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Fischer-Tropsch Synthesis: Reaction Pathways for ^{14}C-Labeled Acetic Acid

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Abstract Reaction pathways for ^{14}C labeled acetic acid (at both carboxylic and methyl positions) added during Fischer-Tropsch synthesis over a doubly promoted fused iron catalysts were studied in a CSTR at 100 psig, 270 °C and ca. 90% CO conversion. The addition of acetic acid slightly affected the CO conversion but results in a significant reduction in H_2 conversion. Both the unlabeled and labeled acetic acid addition caused a large decrease in the alkene ratio for C_2 hydrocarbons as compared to an increase for the C_3 and C_4 hydrocarbons suggesting a direct formation pathway of ethane from added acetic acid. The 1-alkene/2-alkene fraction was found to increase significantly when acetic acid was added and returned to the original value once the addition is terminated, indicating inhibition of hydrogenation activity of the catalyst by acetic acid. Distribution of ^{14}C suggests some C–C bond rupture and direct formation of ethane from labeled acetic acid. In the case of 1-^{14}C labeled acetic acid addition, the gradual increase of the relative molar activity (^{14}C content per mole) with carbon number reveals that ^{14}C containing part of acetic acid initiate chain growth and also participates in the chain propagation for hydrocarbon formation in FTS. When acetic acid labeled at methyl position was added, the results indicated that ^{14}C containing part of acetic acid participates in chain initiation only. The addition of acetic acid decreases methane and methanol selectivity while it increases ethanol, acetaldehyde and acetone selectivity in FTS. Reaction of acetic acid during FTS was found to produce products like ethyl butanoate, ethylene glycol, and its ether, 1,2-diethoxyethane which are not generally observed in the normal FTS product spectrum. The results indicate that acetic acid is not a significant intermediate in FTS with an iron catalyst. ^{14}C-distribution in most of the labeled oxygenate compounds are consistent with the hydrogenation of the acetic acid to acetaldehyde and/or ethanol as primary products followed by secondary reaction of these two primary oxygenate products.

Keywords Fischer-Tropsch synthesis · Iron catalyst · Tracer · Labeled acetic acid · Reaction pathways · Oxygenates

1 Introduction

Among the products of the Fischer-Tropsch synthesis (FTS) with an iron catalyst are oxygenates, especially at lower CO conversions. The CO insertion mechanism to produce oxygenates was an accidental discovery during addition of high concentrations of ethene and this reaction has become known as the oxo or hydroformylation reaction [1]. Both iron and cobalt carbonyls are catalysts for the hydroformylation reaction but are frequently utilized for this reaction under conditions that may differ from normal FTS conditions [2].

Syntheses pathways of oxygenates from syngas are relevant for a fundamental understanding of FTS. Mechanistic investigations of FTS have shown that that surface hydrocarbon species appear, either as intermediates on the path to oxygenate formation, or as products of oxygenate decomposition. For example, higher oxygenate synthesis from syngas has been performed on Rh and other Group

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VIII metals. It is typically proposed that hydrocarbon ligands are assembled by stepwise addition of CH_x-monomeric units, and the chain-growth of the hydrocarbon backbone is terminated by CO-insertion to form surface-bound acyl species. Hydrogenation of acyl species may lead to aldehyde or alcohol [3–5]. Microscopic reversibility suggests that elementary reaction steps involved in oxygenate synthesis should be same as those characterizing the decomposition of the same oxygenates on the corresponding surfaces used as catalysts for their synthesis. Hence by studying the reaction pathways followed by oxygenates during their conversion on FTS catalysts, it is possible to gain substantial insight into mechanistic details concerning oxygenate formations in FTS.

Comparison of ^{14}C distribution when labeled alcohols were added to the synthesis gas revealed that alcohols initiate chain growth but do not propagate chain growth in FTS [6]. Alcohols also undergo direct hydrogenolysis to eliminate water and to produce the same carbon number hydrocarbons that are predominately alkanes. Kummer and Emmett [7] studied FTS with added ^{14}C-labeled primary alcohols (1.5 vol% to a 1:1 H_2:CO synthesis gas) using promoted and unpromoted iron catalysts at about 235 °C and 1 atmosphere pressure. The results indicated that the primary alcohol adsorbed on the iron catalyst acts as an initiator to build up higher hydrocarbons. It was also found that n-alcohol initiation leads to predominantly *n*-hydrocarbons whereas the iso-alcohol initiates chain growth that leads predominantly to iso-hydrocarbons.

Oxygenates produced during the FTS undergoes secondary reactions. It was found that at the exit of a fluidized iron catalyst bed, ethanol, acetic acid and acetaldehyde are in thermodynamic equilibrium in the temperature range 473–600 K [8]. When ethanol, acetaldehyde or ethyl acetate was added individually to the syngas, additional amounts of the other two compounds are always found in the exit gas. At higher temperature acetone was always found and at 510 K the ratios of these compounds were much higher than the thermodynamically expected ratios. This implies that acetic acid was not formed by subsequent oxidation of the primary alcohol by water, nor was acetaldehyde formed by de-hydrogenation of ethanol. The reverse reactions, i.e., the hydrogenation of acetic acid or of acetaldehyde to form ethanol, are also feasible. Little consideration has been given to the conversion of added acetic acid during FTS, although very high selectivity towards acetic acid in oxygenates synthesized from syngas has been observed in special cases [9–10]. The objective of the present study is to examine the secondary reactions of acetic acid (unlabeled and ^{14}C labeled at carboxylic and methyl carbon positions) under medium pressure Fischer-Tropsch synthesis condition with a doubly promoted iron catalyst.

2 Experimental

The experiments were conducted in a 1 l continuous stirred tank reactor (CSTR) equipped with a magnetically driven stirrer with turbine impeller, gas-inlet lines, and a vapor outlet line with a SS fritted filter (2 micron) placed external to the reactor. A tube fitted with a SS fritted filter (0.5 micron opening) extends below the liquid level of the reactor for withdrawing reactor wax (rewax) to maintain a constant liquid level in the reactor. Separate mass flow controllers were used to control the flow of hydrogen and carbon monoxide at the desired rate. The gases were premixed before entering to the reactor. Carbon monoxide was passed through a vessel containing lead oxide-alumina pellets to remove traces of iron carbonyl. The mixed gases entered the CSTR below the stirrer operated at 750 rpm. The reactor temperature was regulated (±1 °C) using a temperature controller. Polywax 3,000 (polyethylene fraction with average molecular weight of 3,000), purchased from Baker Petrolite, Inc., was used as start-up solvent.

A doubly promoted fused iron catalyst (C-73, United Catalysts, Inc.) was used. The particle size of the C-73 catalyst was in the range of 0.035–0.18 mm. The catalyst was reduced in a fixed bed reactor under flowing hydrogen for 72 h at 400 °C, cooled down to room temperature under hydrogen, passivated with 1% oxygen in nitrogen, transferred to the CSTR (containing 300 g of melted Polywax 3,000) pneumatically using UHP nitrogen, and then re-reduced in situ at 300 °C for 48 h with H_2. A total of 99.1 g catalyst was loaded into the reactor.

The FTS was effected at 270 °C, 100 psig total pressure with an initial syngas space velocity (SV) of 18 slph. The H_2/CO ratio in the feed gas was 1.2. The conversions of CO and H_2 were obtained by gas-chromatography analysis (with a thermal conductivity detector) of the exit gas. Conditions were adjusted to give approximately (85–90)% conversion of the CO. The reaction products were collected in three traps maintained at different temperatures—a hot trap (200 °C), a warm trap (100 °C) and a cold trap (0 °C). The products were separated into different fractions (rewax, wax, oil and aqueous) for quantification. However, the oil and the wax fraction, after separation from water, were mixed prior to GC analysis.

The sodium salt of ^{14}C-labeled (at carboxylic and methyl positions) acetic acids (CH_3^{14} COONa, (MC125, 1 mCi; and $^{14}CH_3$ COONa, (MC213, 1 mCi) were procured from Moravek Biochemicals and Radiochemicals, CA, USA and hydrolyzed with deionized water to convert the salt to the corresponding acid form. The total run with one catalyst loading lasted for 4536 h time-on-stream (TOS). The addition of unlabeled acetic acid (ACS reagent, ≥99.7%, Sigma-Alrdich, Inc.) was started at 1294 h TOS with a flow rate of 1.43 mL/h and continued for 7 h (end of addition at 1,301 h TOS). The addition of carboxylic labeled acetic acid ($CH_3\,^{14}COOH$) was started at 1,797.5 h TOS with a flow rate of 1.51 mL/h and continued for 7 h (end of addition at 1,804.5 h TOS). The addition of methyl labeled acetic acid ($^{14}CH_3COOH$) was started at 1,989 h TOS with a flow rate of 1.49 mL/h and continued for 7.5 h (end of addition at 1,996.5 h TOS). The molar ratio of carbon atom from acetic acid to total carbon (from acetic acid and CO) fed to the reactor (i. e., $C_{AcOH}/C_{AcOH} + C_{CO}$) was maintained at about 0.02.

The ^{14}C content of each gaseous product was determined using a proportional counter (PC) connected in series with the GC equipped with OV-1 column. The effluent from the GC (equipped with thermal conductivity detector) was passed directly to a combustion tube containing CuO and then to a trap to remove water. The dry CO_2 produced in the combustion tube was passed through a proportional counter following the addition of methane quench gas. The GC column and conditions were chosen to effect maximum separation of the compounds eluting near the labeled products. Combining the output from the GC and PC permits an analysis for H_2, CO, CO_2, C_1–C_6 hydrocarbons and other gaseous products containing ^{14}C. This result was sufficient to define the activity per mole of the products relative to the labeled acetic acid, the data of interest for this article.

The radioactive products produced during the addition of labeled acetic acid are diluted with non-radioactive products formed during the normal synthesis; hence, all of the reported relative molar activities (^{14}C per mole) in this paper are corrected for this dilution effect by multiplying the observed relative molar activity of a particular compound with a correction factor. If the concentration of the compound before and during addition of acetic acid are A and B, respectively, then the correction factor (CF) for the component is: B/(B–A). When A = B, no correction factor is needed and in practice the correction was only made when there was a significant difference in the two periods. Thus, the corrected relative molar activity is the observed relative molar activity multiplied by CF.

3 Results and Discussion

The C-73 catalyst had been used in an earlier run for over 4,500 h of synthesis with the starting conversion being the same as the conversion at the end of the run (62% CO conversion); that is, the activity did not decline during this run even though there were periods where alkene and alcohol addition was practiced. Thus, this catalyst was used for this run with acetic acid. The C-73 catalyst was prepared by United Catalysts, Inc. (now Süd-Chemie, Inc.) using a molten metal preparation where the mixture is melted by passing a current through the mass of iron and added catalyst promoters. The composition of the catalyst varied with each preparation and over the years. The sample utilized in this study contained alkali (K, Ca, and others) and structural promoters (alumina, silica, etc.) in low levels. The alkali content was low enough that the catalyst would produce low-alpha products (alpha ca. 0.73 producing products with an average carbon number of four).

The conditions were selected for those typical of low-alpha synthesis conditions (270 °C and 8 atm) similar to those used in our earlier studies with this catalyst which utilized the addition of ^{14}C-labeled compounds [6]. The space velocity in the present study was such that the conversion was higher (ca. 90% CO rather than the 62% used in earlier studies) and the H_2/CO ratio was 1.2 rather than the 0.7 used in most of the earlier studies. The concentration of acetic acid produced by similar low-alpha alkali containing iron catalysts is illustrated in Fig. 1. The fraction of acetic acid is highest at low CO conversion and decreases with increasing CO conversion.

The addition of acetic acid caused a decrease in the conversion of hydrogen during the addition of unlabeled acetic acid at about 1,300 h on-stream and a slight decrease in the conversion of CO (Fig. 2). The conversion of CO and H_2 both decreased after the second addition of labeled acetic acid at 1,989 h TOS. The conversion did not recover after the second addition, suggesting that there was a catalyst poison in the ^{14}C-labeled acid. One severe poison for the iron carbide catalyst is the fluoride ion;

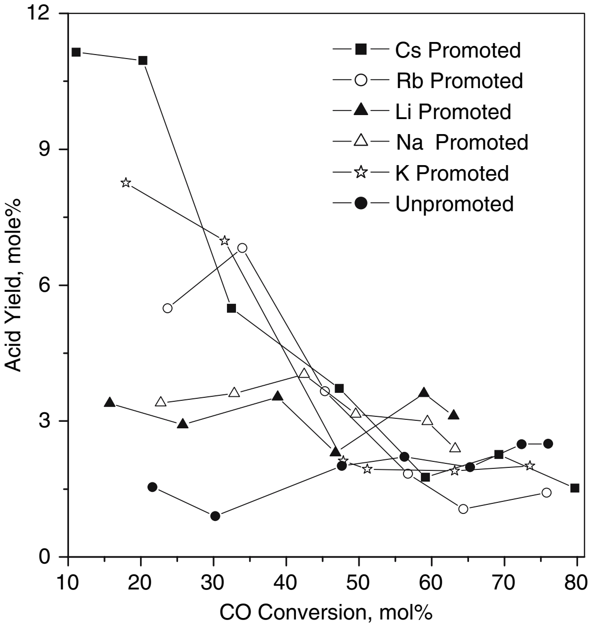


Fig. 1 Total acetic acid production against CO conversion in FTS using Group 1A alkali metal promoted "100 Fe/4.6 Si/1.44 Metal" catalyst

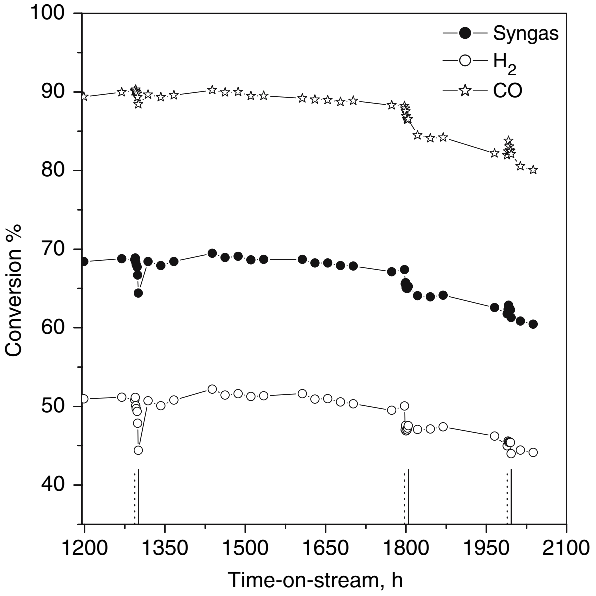


Fig. 2 Conversion profile of CO, H_2 and syngas against reaction time (for the period when acetic acids were added) for FTS at 270 °C, 100 psig. The syngas SV was 18 slph and H_2/CO ratio was 1.2. The dotted line on the X-axis indicates the starting time for acetic acid addition while the immediate solid line indicates the time when the corresponding addition was stopped

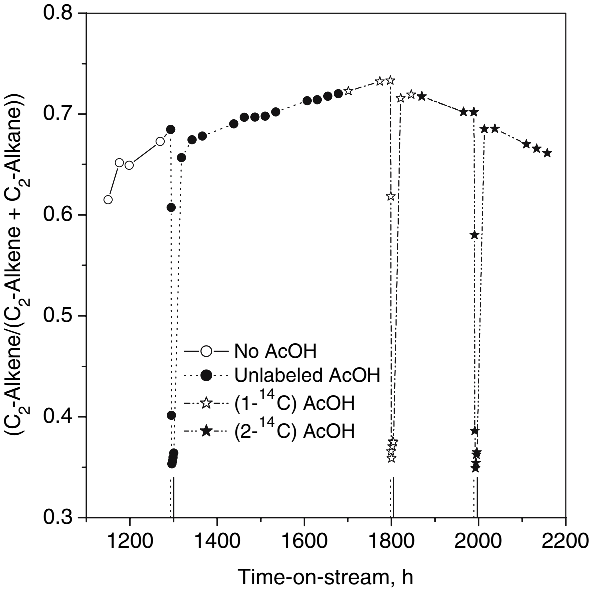
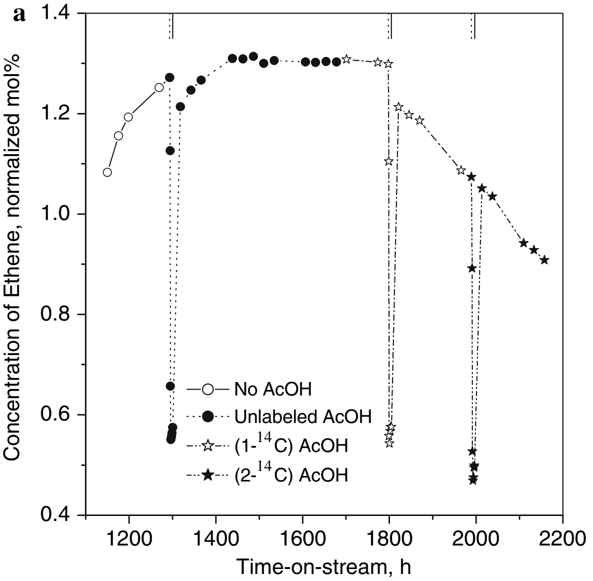


Fig. 3 The variation of the ratio of C_2 alkene to total C_2 hydrocarbon (i.e., alkene and alkane) produced against reaction time during the addition of labeled and unlabeled acetic acid in FTS at 270 °C and 100 psig. The dotted line on the X-axis indicates the starting time for acetic acid addition while the immediate solid line indicates the time when the corresponding addition was stopped

however, since the labeled acetic acid was purchased the nature of the catalyst poison is not known. The behavior for the second addition of ^{14}C-labeled acetic acid was different in that the CO conversion increased during the addition but continued to decline after the addition of the labeled acid was terminated. The alpha value had to be determined using only low carbon (less than about carbon number 40) and did not show a significant difference when acetic acid was added.

The alkene/(alkene + alkane) fraction for C_2 products are shown in Fig. 3. The variation in concentration of ethene and ethane with and without acetic acid addition is also shown in Fig. 4a and b, respectively. Both the unlabeled and labeled acetic acid addition clearly caused a large decrease in the fraction of the alkene which decreased from about 0.65 to about 0.35. The alkene fraction for the C_3-fraction (Fig. 5) and C_4-fraction (Fig. 6) both increase significantly when acetic acid was added. While the increase in the alkene fraction for the C_3- and C_4-hydrocarbons was not as large numerically as was the decrease in the alkene fraction for the C_2-hydrocarbons, it was in the opposite direction. The 1-alkene/2-alkene fraction increased significantly when acetic acid was added and returned to the original value as soon as the addition of acetic acid was terminated (Fig. 7). Considering the above results for the fraction of alkene product, it appears that the low value for the C_2-fraction is due to a combination of the direct formation of ethane from the added acetic acid (and/or ethanol formed from acetic acid) and the increase in the ethane product in contrast to the propane and butane products, which were lower during acetic acid addition. It was shown in earlier experiments that ethane forms directly from ethanol when using the C-73 catalyst [6].

Acetic acid was added in three separate periods and the conversion of acetic acid was almost complete during the synthesis (98.9–99.3%). The significant change in H_2 conversion compared to slight change in CO conversion might indicate weak adsorption of acetic acid relative to CO but stronger adsorption relative to H_2, and/or, competitive adsorption of acetic acids to the catalytic sites active for H_2 adsorption. The added acetic acid decreased the hydrogenating characteristic of the C-73 catalyst as reflected in the increase in the alkene ratio for C_3 and C_4 hydrocarbons (alkene ratio for C_2 hydrocarbons is not considered due to proposed direct production of ethane from added acetic acid). This may be due to inhibited adsorption of hydrogen by acetic acid. The increase in olefin ratio for C_3 and C_4 hydrocarbons suggests competitive adsorption of acetic acid and 1-alkene in the same active sites on the catalyst surface, thus inhibiting the secondary reactions of 1-alkene. This can be further supported by the observed increase in 1-alkene/2-alkene ratio for C_4 hydrocarbons as presented in Fig. 7. The observation of a decrease in the hydrogenation activity by the addition of oxygenates is in agreement with the results reported by several researchers using promoted iron catalysts [11–13].



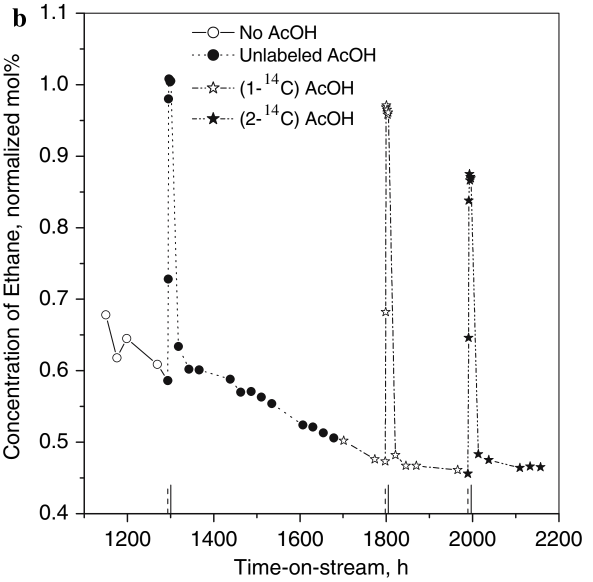


Fig. 4 The variation of (**a**) concentration of ethane; and (**b**) ethane during Fischer-Tropsch synthesis with and without acetic acid addition. The dotted line on the X-axis indicates the starting time for acetic acid addition while the immediate solid line indicates the time when the corresponding addition was stopped

The conversion of a synthesis gas containing ^{14}C-labeled acetic acid with doubly promoted iron catalyst provides products which contained radioactivity. Raje and Davis [14] presented a mechanistic description of different scenarios regarding the incorporation of labeled atom generated from radioactive tracer molecules added during the synthesis. If the ^{14}C labeled molecules are added during FTS, then a plot of relative molar activity against increasing carbon number of products can reveal four different reaction pathways. If the added labeled molecule served only to initiate chain growth, the activity per mole of products should remain constant with increasing carbon number. If the added labeled molecule functions as a chain propagator, the plot of ^{14}C per mole of product should increase by a constant amount with each increase in carbon

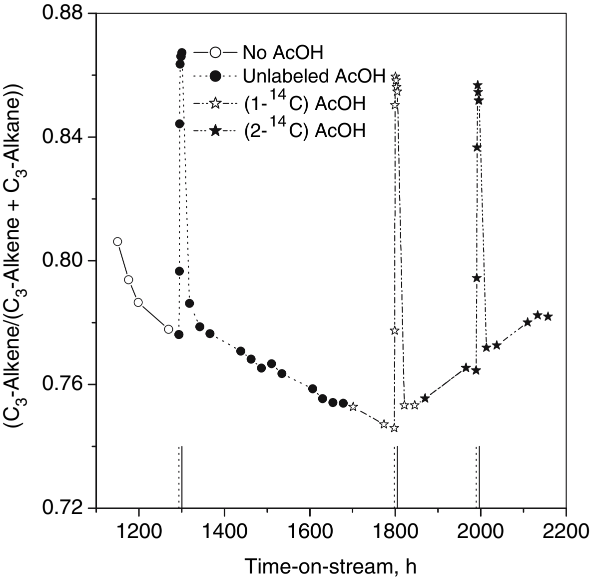


Fig. 5 The variation of the ratio of C_3 alkene to total C_3 hydrocarbon (i.e., alkene and alkane) produced against reaction time during the addition of labeled and unlabeled acetic acid in FTS at 270 °C and 100 psig. The dotted line on the X-axis indicates the starting time for acetic acid addition while the immediate solid line indicates the time when the corresponding addition was stopped

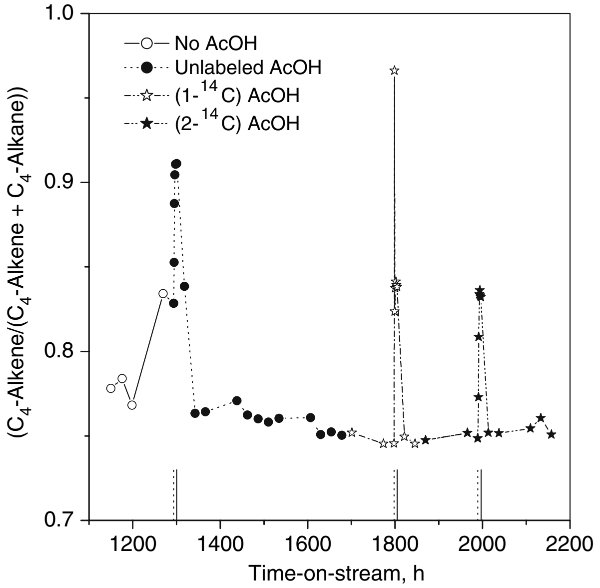


Fig. 6 The variation of the ratio of C_4 alkene to total C_4 hydrocarbon (i.e., alkene and alkane) produced against reaction time during the addition of labeled and unlabeled acetic acid in FTS at 270 °C and 100 psig. The dotted line on the X-axis indicates the starting time for acetic acid addition while the immediate solid line indicates the time when the corresponding addition was stopped

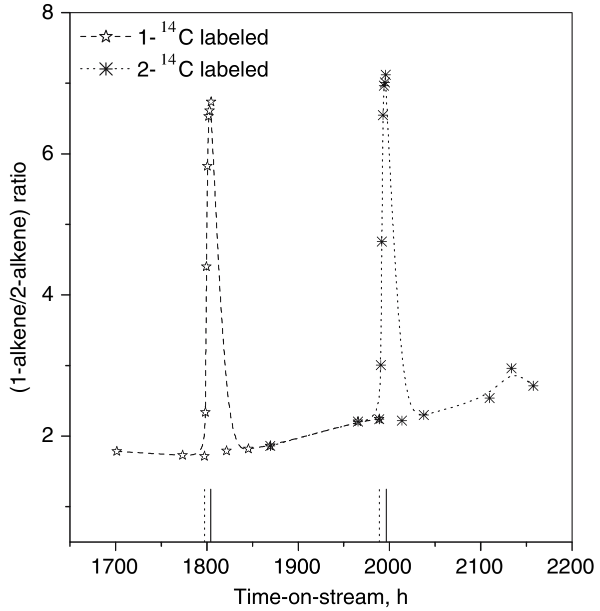


Fig. 7 The variation in the (1-alkene/2-alkene) with the addition of labeled and unlabeled acetic acid during FTS at 270 °C and 100 psig, $H_2/CO = 1.2$ with a doubly promoted iron catalyst (CO conversion ca. 85%). The dotted line on the X-axis indicates the starting time for acetic acid addition while the immediate solid line indicates the time when the corresponding addition was stopped

number so that the slope of the straight line should be one. Similarly, if the carbon from ^{14}C-labeled tracer molecule become equivalent to that of unlabeled CO from syngas, then the slope of the line should be one. If the added ^{14}C-labeled molecules were to initiate and propagate chains in a pathway that is independent of the FTS network, then the distribution of ^{14}C per mole of product should increase with increasing carbon number to yield a straight line of slope one, but the odd-carbon number compounds should not contain any activity.

The plot of relative molar activities of C_1–C_6 hydrocarbons, CO_2 and ethanol determined from the analysis of product gas mixture formed during the FTS when 1-^{14}C labeled or 2-^{14}C labeled acetic acid was added are shown in Figs. 8 and 9, respectively. The gradual increase of the relative molar activity with carbon number (from one to six) shown in Fig. 8 (inset) reveals that acetic acid labeled with ^{14}C at carboxylic position initiate chain growth and also participates in the chain propagation for hydrocarbon synthesis pathways in FTS. The molar activity of ethanol and CO_2 was significant. The activity of ethane was higher than ethene which supports the direct formation of ethane from acetic acid (and/or ethanol) as discussed earlier. A different distribution of relative molar activity of the compounds in the gas phase was obtained when acetic acid labeled with ^{14}C at methyl position was added (Fig. 9). Ethanol, as in the case of 1-^{14}C labeled acetic acid addition, was found to contain high activity; however, CO_2 did not contain a measurable amount of ^{14}C. The relative molar activity of methane was much higher than what was observed with 1-^{14}C labeled acetic acid addition. The relative molar activity of ethane was found to be highest in magnitude among the C_1 to C_6 hydrocarbons, supporting earlier claims of a direct formation pathway. The higher

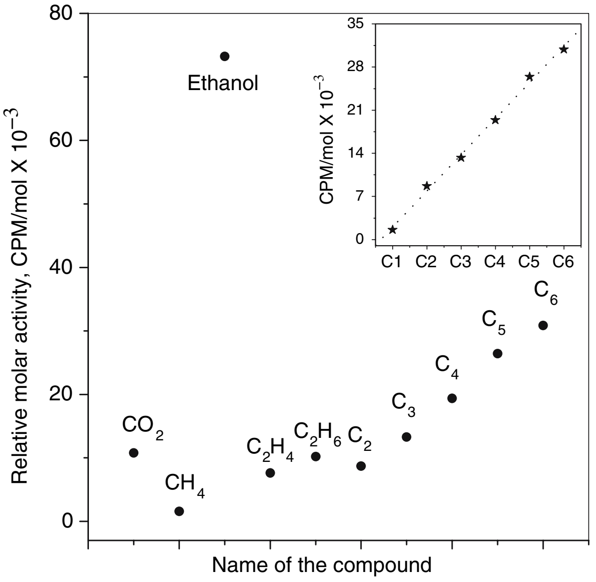


Fig. 8 The relative molar ^{14}C activity of gaseous products after 7 h of addition of 1-^{14}C labeled acetic acid at a flow rate of 1.51 mL/h during FTS at 270 °C and 100 psig, $H_2/CO = 1.2$ with a doubly promoted iron catalyst (CO conversion ca. 85%)

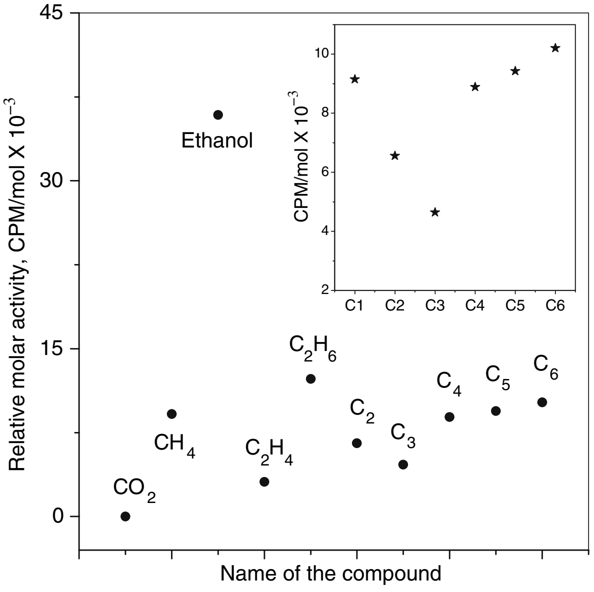


Fig. 9 The relative molar ^{14}C activity of gaseous products after 7.5 h of addition of 2-^{14}C labeled acetic acid at a flow rate of 1.49 mL/h during FTS at 270 °C and 100 psig, $H_2/CO = 1.2$ with a doubly promoted iron catalyst (CO conversion ca. 85%)

activity of methane and ethane than the other hydrocarbon suggests that these two components are generated directly by decarboxylation/hydrogenolysis of labeled acetic acid and not via stepwise chain growth/propagation. The relative molar activities of C_4–C_6 hydrocarbons were essentially constant, suggesting that 2-^{14}C labeled acetic acid participated in chain initiation only.

The changes in the concentration of oxygenates in the aqueous phase when unlabeled acetic acid was added are shown in Figs. 10 and 11. Similar changes were noted when the ^{14}C-labeled acetic acid was added. It is clear that a major conversion of acetic acid was the hydrogenation to ethanol, and acetaldehyde is anticipated to be formed also by hydrogenation. Acetone is formed and this is likely to be the result of the ketonization reaction where two acetic acid molecules extrude CO (or CO_2) and the remaining fragments combine to form acetone, and isopropanol by hydrogenation of the acetone. The above mentioned pathway for acetone formation can be justified from Fig. 12 where the relative molar activity of ethanol, acetaldehyde and acetone are compared when 1-^{14}C and 2-^{14}C labeled acetic acids are added. The relative molar activity of acetone in the case of 2-^{14}C labeled acetic acid was much higher than the 1-^{14}C labeled case although the activities of ethanol and acetaldehyde were comparable in both cases. The increase in 1-butanol can result from the aldol reaction of acetaldehyde and the subsequent hydrogenation of the initial product:

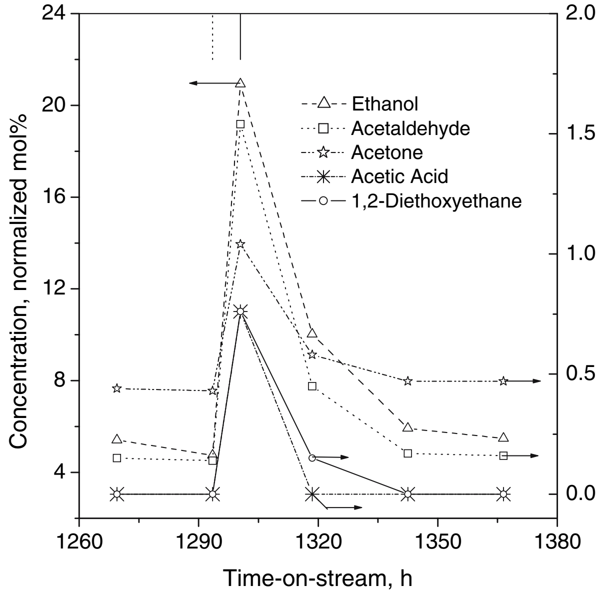


Fig. 10 The variation in the concentration (in the aqueous phase) of different oxygenates produced in FTS at 270 °C and 100 psig with addition of unlabelled acetic acid (flow rate of acetic acid = 1.43 mL/h and total duration of addition = 7 h). The dotted line on the X-axis indicates the starting time for acetic acid addition while the immediate solid line indicates the time when the corresponding addition was stopped

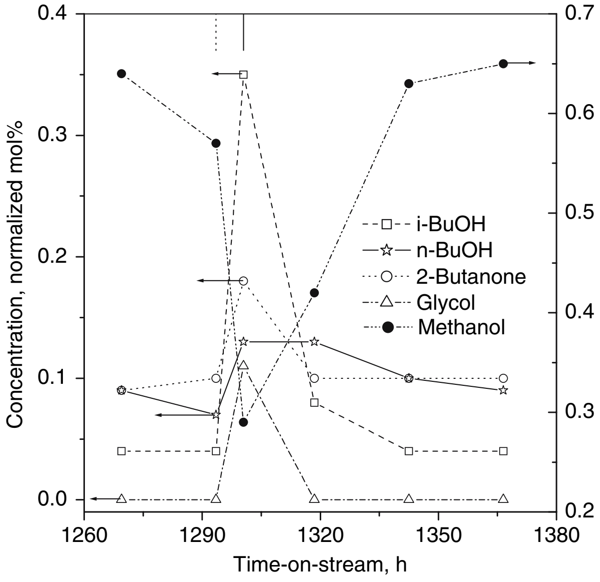


Fig. 11 The variation in the concentration (in the aqueous phase) of different oxygenates produced in FTS at 270 °C and 100 psig with addition of unlabelled acetic acid (flow rate of acetic acid = 1.43 mL/h and total duration of addition = 7 h). The dotted line on the X-axis indicates the starting time for acetic acid addition while the immediate solid line indicates the time when the corresponding addition was stopped

$$2CH_3CHO \rightarrow CH_3CHOHCH_2CHO \rightarrow CH_2 = CHCH_2CHO \xrightarrow{H_2} CH_3(CH_2)_2CH_2OH$$

The increase in the formation of 2-butanol and 2-butanone during the addition of acetic acid is more difficult to explain.

The concept of common reaction pathways and intermediates for synthesis of hydrocarbons and oxygenates in FTS has been debated for a long time. It was proposed by Tau et al. [15] that an alkane comprises about 20% of hydrocarbon products of FTS for each carbon number. On the other hand, the labeled C_3 products formed from 1-propanol indicated that the relative amounts of propane and propene are 4:1, respectively, which implied that if an adsorbed oxygenate that resembles an alcohol is to be the primary source of hydrocarbons in FTS, then (1) hydrogenolysis of the added alcohol must occur at least 16 times faster on catalytic sites that are inactive for chain growth than occurs with the growing chain; and (2) surface migration of growing chains to these active hydrogenolysis sites does not occur at a significant rate [6]. From this view, a common intermediate to the formation of hydrocarbons and oxygenates is unlikely. Another view is that oxygen containing surface species (i.e., intermediates for oxygenates) can be formed via CO insertion into an alkyl-metal bond [16]. Johnston and Joyner [17] postulated that the same surface species might be formed via addition of a hydroxyl group to an alkylidene species. The desorption of

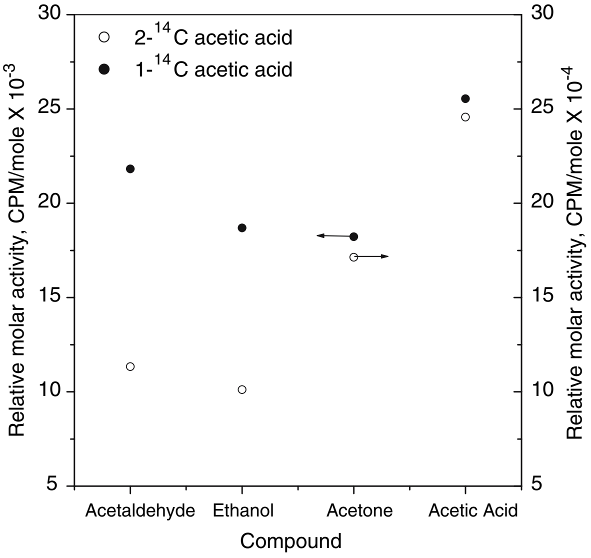


Fig. 12 The relative molar activity of main oxygenates (acetaldehyde, acetone, ethanol and acetic acid in the aqueous phase) addition of 1-^{14}C and 2-^{14}C labeled acetic acid during FTS at 270 °C and 100 psig, $H_2/CO = 1.2$ with a doubly promoted iron catalyst (CO conversion ca. 85%)

such a species would result in primary formation of oxygenates. Alkoxide and carboxylate groups appeared to be the most stable species in the infrared spectra during FTS and were considered as the intermediates to oxygenate in FTS [18]. Thus, the formation of oxygenates via a parallel pathways to that of hydrocarbons is most likely.

The decrease in methanol selectivity upon addition of acetic acid can be attributed to the inhibition of the active catalytic sites for methanol synthesis by the added acetic acids. Hall et al. [19] found the radioactivity of FTS products obtained during the conversion of a mixture of $^{14}CH_3OH$ and unlabeled syngas increases approximately linearly with increasing carbon number as would be expected if methanol both initiated and participated in the growth of hydrocarbon chains. This is due to reversible decomposition of methanol to produce CO and H_2 which is unique among primary alcohols that generally undergo irreversible reactions. It is inferred in the present study that the added acetic acid adsorbs on the active catalytic sites responsible for the reversible methanol synthesis and that this results in a decrease in the methanol selectivity in FTS.

Addition of 1-^{14}C labeled acetic acid results in $CO_2$with high relative molar activity and methane with very low activity, whereas, 2-^{14}C labeled acid results in CO_2 with no measurable activity and methane with high relative molar activity. These results are consistent with a direct decarboxylation of adsorbed acetic acid to produce methane and carbon dioxide.

Some products are formed when acetic acid is added that are not formed in measurable amounts during normal FTS. For example, glycol and its ether, 1,2-diethoxyethane, are formed in significant amounts during the addition of acetic acid and are formed in very small quantities, or are not formed, when acetic acid is not added. While learning the nature of the intermediates leading to these products would be of interest, it does not appear that they are important for the FTS, at least under conditions of high CO conversion.

Table 1 Distribution of relative molar activity in the liquid hydrocarbon fraction (C_5–C_{10}) when adding labeled acetic acid

Hydrocarbon fraction	$CH_3{}^{14}COOH$ (%)	$^{14}CH_3COOH$ (%)
C_5	1.9	0.8
C_6	12.6	9.9
C_7	33.6	37.7
C_8	26.7	30.3
C_9	19.7	16.9
C_{10}	5.5	4.4

During the short run with the labeled acetic acid, the results for the higher hydrocarbon samples will be impacted in the duration of the run before the labeled acetic acid enters the reactor, the vapor pressure control of product accumulation, the retention of products in the collection vessel, etc. Even so the data in Table 1 for the C_5–C_{10} hydrocarbons show a similar trend in the ^{14}C-distribution.

The purchased labeled acetic acid appeared to contain a catalyst poison that caused a decrease in catalytic activity that was not recovered when the addition of acetic acid was terminated. The data clearly show that acetic acid, like methanol and unlike ethanol, undergoes some C–C bond rupture under synthesis to produce CO and/or CO_2, and presumably an adsorbed CH_3 group. This is similar to methanol where Emmett and coworkers clearly showed that the formation of methanol is reversible and the labeled products were consistent with those produced from labeled CO [1957]. The present results show that $CH_3{}^{14}COOH$ produces labeled CO/CO_2 and that the relative radioactivity in the products increases with carbon number as expected if a significant fraction of these products were formed by the normal FTS route using ^{14}CO. Most of the labeled oxygenate compounds are consistent with the hydrogenation of the acetic acid to produce acetaldehyde and ethanol as primary products and the labeled oxygenate compounds are formed by the reactions of these two primary oxygenate products.

4 Conclusions

Addition of acetic acid during FTS with C-73 catalyst results in a significant decrease in H_2 conversion and a slight reduction in CO conversion. Acetic acid addition decreases the alkene ratio for C_2 hydrocarbons and increases the alkene ratio for C_3 and C_4 products. The 1-alkene/2-alkene fraction is found to increase significantly with acetic acid addition. Distribution of ^{14}C in the products suggests C–C bond rupture in acetic acid direct formation of ethane from labeled acetic acid. Results indicate that ^{14}C containing part of 1-^{14}C labeled acetic acid participates in the chain initiation and propagation for hydrocarbon formation in FTS. However, for methyl labeled acetic acid the ^{14}C containing part participates only in chain initiation step. ^{14}C-distribution in major oxygenate compounds indicate hydrogenation of the acetic acid to acetaldehyde and ethanol as primary products followed by secondary reactions. The additions of acetic acid cause decrease in methane and methanol selectivity while it increases ethanol, acetaldehyde and acetone selectivity in FTS. Addition of acetic acid results in formation of several products, like glycol and its ether, 1,2-diethoxyethane, and ethylbutanoate in significant amounts which are not generally observed in the normal FTS product spectrum. The results indicate that acetic acid is not a significant intermediate in low-temperature FTS with an iron catalyst.

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