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Olefin Addition in Fischer–Tropsch Synthesis on an Iron Catalyst

The possibility of altering the molecular weight distribution of Fischer–Tropsch products by addition of olefins to the synthesis gas is of practical interest. Two early studies with C-labeled ethylene or propylene (*1, 2*) indicated that on iron catalysts only a few percent of the added olefins were incorporated into higher hydrocarbons but in a more recent study (*3*) it was reported that the addition of ethylene or propylene markedly shifted the selectivity to heavier products. Our study was designed to help resolve this seeming disagreement.

Hall *et al.* (*1*) passed synthesis gas of H_2/CO ratio equal to 1 and containing 1 to 1.25 mole% radioactive ethylene over either of two reduced fused-iron catalysts in a fixed-bed reactor at 224°C. With an iron catalyst promoted with 0.6% SiO_2, 0.6% Cr_2O_3, 4.6% MgO, and 0.6% K_2O, about 6 mole% of the ethylene was incorporated into higher hydrocarbons at 790 kPa. With an iron catalyst promoted with 0.64% Al_2O_3 and 2.0% ZrO_2 but containing no potassium, about 12% of the ethylene was incorporated into higher hydrocarbons at 100 kPa. In both experiments the principal reaction of the labeled ethylene was hydrogenation to ethane.

Schulz *et al.* (*2*) investigated the effect of ^{14}C-labeled ethylene or propylene over an alkalized iron catalyst in a fixed-bed reactor at 2.1 MPa and 220°C. They added 0.2 to 0.3 mole% olefin to synthesis gas with a H_2/CO molar ratio of 2.0. About 9% of the ^{14}C-labeled ethylene but only 1% of the propylene was converted to higher hydrocarbons. In both cases, the major portion of the tagged olefins was hydrogenated to the saturated parafins.

In a more recent study, Dwyer and Somorjai (*3*) reported that the addition of 0.04 to 2.7 mole% ethylene or propylene to synthesis gas with a H_2/CO molar ratio of 3 noticeably shifted the selectivity to heavier products. Experiments were conducted with an initially evacuated, unalkalized iron foil at 610 kPa and 300°C in an isolation cell over a catalyst lifetime of 2 to 3 hr, and total conversion of CO was less than 1%. Loss of activity was attributed to excessive carbon deposition on the catalytic surface. In a representative experiment, after 90 min of reaction most of the ethylene had been hydrogenated to ethane; however, 8 mole% of the original ethylene at 2.7 mole% concentration had been converted to higher hydrocarbons. A chain growth probability factor α of 0.56 was calculated, based on the Schulz–Flory distribution for C_1 and C_3 to C_5 hydrocarbons. A much lower value of $\alpha = 0.30$ was observed when only 0.04 mole% ethylene was added. When propylene was added, a value of $\alpha = 0.70$ was reported. Dwyer and Somorjai reasoned that the increase in α with increasing ethylene partial pressure showed that incorporation of α-olefins into growing chains could be a major reaction pathway for producing higher-molecular-weight products.

EXPERIMENTAL

The apparatus and analytical procedures used in this study are described in detail elsewhere (*4, 5*). Synthesis gas either with or without added ethylene or 1-butene was passed continuously into a 1-liter, mechanically stirred autoclave about half-filled with an essentially nonvolatile and inert liquid, normal-octacosane of >99% purity, in which the catalyst was suspended. The contents were well mixed so the reactor behaved as a continuous stirred-tank reactor (CSTR). Volatile products were removed

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overhead continuously while the catalyst and inert liquid remained in the reactor for the duration of a run. After an initial period, steady-state operation with regard to catalytic activity and selectivity was obtained over the entire run.

The catalyst (from United Catalysts, Inc., and designated C-73) was a fused magnetite containing 2.0–3.0% Al_2O_3, 0.5–0.8% K_2O, 0.7–1.2% CaO, and <0.4% SiO_2, on an unreduced basis. About 75 g of crushed catalyst (170- to 270-mesh size) was prereduced in a separate vessel with hydrogen at a space velocity of 10,000 hr^{-1}, 400°C, and atmospheric pressure, for at least 72 hr. It was then slurried with the octacosane to produce a 15 wt% suspension (unreduced basis).

The H_2/CO mole ratio in the synthesis gas was 1.27 for Runs 1-1 and 1-2 and 1.20 for all others. An olefin was added to comprise about 1.5 mole% ethylene or 0.86 mole% 1-butene in this mixture. This increased the ethylene or the 1-butene concentration in the product gases over twofold. Reaction conditions were 248°C, and either 790 or 1480 kPa. The space velocity of the feed gas was approximately 6.5 L gas (at STP)/min-kg catalyst (unreduced basis), chosen to give CO conversions greater than 90%. This was sought since significant readsorption of olefins would seem to be most likely when competition with carbon monoxide, which is strongly bound onto the catalyst, is minimized.

RESULTS

The products, analyzed by gas chromatography, were characterized by carbon number on a total organic basis, which included hydrocarbons plus oxygenates. We will show that they follow the same Flory distribution in the presence of added ethylene and 1-butene as they do in the absence of added olefin. A significant fraction of the ethylene was hydrogenated to ethane but the 1-butene remained unreacted.

TABLE 1

Experimental Results

Run No.	Time on stream (hr)	Exit $P_{C_2H_4}$ (kPa)	Exit $P_{C_4H_8}$ (kPa)	P_{total} (kPa)	Percentage conversion	
					H_2	CO
		Catalyst Batch 1				
1-1	220	21.8	15.2	1480	57	97
1-2[a]	290	21.6	41.2	1480	60	97
1-3[b]	625	25.1	6.4	790	49	93
1-4	675	9.9	6.1	790	51	93
		Catalyst Batch 2				
2-1	120	10.0	6.1	790	48	90
2-2	150	19.9	14.7	1480	57	96
2-3[b]	170	24.2	5.6	790	48	89
2-4[b]	210	43.9	13.5	1480	56	95

[a] 0.86 mole% 1-butene added to feed.
[b] 1.5 mole% ethylene added to feed.

To avoid complexities associated with the C_1 and C_2 products, we considered only the C_3 to C_8 fraction of the product for calculation of the chain growth probability, α, in the Flory equation. This becomes here

$$m_n' = (M_T/M_{3\text{-}8})(1 - \alpha)\alpha^{n-1}, \qquad (1)$$

where m_n' is the mole fraction of carbon number n (where $3 \leq n \leq 8$), within the C_3 to C_8 portion, $M_{3\text{-}8}$ is the total moles of C_3 through C_8 organic, and M_T is the total moles of organic produced by the synthesis. Taking the logarithmic form of Eq. (1), a plot of $\ln(m_n')$ as a function of n yields the value of α from the slope.

Runs with and without added olefin were conducted at various times on stream with each of two batches of catalyst. Table 1 gives the percentage conversion of H_2 and of CO (note that some CO disappears and H_2 is formed by the water gas shift reaction) and the ethylene and butylene partial pressures in the exit gas. The production distribution by carbon number for each of the four data sets without added olefin (Runs 1-1, 1-4, 2-1, and 2-2) is plotted in Fig. 1 according to the logarithmic form of Eq. (1), yielding $\alpha = 0.59$. There was no trend with time on stream, catalyst batch, carbon monoxide conversion, or partial pressure of ethylene or butene, which in this case were all formed by the synthesis.

Figure 2 shows data for Runs 1-3, 2-3,

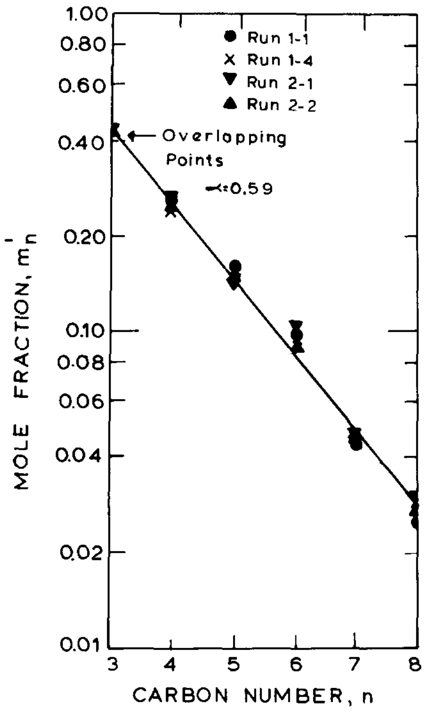

FIG. 1. Flory distribution; synthesis gas alone.

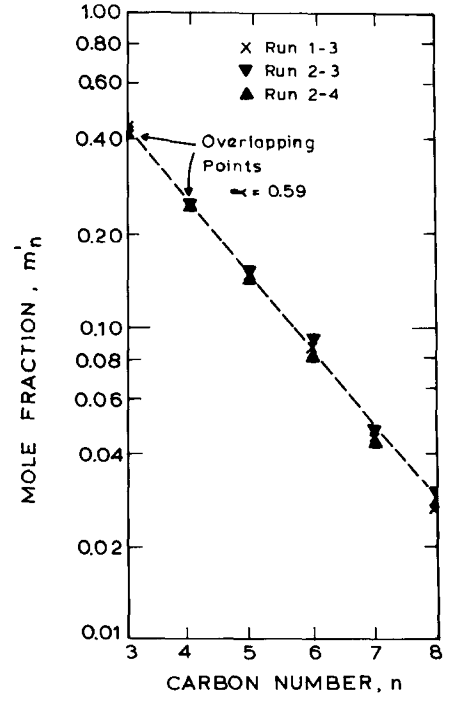

FIG. 2. Flory distribution; 1.5 mole% ethylene added to the synthesis gas.

and 2-4 in which 1.5 mole% ethylene was added to the synthesis gas. The value of α was again 0.59, signifying that adding ethylene did not alter the molecular weight distribution.

Table 2 compares matched pairs of runs with and without added ethylene (e.g., 2-2 with 2-4, 1-4 with 1-3, and 2-1 with 2-3). From 18 to 32% of the added ethylene was hydrogenated to ethane, more at the higher pressure. Dry (*6*) also observed that ethylene appreciably reacted with hydrogen when it was added to the feed gas over an iron catalyst at 335°C. He reported that C_{3+} olefins were not hydrogenated under similar conditions. Comparison of matched pairs shows no significant effect of ethylene addition on the olefin–paraffin ratio of, for example, the C_4 or C_6 product.

Material balances on the C_2 fraction, made by comparing matched runs with and without added ethylene, indicated that a slight amount of ethylene seemed to disappear beyond conversion to ethane. This averaged less than 10% and seemed to be greater at higher-percentage CO conversions.

Upon the addition of 1-butene, less than 0.5% was hydrogenated to *n*-butane under the synthesis conditions. The product distribution was similar to that obtained with pure synthesis gas (data not shown) and the

TABLE 2

Effect of Added Ethylene on Molar Ratio of α-Olefin/Normal Paraffin

Run No.	C_2[a]	C_4	C_6	Mole% of added C_2H_4 hydrogenated	P_{total} (kPa)
			Pure synthesis gas		
2-2	1.4	4.7	3.9	—	1480
1-4	1.9	4.9	3.9	—	790
2-1	1.8	5.2	4.2	—	790
			Synthesis gas + 1.5 mole% C_2H_4		
2-4	0.1	4.6	3.4	32	1480
1-3	0.5	5.0	4.0	22	790
2-3	0.5	5.5	4.3	18	790

[a] (moles C_2H_4 in effluent − moles C_2H_4 in feed)/moles C_2H_6 in effluent.

same probability of chain growth $\alpha = 0.59$ was calculated, subtracting the 1-butene added.

DISCUSSION

A slight degree of incorporation of an olefin into the product may be difficult to identify as a perturbation from a straight line on a semilogarithmic plot, as emphasized by the analyses recently published by Novak *et al.* (*7*). The principal conclusion of our study is that addition of olefin to the reactant stream is not a viable method of altering molecular weight distribution over an iron catalyst.

This finding agrees with studies conducted at SASOL (*6*) in which a fluidized-bed reactor was operated at 335°C with an iron catalyst. An olefin-rich oil cut in the gasoline boiling range was extensively recycled to the reactor (2 vol oil recycled/vol oil produced). There was no indication that the oil had been chemically altered even with 93% synthesis gas conversion; incorporation of the light oil into fresh product did not occur.

Studies by Feimer *et al.* (*8*) also support this conclusion. They studied a precipitated, copper–potassium-promoted, iron catalyst operating at steady state in a fixed-bed reactor. The C_1 to C_5 hydrocarbon product distribution, measured at five points along the bed, was independent of reactor length, and hence ethylene partial pressure, at 233°C, 1490 kPa, and H_2/CO molar feed ratio of 2.3 and CO conversions up to 67%. At very high CO conversions, the reactor profile for ethylene and ethane suggested that ethylene hydrogenation and/or incorporation into product might be more important.

The most significant condition in the Dwyer and Somorjai study may have been that the conversion was always less than 1%. Hence the olefin addition caused an increase in its concentration by an order of magnitude or more, which would magnify effects. Their results might also be related to the absence of alkali in their catalyst. In pulsing-type studies with a Ru catalyst Nijs and Jacobs (*9*) reported that incorporation of α-olefins into growing organic chains was significantly higher on an acidic support than on a neutral support, and the results of Hall *et al.* (*1*) could be interpreted as primarily an effect of potassium content causing lesser ethylene incorporation into products.

More probably, Dwyer and Somorjai's results can be attributed to the fact that their catalyst had not reached steady-state activity and was probably an incompletely carburized, polycrystalline iron. Krebs *et al.* (*10*) showed with a reduced magnetite catalyst that the product distribution and value of α changed markedly during the first few hours on stream, and Raupp and Delgass (*11*) and Amelse *et al.* (*12*) related major changes in catalyst properties over the first few hours to surface reconstruction and iron carbide formation.

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