Fischer-Tropsch Synthesis: Comparison of $^{14}$C Distributions and Analysis of Reaction Pathways When Labeled Acetic Acid Is Added

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1. INTRODUCTION

The molecular detail of Fischer-Tropsch Synthesis (FTS) has been a very controversial subject since the synthesis was first reported and several mechanisms, and variations thereof, have been proposed. The product spectrum of Fischer-Tropsch synthesis consists of a complex mixture of hydrocarbons and oxygenated compounds. Syntheses pathways of oxygenates from syngas are relevant for a fundamental understanding of FTS. Mechanistic investigations on FTS has revealed that that surface hydrocarbon species appear, either as intermediates on the path to oxygenate formation, or as products of oxygenate decomposition. 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 decomposition on FTS catalysts, it is possible to gain substantial insight into mechanistic details concerning oxygenate synthesis during FTS.

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 200-327 °C. When ethanol, ethyl acetate, or acetaldehyde was added individually to the syngas, additional amounts of the other two compounds are always found in the exhaust gas. At higher temperature acetone was always found and at 237 °C 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 dehydration 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 although very high selectivity towards acetic acid in oxygenates synthesized from syngas has been observed in special cases. There is clearly evidence for the participation of an oxygenate intermediate in the FTS using an iron catalyst. The objective of the present study is to examine in more detail the transformation of acetic acid labeled with radioactive and stable $^{14}$C isotope (both at carboxylic and methyl carbon) under medium pressure FTS using a doubly promoted fused iron catalyst.

2. EXPERIMENTAL

A doubly promoted fused iron catalyst (C-73, United Catalysts) was used. The catalyst was reduced with $\text{H}_2$ at 400 °C for 72 h, passivated with 1% oxygen in nitrogen, transferred pneumatically to the CSTR (containing 300 g of melted Polywax 3000, polyethylene fraction with average molecular weight of 3000), and then re-reduced in situ at 300 °C for 48 h with $\text{H}_2$. A total of 99.1 g catalyst was loaded into the reactor. Sodium salt of $^{14}$C labeled (at
carboxylic and methyl positions) acetic acids (CH$_3^{14}$COONa, # MC125, 1 mCi; and
CH$_3^{14}$COONa, # MC213, 1 mCi) were procured from Moravek Biochemicals and
Radiochemicals, CA, USA and hydrolyzed with deionized water to convert to corresponding
acid forms prior to use. The experiments were conducted in a 1 L CSTR equipped with a
magnetically driven stirrer with turbine impeller, a gas-inlet line, and a vapor outlet line with a
SS fritted filter (2 $\mu$m) placed external to the reactor. A tube fitted with a SS fritted filter (0.5
$\mu$m opening) extends below the liquid level of the reactor for withdrawing reactor wax (rewax)
maintains a constant liquid level in the reactor. Separate mass flow controllers were used to
control the flow rate of H$_2$ and CO. The gases were premixed in a mixing vessel before
entering to the reactor. CO was passed through a vessel containing lead oxide-alumina pellets
to remove any traces of iron carbonyl. The mixed gases entered the CSTR below the stirrer
operated at 750 rpm. The reactor was operated at a constant temperature (±1 °C). The FTS
was effected at 270 °C, 100 psig, H$_2$/CO ratio of 1.2, and an initial syngas SV of 18 slph. The
conversions were calculated by GC analysis (with a TCD) of the exit gas. 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
were mixed prior to GC analysis.

Conditions were adjusted to give approximately (85-90) % conversion of the CO. The
total synthesis time (time-on-stream, TOS) with the same catalyst loading was about 4536 h.
The addition of unlabeled acetic acid (ACS reagent, ≥99.7%, Sigma-Aldrich, Inc.) was started
at 1293.5 h TOS with a flow rate of 1.43 mL/h and continued for 7 h. The addition of
CH$_3^{14}$COOH was started at 1797.5 h TOS with a flow rate of 1.51 mL/h and continued for 7 h.
The addition of CH$_3^{14}$COOH was started at 1989 h TOS with a flow rate of 1.49 mL/h and
continued for 7.5 h. The molar ratio of carbon atom from acetic acid to total carbon fed to the
reactor (i.e., C$_{AcOH}$/C$_{AcOH + C_{CO}}$) was maintained at about 0.02. The $^{14}$C content of each
product was determined by use of a proportional counter (PC) connected in series with the GC
equipped with OV-1 column. The effluent from the GC 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 PC following the addition of methane quench gas.
Combining the output from the GC and PC permits an analysis for H$_2$, CO, CO$_2$, C$_1$ – C$_5$
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.

3. RESULTS AND DISCUSSIONS

The C-73 catalyst results in a steady conversion of syngas with an insignificant
deactivation over 4500 h synthesis time. The conversion of added acetic acid was almost
complete during the synthesis (i.e., 98.9% – 99.3%). Addition of unlabeled acetic acid produced a significant change in the product distribution pattern of normal Fischer-Tropsch
synthesis using doubly promoted fused iron catalyst. The change in the concentration (in the
aqueous phase) of different oxygenates produced during FTS with addition of unlabelled acetic
acid is presented in Figure 1a and 1b. Addition of acetic acid results in an immediate and
significant increase of rate of production of ethanol (in maximum magnitude), acetaldehyde, acetone, iso-butanol (iso-BuOH), n-butanol (n-BuOH), and 2-butanone. The rate of production of methanol in FTS showed a steep decline upon the addition of acetic acid. The most interesting observation was that when acetic acid was added during FTS, significant amounts of ethylene glycol and 1,2-diethoxyethane (1,2-DEE) were produced. Neither ethylene glycol nor 1,2-DEE was observed in the product spectrum during normal FTS using the doubly promoted fused iron catalyst. The ratio of olefin to total hydrocarbon (i.e., olefin and paraffin) produced during the addition of labeled and unlabeled acetic acid reveals a significant change as compared to normal FTS. These ratios (analyzed from the exit gas phase) are shown in Figure 2a and 2b for C_{2}, and C_{3} hydrocarbons, respectively. Figure 2a reveals that in the case of C_{2} hydrocarbons, the olefin ratio declines immediately upon the addition of acetic acid. Acetic acid promotes production of more saturated hydrocarbons and less olefinic C_{2} hydrocarbons causing an overall decrease of the olefin ratio. However, the effect of acetic acid addition on the olefin ratio for C_{3} and C_{4} hydrocarbons was different from the result obtained for C_{2} hydrocarbons, as can be seen in Figure 2b (for C_{3} hydrocarbons). The olefin ratio increased immediately with the addition of acetic acid and came back to the original values when addition of acetic acid was stopped. It is found that addition of acetic acid results in the declination of rate of production of both olefins and paraffins during FTS; however, the magnitude of decrease in production rate is higher for paraffins than olefins causing an overall increase in the olefins ratio for C_{3} and C_{4} hydrocarbons. It is found that when the addition of acetic acid was stopped, then olefin ratios come back to the normal value immediately and the change is reversible and repeatable (considering slow deactivation of the catalyst with synthesis time). Analysis of exit gas mixture from the CSTR revealed that the addition of acetic acid results in an increased rate of production of CO_{2} along with ethylene glycol and iso-butanol. The methane and methanol production rate decreased significantly upon the addition of acetic acid and concentration of methane and methanol came back to the original value after the addition was stopped. The most significant change of the product distribution upon addition of acetic acid in the oil phase was the appearance of ethyl butanoate, which was not observed in the product spectrum of normal FTS. Once the addition of acetic acid was stopped, the concentration of ethyl butanoate became too low to detect.

The conversion of syngas containing ^{14}C-labeled acetic acid provides products which contained radioactivity. The radioactive products become diluted with non-radioactive products from normal synthesis pathways; hence all the reported relative molar activities (^{14}C per mole) in this article are corrected for this dilution effect. Raje and Davis^{2} have presented a mechanistic description of different cases regarding the incorporation of labeled atom generated from tracer molecules added during 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/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/mole of product should increase by a constant amount with each increase in carbon 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/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.

Figure 1. Variation in the concentration (in aqueous phase) of different oxygenates produced in FTS at 270 °C and 100 psig with addition of unlabelled acetic acid (flow rate of 1.43 mL/h for 7 h). The dotted line on the TOS axis indicates the starting time for acetic acid addition while the solid line indicates the time when the addition was stopped.

Figure 2. Variation of olefin/hydrocarbon ratio against reaction time during addition of labeled and unlabelled acetic acid in FTS at 270 °C and 100 psig: (a) C$_2$ olefin/C$_2$ hydrocarbons; (b) C$_3$ olefin/C$_3$ hydrocarbons. The dotted line on the TOS axis indicates the starting time for acetic acid addition while the solid line indicates the time when the addition was stopped.
Figure 3. The relative molar $^{14}$C activity of gaseous products after addition of labeled acetic acid during FTS at 270 °C, 100 psig, H$_2$/CO = 1.2 with a doubly promoted iron catalyst (CO conversion ca. 85%): (a) 1-$^{14}$C labeled acetic acid at a flow rate of 1.51 mL/h for 7 h; (b) 2-$^{14}$C labeled acetic acid at a flow rate of 1.49 mL/h for 7.5 h.

Figure 4. The relative molar $^{14}$C activity of oxygenates (in the aqueous phase) after addition of labeled acetic acid during FTS at 270 °C, 100 psig, H$_2$/CO = 1.2 with a doubly promoted iron catalyst (CO conversion ca. 85%): (a) 1-$^{14}$C labeled acetic acid at a flow rate of 1.51 mL/h for 7 h; (b) 2-$^{14}$C labeled acetic acid at a flow rate of 1.49 mL/h for 7.5 h.
The plots of relative molar activity of different compounds determined from the analysis of product gas mixture formed during the FTS when 1-\(^{14}\)C labeled and 2-\(^{14}\)C labeled acetic acid are added are shown in Figures 3a and 3b, respectively. The gradual increase of the relative molar activity with carbon number (from one to six) shown in Figure 3a (inset) reveals that acetic acid labeled with \(^{14}\)C at carboxylic position initiate chain growth and also participates in the chain propagation during FTS for hydrocarbons. The molar activity of ethanol and CO\(_2\) was significantly high. The activity of ethane was higher than ethylene which support the earlier observation that addition of acetic acid results in enhanced rate of ethane production and decreases the rate of ethylene production causing an overall decrease of olefin to total hydrocarbon ratio. A different distribution of relative molar activity of the compounds in the gas phase was obtained as \(^{14}\)C per mole of compounds are plotted when acetic acid labeled with \(^{14}\)C at methyl position was added (shown in Figure 3b). Ethanol, as in the case of 1-\(^{14}\)C addition, was found to contain high activity; however, CO\(_2\) produced with 2-\(^{14}\)C labeled acetic acid addition during the synthesis did not contain \(^{14}\)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 C\(_1\) to C\(_6\) hydrocarbons supporting earlier observations. The higher activity of methane and ethane than the other hydrocarbon products suggests that these two components are generated directly by decarboxylation/hydrogenolysis of labeled acetic acid and not via stepwise chain growth/propagation as the activity distribution does not follow Anderson-Schulz-Flory model. Contribution from the higher activity of ethane results in an overall higher activity of C\(_2\) hydrocarbons and can be misleading if considered together with C\(_1\) to C\(_6\) hydrocarbons. The very small slope of the \(^{14}\)C distribution plot among C\(_4\) – C\(_6\) hydrocarbons indicates that 2- \(^{14}\)C labeled acetic acid essentially initiate chain growth and the \(^{14}\)C containing fraction of acetic acid does not contribute into the chain propagation step. This claim can be verified from the almost constant relative molar activity in the \(^{14}\)C distribution plot of C\(_1\) to C\(_6\) hydrocarbons as shown in Figure 3b (inset).

The distribution of \(^{14}\)C in the oxygenates found in the liquid phase when 1-\(^{14}\)C and 2-\(^{14}\)C labeled acetic acid were added are represented in Figures 4a and 4b, respectively. Only four oxygenates (a total of 95.1% relative molar activity in both cases) were identified in the liquid phase; the concentration of other components present were too small for an accurate identification. With the addition of 1-\(^{14}\)C labeled acetic acid, the relative molar activity of ethanol and acetone are comparable and acetaldehyde was found to have higher activity than both ethanol and acetone (Figure 4a). However, a different scenario was observed with the addition of 2-\(^{14}\)C labeled acetic acid as shown in Figure 4b. In this case, the activity of acetone was almost double to that of ethanol, which has a comparable activity to acetaldehyde. The activities of unconverted acetic acid were highest in both cases.

The most significant and interesting observation of the present study is the difference in the relative molar activity distribution against carbon number of hydrocarbons for 1-\(^{14}\)C labeled acetic acid as compared to 2-\(^{14}\)C labeled acetic acid. In the case of 1-\(^{14}\)C labeled acetic acid, the relative molar activity increased with carbon number; furthermore, the linear
plot extrapolated to the origin for zero carbon number (Figure 3a, inset) as contrary to the case of 2-^{14}C labeled acetic acid addition when a sudden high activity for methane and ethane was observed and the activity of other hydrocarbons remained essentially similar. The results for the 1-^{14}C labeled acetic acid are consistent with water-gas-shift reaction producing ^{14}CO and subsequent standard FTS. From the result of 1-^{14}C labeled acetic acid study, it can be proposed that the carbonyl carbon containing part serves as the source of carbon for chain growth (i.e., this species takes part into chain propagation). Similarly, from the observations of 2-^{14}C labeled acetic acid experiments, together with 1-^{14}C labeled study it can suggested that the alkyl carbon containing species initiates chain growth, but do not participate into the chain propagation steps.

The addition of acetic acid did not significantly affect the conversion of CO, but the conversion of hydrogen was found to decrease immediately which suggests weak adsorption of acetic acid relative to CO but stronger adsorption relative to H2, or, competitive adsorption of acetic acids to the catalytic sites active for H2 adsorption. The added acetic acid decreased the hydrogenating characteristic of the C-73 catalyst as reflected in the decrease of methane selectivity and the increase in the olefin to total hydrocarbon ratio for C3 and C4 hydrocarbons (olefin ratio for C2 hydrocarbons is not considered due to the potential direct generation of ethane via decarboxylation/hydrogenolysis of added acetic acid). Both of these trends could be due to the inhibited adsorption of hydrogen by acetic acid. The increase in olefin ratio for C3 and C4 hydrocarbons suggests competitive adsorption of acetic acid and \( \alpha \)-olefins in the same active sites on the catalyst surface; thus inhibiting the secondary reactions of \( \alpha \)-olefins. This can be supported by the observation that the \( \alpha \)-olefin/\( \beta \)-olefin ratio also increased for C4 hydrocarbons with the addition of acetic acid. The observation of decrease in hydrogenation activity by the addition of oxygenates are in agreement with the result reported by several researchers using promoted iron catalysts.7-9

Higher carbon number oxygenates formed during the FTS with the addition of acetic acid co-elute with isoalkanes and are therefore difficult to analyze by using the gas radiochromatographic technique. Thus the present data only indicate that C4 \(^+\) oxygenates do not appear to be produced in significantly larger quantities when acetic acid is added to the syngas. Hydrogenation of added acetic acid during FTS was found to produce ethanol and acetaldehyde mainly. Aldol condensation of acetaldehyde followed by dehydration and hydrogenation of the double bond produces butyraldehyde which can further oxidized to butyric acid. The esterification of bytyric acid with ethanol will lead to ethyl butanoate, which was observed in the product spectrum with the addition of acetic acids. However, the contributions of these routes to the reaction pathways of added acetic acid during FTS are insignificant.

4. CONCLUSIONS

Addition of acetic acid does not reduce the CO conversion but result in a significant decrease in H2 conversion level. The results obtained with \(^{14}\)C labeled acetic acid addition to the syngas during FTS with a doubly promoted iron catalysts are consistent with the added acetic acid serving to both initiate and participate in the hydrocarbon chain growth actively. A major portion of acetic acid results in direct decarboxylation or hydrogenolysis to produce
methane and ethane mainly. Addition of acetic acid decreases methane, methanol and hydrogenation selectivity of the catalyst. The ethanol, acetaldehyde and acetone selectivity of the catalyst during FTS is significantly increased by the addition of acetic acid. It also inhibits the secondary reactions of \( \alpha \)-olefins. Conversion of acetic acid during FTS also produced products like ethylene glycol, 1,2-diethoxy ethane and ethyl butanoate which are not generally observed in the normal product range. It is concluded that an acetic acid intermediate acts to produce Fischer-Tropsch synthesis products in parallel with another synthesis mechanism. More specifically, acetic acids are not an intermediate in the FTS.

5. REFERENCES