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NOTES

Study of Fischer–Tropsch Synthesis over Fe/SiO$_2$: Effect of Diethylamine on Hydrocarbon and Alcohol Production

Iron is known to be an effective catalyst for Fischer–Tropsch synthesis (*1*). Scavenging work in our laboratory on Fe$_2$O$_3$/SiO$_2$ has shown that alkyl fragments are the immediate precursors to alkanes and olefins and are most likely involved in the chain-growth step (*2, 3*). Others have shown that the chain-growth step can proceed via a nonoxygenated intermediate (*4–6*) and that the most probable chain-growth step involves methylene inserting into a metal–alkyl bond (*7*). The catalytic route to oxygenated products (mainly alcohols and aldehydes) is still unresolved. Bell (*8*) has proposed that these are formed only as a termination step in which carbon monoxide inserts into a metal–alkyl bond to form an acyl species which is subsequently hydrogenated to the alcohol or aldehyde product. This mechanism is supported by the recent work of Pijolat and Perrichon (*9*) who found that the addition of 1-butene to the CO/H$_2$ feed resulted in an enhancement in the formation of 1-pentanol over an iron catalyst. The work reported herein was initiated to scavenge the proposed acyl intermediate over an iron catalyst.

The iron catalyst (20.4 wt% Fe$_2$O$_3$/SiO$_2$) used in this study and the experimental apparatus has been described earlier (*2*). The hydrocarbon analyses were performed online with a Varian 3700 gas chromatograph (GC), using a packed OV-101 column and a flame ionization detector. Alcohol analyses were performed by trapping reactor effluent in a liquid-nitrogen-cooled trap for 30 min and then injecting it on a Hewlett–Packard 5880 GC fitted with a 5% phenylsubstituted methyl silicone capillary column. Calibrations were done with known standards and GC–mass spectroscopy.

Experiments were conducted at 220°C, H$_2$/CO ratios of 1.0 to 3.6, and total pressure of 1 to 10 atm. The Flory plots in Figs. 1 and 2 for total hydrocarbons (alkanes and olefins) and alcohols, respectively, are representative of the results. The different quantities plotted on the ordinates of the figures are based on Flory-type analyses (*8, 10*) and were selected to conform with the different form of data each GC analysis provided. Each figure has a slope defined as the natural logarithm of the chain-growth probability α. The deviation for carbon numbers 6 and 7 in Fig. 1 was caused by excessive column bleed and poor elution characteristics of these products from the OV-101 column.

Different α's were found for the hydrocarbons and for the alcohols. Other researchers have reported different chain-growth parameters for hydrocarbons and alcohols on a variety of catalysts (*11–13*) and have proposed that this suggests that the hydrocarbons and alcohols are formed by different pathways (*11*) or on different sites (*12, 13*). Pijolat and Perrichon (*9*) and Huff and Satterfield (*14*) observed nearly similar α's for low-weight hydrocarbons and alcohols over iron-based catalysts. The similar α's were used by Pijolat and Perrichon to argue that a common alkyl intermediate was converted into either the hydrocarbons or the alcohols. Huff and Satterfield found, as did Egiebor and Cooper (*15*), that a different α described the hydrocarbon distribution for higher weight products, C$_{10+}$ and C$_{13+}$, respectively. This change in α with chain length was associated with different sites for production of low- and high-weight products (*14, 15*). We propose that the different α's observed in

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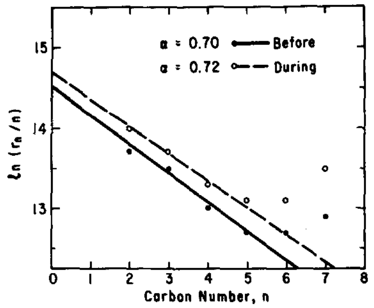

FIG. 1. Flory distribution for hydrocarbons before (—) and during (---) the addition of diethylamine to the feed; 220°C, H_2/CO feed ratio = 3.6, 9.95 atm total pressure.

our study are associated with different sites for the production of hydrocarbons and alcohols.

Diethylamine was added to the CO/H_2 feed gas in attempts to scavenge the alcohol precursor, which has been postulated to be an acyl species (*8*). A nucleophilic reaction between the acyl's carbon and diethylamine, in the presence of hydrogen, was expected to produce either *N,N*-diethylamides or *N*-alkyldiethylamines (*16, 17*). *N,N*-Diethylformamide and *N,N*-diethylacetamide, and C_1 to C_4 *N*-alkyldiethylamines were formed.

Control experiments established that the amides may have formed between diethylamine and formic and acetic acid, which are possible synthesis products over iron (*1*), but were never detected in our study. Additional control experiments demonstrated that diethylamine reacted, in the presence of H_2, with itself and with ethylene to form triethylamine. The route to *N*-alkyldiethylamines during scavenging could not be established. Three possible routes are (1) surface reaction of the amine with an acyl/formyl intermediate; (2) exchange reactions of the adsorbed amine with alkyl fragments known to be on the iron surface during Fischer–Tropsch synthesis (*2, 3*); and (3) disproportionation of the amine with itself (*18*).

Klier and co-workers (*11, 19*) used isopropylamine to probe the alcohol forming reaction over an Fe/Cu/ZnO catalyst. They observed *N*-alkylisopropylamines to form. The addition of isopropylamine to the CO/H_2 feed caused the production of alcohols to be completely suppressed, while the synthesis of hydrocarbons was only partially inhibited and the Flory distribution of hydrocarbons was shifted to higher weights. They found that the isopropylamine trapped methyl and ethyl groups and also proposed that the amine primarily attacked the alcohol precursor (*11*). (The alcohol precursor was not identified.)

The effect of diethylamine on the hydrocarbon and alcohol product distributions is shown in Figs. 1 and 2, respectively. The chain-growth parameter did not change significantly upon the addition of the amine. There was a shift toward a higher olefin/alkane ratio as the amine competed with hydrogen for adsorption sites, and there was a slight enhancement in the total hydrocarbon production. The latter enhancement is reasonable and may have been caused by the ethyl fragments from diethylamine participating in Fischer–Tropsch chain growth. It is not possible to comment on the absolute yields of alcohols prior to and during the addition of diethylamine because of the sampling techniques used to analyze for alcohols. There was definitely no precipitous drop in alcohol production as was observed by Klier and co-workers in their study.

A cessation of alcohol production with

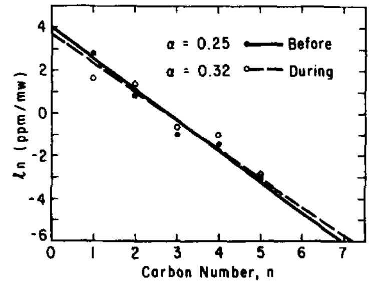

FIG. 2. Flory distribution for alcohols before (—) and during (---) the addition of diethylamine to the feed; 220°C, H_2/CO feed ratio = 3.6, 9.95 atm total pressure.

little effect on hydrocarbon production by diethylamine would suggest that diethylamine was either inhibiting chain growth on the sites where alcohols are produced or was titrating the precursors to alcohols. Diethylamine had little effect on the distribution of alcohols and hydrocarbons and did not inhibit either from forming. These observations suggest a similar chain-growth mechanism occurred on the sites which produced alcohols and on the sites which produced hydrocarbons. These sites may differ only in the type of termination step allowed, alkyl hydrogenation/dehydrogenation to hydrocarbon products and CO insertion leading to oxygenates.

The concept of different sites producing different synthesis products has been reported recently (*12–15*). Egiebor and Cooper (*15*) reported modified-iron catalysts in which the two sites differed in their ability to hydrogenate the alkyl fragment; site 1 (the low-weight site) produced alkanes and olefins and site 2 (the high-weight site) produced only alkanes. Huff and Satterfield (*14*) also found two sites over iron catalysts with site 1 producing 1-olefins, paraffins and oxygenates, and site 2 not producing oxygenates. The origin and nature of the sites in our study remain unknown. Iron is a very complex catalyst. Several bulk phases were shown to be present under synthesis conditions (*2*) and the surface is likely to involve different phases and/or oxidation states of iron as well.

In summary, the iron/silica catalyst displayed a polyfunctionality with regard to oxygenate and hydrocarbon formation. These products appear to form on different sites. The α's for both hydrocarbons and alcohols did not significantly change upon addition of diethylamine suggesting that the mechanism for chain growth on both sites was similar, differing only in the termination step.

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