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Oxygenates Formed from Ethanol during Fischer–Tropsch Synthesis

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Addition of ^{14}C labeled ethanol to a syngas feed ($H_2/CO = 0.78$) results in dehydrogenation to acetaldehyde to establish an equilibrium ratio of alcohol to aldehyde. In addition, ethyl acetate and acetal have been identified, using both gas chromatographic–mass spectroscopic and gas chromatographic–infrared techniques, as significant reaction products that, because of ^{14}C content, are shown to be derived from the added ethanol. Alcohols with greater than two carbons are also formed from ethanol; their relative concentrations suggest that aldol condensation of acetaldehyde contributes to the overall reaction mechanism. In the stirred autoclave reactor, more ethanol is converted to other oxygenates than is incorporated into higher carbon number hydrocarbons; however, ethanol is a chain growth initiator. The data is consistent with significant accumulation of ethanol in the reactor above the concentration in the gas feed when octacosane is used as a solvent with a 10 wt% Fe on high surface area (700 m^2/g) silica support.

INTRODUCTION

Oxygen-containing compounds are found in Fischer–Tropsch products when iron catalysts are employed in the synthesis. These oxygen-containing products have received much attention since the pioneering work of Emmett and co-workers (*1–8*). Emmett's results from a series of isotope labeling studies clearly showed that alcohols could serve as chain initiators for the polymerization reactions. Mechanistic views based on Emmett's results dominated the field for many years. To carry out his studies, Emmett had to resort to gross separation by distillation and to obtain an "average" hydrocarbon composition and ^{14}C label. High-resolution gas and liquid chromatographic techniques were unavailable to Emmett and co-workers and it is truly amazing that they were able to accomplish as much as they did. Schulz and co-workers (*9–14*) have confirmed, and extended, many of the ^{14}C isotope labeling results obtained by Emmett and co-workers. However, these workers did not report the details of the oxygenates formed when alcohols are added to a syngas feed. Since oxygenates, or at least surface oxygen-containing species, play such an important role in mechanistic considerations for synthesis using iron catalysts, a better understanding of the role of these compounds is needed.

EXPERIMENTAL

The experimental system consisted of gas flow regulators, a 1-liter stirred autoclave reactor, hot and cold product traps, and in-line gas chromatography (GC) for gas stream analysis. The catalyst contained 9.2% Fe and was prepared by adding aqueous ferric nitrate to a Davison 923 silica gel (700 m^2/g) using an incipient wetness technique. The impregnated silica was dried at 120°C and then calcined at 450°C for 4 h. The material (120 g) was reduced for 24 h at 450°C in ca. 100 cm^3/min hydrogen flow; the reduced catalyst was then charged to the stirred autoclave reactor. Approximately 500 cm^3 of *n*-octacosane, purified by recrystallization from THF, was added to the reactor and the catalyst rereduced *in situ*. Synthesis runs were carried out at 265°C, 90 psig, CO/H_2 ratio of 0.78, 5 cm^3/sec syngas flow, and 600 rpm reactor stirrer speed. Ethanol, labeled in position 1, was

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pumped into the heated (ca. 100°C) syngas stream immediately prior to entering the reactor; the pump rate was adjusted to provide a 3 vol% ^{14}C label (based on total gas flow). Liquid products were collected in hot (ca. 60°C) or cold (ca. 5°C) traps. Gas passing through the cold trap was sampled and analyzed by one of two GC's: (1) a Carle valve GC (Hacks) using a combination of six columns to effect analysis of CO, H_2, CO_2, and all the hydrocarbons below C_5, and (2) a 6 ft $\frac{1}{8}''$ Porpack R column (Supelco) to obtain analysis of C_5^+ hydrocarbons. Thermal conductivity GC detectors were used so that the GC effluent could be passed through a short heat-traced line directly to a Packard Model 894 gas proportional counter. Prior to ^{14}C detection each effluent peak was burned to CO_2 and mixed with methane quench gas.

Gas chromatographic–mass spectrometric (MS) analyses were performed on a Hewlett-Packard 5985A capillary GC/quadrupole mass spectrometer system. GC separation was carried out on an OV1 WCOT column and mass spectra were recorded every 2 s. The spectrometer was operated in the EI mode at 70 V electron energy and at a source temperature of 150°C. Component identification was aided by search of a mass spectral library.

The infrared (IR) spectra were obtained using Capillary GC/Matrix Isolation-FTIR (GC/MI-FTIR). A commercially available system (Cryolect, Mattson Instruments, Madison, WI) was used. The system consists of a Varian 3700 GC equipped with a split/splitless injector, a Sirius 100 FTIR spectrometer, a Matrix Isolation interface, and a Starlab computer. The configuration of the system is shown in Fig. 1.

Helium doped with 1.2% argon is used as the carrier gas. As the effluent exits the capillary column (DB-5, J & W Scientific) approximately 20% is diverted to the FID. The remainder is directed to the collection disk via a capillary transfer line. The collection disk, which is plated with optically polished gold, is cooled to 13 K by a closed cycle He compressor and cryogenic cold finger. A precision compumotor is used to rotate the disk during deposition. The Ar freezes the components of the sample on the disk as they elute from the column. The FID tracing is then used to locate the peaks on the disk after the GC run is complete. By

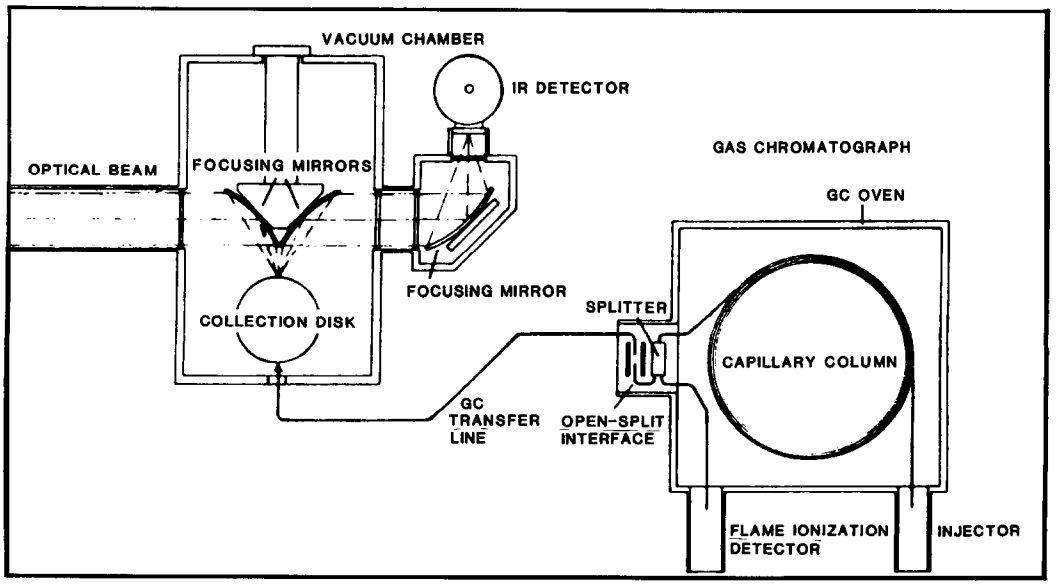

FIG. 1. Schematic of the capillary gas chromatograph/Matrix Isolation/FTIR instrument.

positioning the peaks of interest in front of the focusing mirrors, IR spectra may be obtained (*15*). Because the components are frozen in a fixed position that may be accurately positioned by the precision computer, an optimum number of scans may be taken and averaged to increase the S/N ratio. The spectra used in this paper were taken using 32 scans at 4 cm^{-1} resolution.

RESULTS

Results for the paraffin product distribution (defined as % paraffin = (C paraffin)$_i$/(C total products)$_i$) are presented in Fig. 2 for (a) CO/H_2 syngas feed only (■) and CO/H_2 syngas with added ethanol (○). The product distributions are similar for the two runs. Thus, adding ethanol at this concentration does not materially alter each carbon number product distribution in this carbon number range.

Several oxygenated products were formed from ethanol (Table 1). Possible

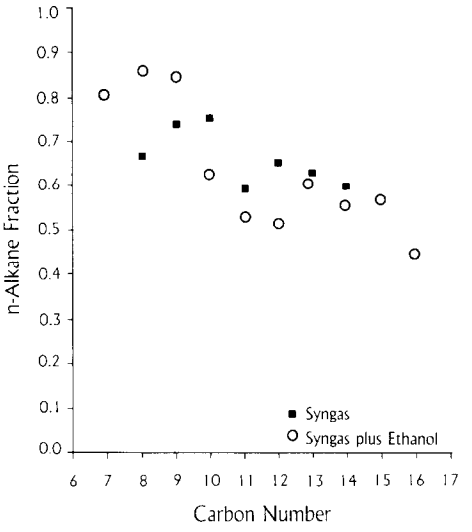

FIG. 2. Fraction of *n*-alkane, based upon *n*-alkane plus *n*-alkenes, formed for each carbon number from C_7 to C_{16} for syngas (■) and for syngas plus ethanol (○) conversions.

TABLE 1

Oxygenated Compounds Formed from Syngas alone and When ^{14}C Labeled Ethanol Was Added

Compound	Reaction mixture		Relative radioactivity ^{14}C/mole[a]
	CO/H_2 (g)	$CO/H_2/C_2H_5OH$ (g)	
Alcohols			
CH_3OH (methanol)	0.373	0.912	
C_2H_5OH (ethanol)	0.536	12.6	1.0
C_3H_7OH (1-propanol)	0.210	0.293	[b]
C_4H_9OH (1-butanol)	0.038	0.067	[b]
$C_5H_{11}OH$ (1-pentanol)	0.01		
Aldehydes			
CH_3CHO (acetaldehyde)	0.07	1.27	1.09
Esters			
$CH_3CO_2CH_3$ (methylacetate)	—	0.40	0.94
$CH_3CO_2C_2H_5$ (ethylacetate)	—	6.11	1.93
Acetals			
$CH_3CH(OC_2H_5)_2$ (acetal)	—	0.134	[b]
$CH_3CH(OCH_3)(OC_2H_5)$		0.084	[b]
$CH_3CH(OCH_3)$		0.050	[b]
$CH_3CH(OC_2H_5)(OC_3H_7)$		0.025	[b]

[a] Activity relative to ethanol = 1.0.

[b] Small amounts of compound and/or absence of reliable thermal conductivity response factor allows only approximate relative activity determinations.

pathways for these products are outlined below:

$$C_2H_5OH \rightarrow CH_3CHO \text{ (acetaldehyde)} + H_2 \quad (1)$$

$$2CH_3CHO \rightarrow CH_3C{-}O_2C_2H_5 \text{ (ethylacetate)} \quad (2)$$

$$CH_3CHO + 2C_2H_5OH \rightarrow CH_3CH(OC_2H_5)_2 \text{ (acetal)} \quad (3)$$

$$CH_3CHO + HCHO \rightarrow CH_3CO_2CH_3 \text{ (methylacetate)} \quad (4)$$

Mixed acetals are formed in a manner similar to acetal except that another alcohol is substituted for ethanol.

The GC trace for a sample of the aqueous layer from the cold trap is shown in Fig. 3; no attempt was made to optimize the GC analysis since it was used for qualitative purposes only. Of interest for this study was the identification of the peaks at retention times 3.13 and 5.75 min. The IR spectrum for the compound eluting at 3.13 min

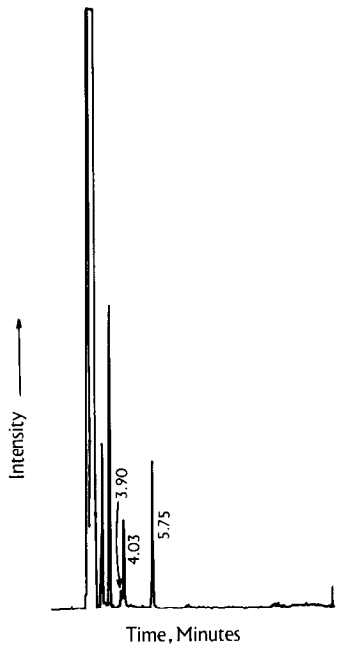

FIG. 3. Capillary GC trace for an aqueous phase of a cold trap sample; the peaks correspond to the GC–IR spectra shown in the following figures.

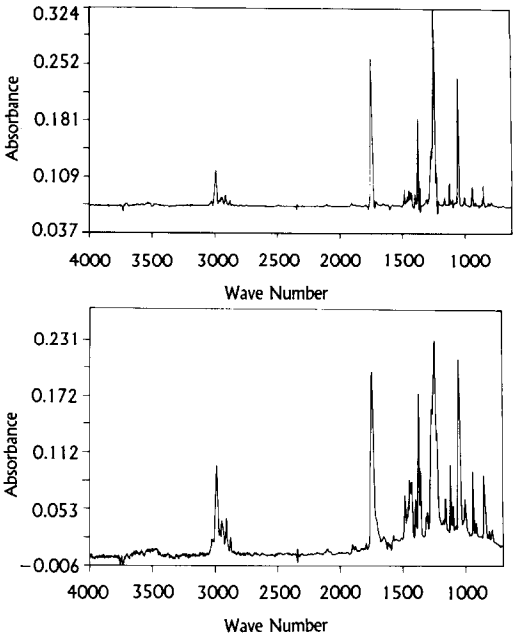

FIG. 4. Ethyl acetate GC–IR spectrum (top) and the GC–IR spectrum (bottom) of the peak eluting at 3.13 min. in Fig. 3.

is shown in Fig. 4 (bottom) together with the spectrum for a sample of ethyl acetate (top). The agreement between the two spectra is excellent and identifies the compound responsible for the 3.13-min peak as ethylacetate. Likewise, the infrared spectrum of diethylacetal and the peak eluting at 5.47 min clearly confirm that the peak eluting at 5.47 min is acetal as clearly as the spectra in Fig. 4 identify ethylacetate.

An ion current GC–MS spectrum, with peak identification, is shown in Fig. 5. The identification of the indicated peaks was accomplished by matching the electron impact (EI) spectrum with published EI spectra.

Acetaldehyde eluted so quickly that it was not amenable to identification by either GC–MS or GC–IR techniques without considerable additional effort. Hence, this compound was identified by confirming its retention time by doping a Fischer–Tropsch sample with an authentic sample of acetaldehyde.

A sample of the silica used as a support

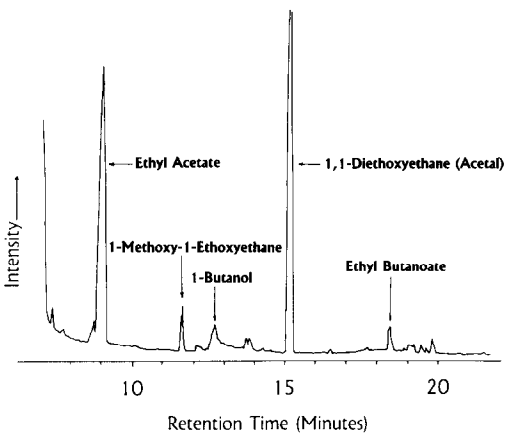

FIG. 5. GC–MS ion current trace for an aqueous phase from a cold trap sample.

for the iron catalyst was examined for catalytic activity. A syngas mixture, when passed over the silica at 260°C and 1 atm, did undergo measurable conversion. When ethanol was added to the syngas feed at a level equivalent to that utilized in the runs with the Fe–SiO_2 catalyst, both dehydrogenation and dehydration occurred. During the initial 5 h the dehydration activity declined to an insignificant level; however, a low level of dehydrogenation to form aldehyde persisted during 24 h. At this time the ethanol feed was replaced by an equal molar mixture of ethanol and acetaldehyde. This mixture underwent conversion over the silica support to produce significant quantities of ethyl acetate and acetal.

DISCUSSION

Analytical limitations prevented Emmett and co-workers from making a detailed analysis of the oxygenates in their ^{14}C tracer studies. The introduction of gas chromatographic analysis allowed for more detailed analysis of the products as was done, for example, by one of the pioneers, Pichler, of Fischer–Tropsch synthesis (*14*). Included in Ref. (*14*) was an analysis for C_1 through C_5 alcohols but other oxygenates were not indicated by the GC for alcohols that were produced by a promoted Co catalyst; Ref. (*11*) presents analysis of oxygenates formed using an iron catalyst.

The oxygenates produced in the current study are readily identified by the ^{14}C label if they are derived from the added ^{14}C labeled alcohol. A number of these oxygenates have been identified by GC–MS and/or GC–IR techniques. The use of GC–IR techniques is in its infancy and the quality of the IR spectra, combined with the high-resolution capability of capillary GC and the unique quantitative capabilities of GC and IR, points toward rapidly expanding usage of this technique. In Fischer–Tropsch studies, the qualitative and quantitative application for analysis for alkenes, alcohol, or carbonyl compounds in peaks comprised of coeluting compounds should make this an important analytical procedure.

The presence of acetaldehyde is not surprising since aldehydes and ketones have been previously reported. The data in Fig. 6 show that ethanol and acetaldehyde are at, or near, equilibrium concentrations for the conditions utilized for this run. The ratio of ethanol/acetaldehyde in the gas phase is essentially the same when the reactant feed is CO/H_2/ethanol or when ethanol in the feed is replaced by an approximately equimolar mixture or ethanol and acetaldehyde (Fig. 6). thus, dehydrogenation of the ethanol added as a ^{14}C labeled reactant to acetaldehyde (reaction (1)) readily accounts for the

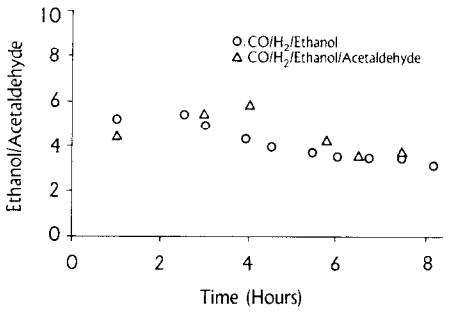

FIG. 6. Plot showing that similar ethanol/acetaldehyde ratios are obtained when the syngas feed contains only ethanol (○) or an equal molar mixture of ethanol and acetaldehyde (△).

presence of acetaldehyde. The ethanol and acetaldehyde have essentially the same specific activity (Table 1) as is required for a rapidly equilibrating mixture of these two compounds.

For homogeneous catalytic systems, the synthesis of a series of low-molecular-weight alcohols and esters is readily accomplished (*16–21*). For example, Knifton *et al.* (*21*) found that, for a series of ruthenium bimetallic catalysts, alcohol carbonylation of methanol provided a reaction pathway to produce acetic acid and ethanol. In the present study, however, the pathway to ethylacetate formation cannot be through carbonylation to form the acetic acid. First, while more methanol is formed when ethanol was added than when it was absent, the amount of ethylacetate exceeds by a factor of 10 the total methanol plus methylacetate formed when syngas only was used as a feed. Second, and more convincing, is that the relative ^{14}C activity of ethylacetate is essentially twice that of ethanol. Methanol and CO present when ^{14}C labeled ethanol was added to the feed does not contain a detectable level of ^{14}C. Thus, any acetic acid formed from methanol and CO is, at our detection level, unlabeled. If this unlabeled acetic acid reacted with ^{14}C labeled ethanol, the relative activity of the ester would be 1 rather than the 1.9 observed experimentally. This means that the predominate quantity of both the acid and alcohol that forms the ester must have come from the added ^{14}C labeled alcohol.

Aldol condensation of acetaldehyde, followed by dehydration and hydrogenation of the c=c unsaturation, produces butyraldehyde; the presence of a larger quantity of ^{14}C labeled ethyl butanoate than of ethyl propanoate is indicative of a minor amount of product being formed by aldol condensation.

The presence of small amounts of ^{14}C containing normal alcohols with three or more carbons suggests that either a small amount of ethanol undergoes carbonylation with subsequent reduction and/or that ethanol initiates a chain that is followed by CO propagation and then a termination step that produces an alcohol. The present data does not permit us to discriminate between these two possibilities. Likewise, 5 to 15% of the added ^{14}C appears to be incorporated into hydrocarbons; a discussion of this aspect of the synthesis is beyond the scope of this paper.

The results of the conversion of ethanol and acetaldehyde with the silica support in the absence of iron suggest that the conversion with the 10 wt% $Fe–SiO_2$ indicate that some of the oxygenates are formed as a bifunctional reaction. Hence, it appears that the following reaction scheme is applicable:

$$C_2H_5OH \rightleftarrows CH_3CHO \text{ Fe function}$$

$$2CH_3CHO \rightarrow CH_3C(=O)OC_2H_5 \quad \text{silica support}$$

$$CH_3CHO + 2C_2H_5 \rightleftarrows CH_3C(OC_2H_5)_2H \quad \text{silica support}$$

The above scheme is further supported by results from a doubly promoted, unsupported UCI C-73 catalyst. With this catalyst the ethanol is dehydrogenated to acetaldehyde but ethyl acetate and acetal are formed in insignificant, or undetectable, amounts under similar reaction conditions. Consequently, the silica should not be viewed as an inert support for the Fischer–Tropsch synthesis.

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