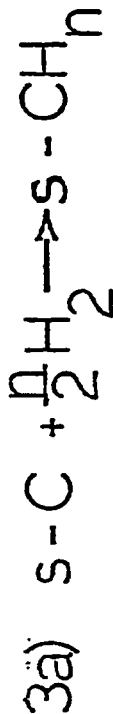
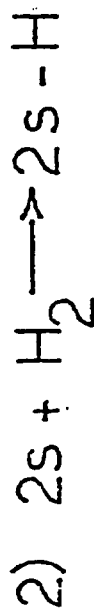
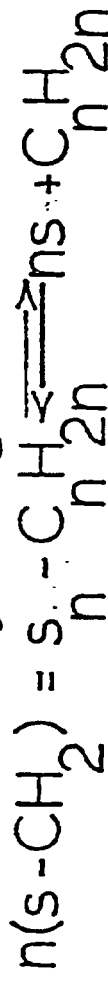


Figure 1

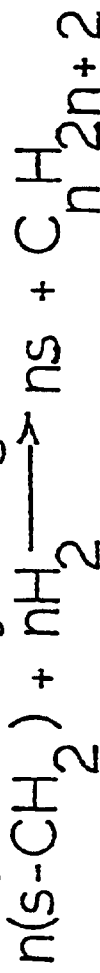
F-T SYNTHESIS

CHAIN LENGTHENING REACTIONS

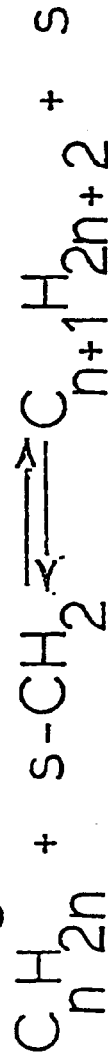
1) Polymerization yielding olefins



2) Hydrogenation yielding saturates



3) Homologation of olefins

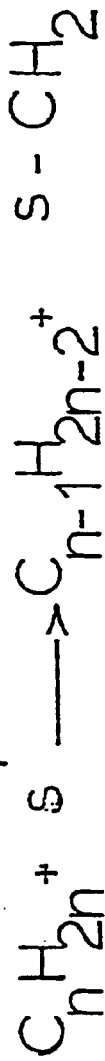


4) Other possible reactions involving

:CHOH, CO insertion, etc.

F-T SYNTHESIS
INCIDENTAL REACTIONS

1) Olefin decomposition



2) Olefin hydrogenation

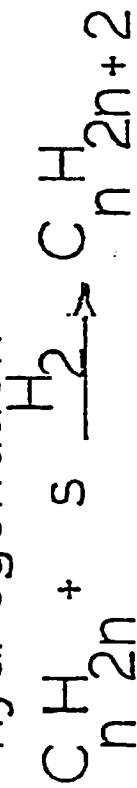


Figure 3