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Role of CO_2 in the initiation of chain growth and alcohol formation during the Fischer–Tropsch synthesis

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Abstract

$^{14}CO_2$ added to the syngas serves to initiate chain growth to produce both oxygenates and hydrocarbons. This observation prompted a closer examination of the production of alcohols during Fischer–Tropsch synthesis with precipitated iron catalysts containing either silica or alumina and various levels of the potassium promoter. Surprisingly, the catalysts containing alumina produced more alcohols than the silica containing catalysts. The oxygenates fraction increased with increasing potassium content. At high potassium loadings, propanal becomes the dominant C_3 oxygenate, suggesting that aldehyde, and not alcohol, is a primary product.

Keywords: Fischer–Tropsch synthesis (FTS); FTS reaction mechanism; FTS chain initiation; FTS oxygenates; Isotopic tracer; Catalyst, iron; Alcohol

1. Introduction

The mechanism of the Fischer–Tropsch Synthesis (FTS) has elicited an ongoing debate since its discovery in the 1920s. Initially, it was viewed that a bulk carbide formed and was then hydrogenated to produce hydrocarbons [1,2]. During the 1950s the oxygenate intermediate received wide acceptance, primarily due to the ^{14}C tracer studies of Emmett et al. [3]. Subsequently, the results from surface science studies led to the revival of the carbide intermediate, but one that involved only the formation of a surface carbide.

The production of methanol from syngas should follow a simpler mechanism than the FTS and, at the same time, provide some insight into the FTS mechanism. However, even the mechanism for the methanol synthesis with a copper-based low-temperature catalyst is complex and involves controversy. Klier et al. [4] advanced the view that methanol is synthesized from the CO component of the reactant mixture and that CO_2 served to maintain the catalyst in a partially oxidized state. On the other hand, other workers have claimed that methanol is formed directly from CO_2 and not from CO [5,6]. It appears that the contribution of CO and CO_2 to the synthesis of methanol depends upon the process conditions, especially partial pressures. While there are many differences between the FTS and methanol synthesis, they do have the commonality of having both CO and CO_2 present in either the reactant feed, or during the synthesis due to the activity of the iron-based catalysts for the water-gas-shift (WGS) reaction. The present work was initiated as an effort to assess the contribution of the WGS to

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the Fischer–Tropsch reaction since it was conceivable that CO_2 could be formed by a mechanism involving the two reaction steps shown below:

$$CO \rightarrow C_{ads} + O_{ads} \quad (1)$$

$$O_{ads} + CO_{ads\,or\,gas} \rightarrow CO_2 \quad (2)$$

Thus, the products from a combination of Eqs. (1) and (2) would be the same as if the WGS had operated. On the other hand, if the WGS reaction was rapid compared to the FTS, we would expect ^{14}C, added in the CO_2, to rapidly redistribute and to be present in the CO. Surprisingly, when this experiment was performed, we found that the radioisotope distribution was such as to indicate that chain initiation could occur from an intermediate derived from CO_2 but that chain growth occurred using carbon derived only from CO [7]. Furthermore, of the CO_2 that was converted, half, or more than half, was converted to hydrocarbons [7].

In view of the incorporation of CO_2, as well as CO, and the similarity to the methanol synthesis, it was of interest to re-examine the formation of oxygenates and their dependence upon the promoter level. Thus, we have compared the amounts of oxygenates in the aqueous phase product fraction from catalysts with various levels of potassium promoter and with either alumina or silica as the added structural promoter. While some oxygenates, and especially the higher carbon number compounds, will be in the hydrocarbon layer, the amount of oxygenates present in the aqueous phase should be related to the total amount of oxygenates formed. In addition, the oxygenates present in the aqueous phase should be more easily recovered for potential use as chemicals than those that are present in the hydrocarbon fractions.

2. Experimental

The run to determine the incorporation of CO_2 was conducted in a 1-l CSTR system [8,9] using a catalyst containing 4.4 Si and 0.71 K (based on Fe=100). The catalyst was pretreated with syngas ($H_2/CO = 0.7$) for 24 h at 270°C and 1 atm absolute. The synthesis was effected at 175 psig and 270°C with the molar gas compositions ($H_2/CO/CO_2$) and flows as follows: 0 to 480 h (50/25/25), 3.4 Nl/h-g Fe; 504 to 720 h (66/0/34), 2.54 Nl/h-g Fe; 744 to 1200 h (60/10/30), 2.83 Nl/h-g Fe (liters (STP) per gram of iron per hour). Starting at hour 1032 and continuing for 72 h, $^{14}CO_2$ was added as a component of the feed gas. The $^{14}CO_2$ was added with the unlabeled CO (0.22 mol% $^{14}CO_2$). The hydrogen, CO and CO_2 streams to a mixing tank were fed, where the gases could be completely mixed prior to entering the continuous stirred tank reactor (CSTR). The analyses for the products have been described earlier [8,9].

The runs to define the production of oxygenates were conducted as described above, but without CO_2 added to the synthesis gas. The catalysts were prepared by precipitation at pH 8.5–9.5 by feeding the required amounts of streams of concentrated ammonium hydroxide and iron nitrate plus either aluminium nitrate or dispersed silica obtained by hydrolysis of tetra-butoxy silicon to a CSTR, where the residence time was about 6 min. The precipitate was washed two times with distilled water by repeated filtration/redispersion cycles. After the solid was dried at 110°C for about 3 days, the required amount of a potassium nitrate solution was added by the incipient wetness technique to produce the desired amount of potassium in the final catalyst. The catalyst was pretreated with CO as described above or with syngas at 1 atm for 24 h at 270°C prior to the synthesis runs. The reaction conditions were those utilized in the above example for a flow of synthesis gas of 3.4 Nl/h-g Fe; the temperature used to effect the synthesis was 270° or 230°C. The aqueous phase was collected separately and the content of alcohols was measured using g.c. with a Porpack column. The FTS with an iron catalyst involves two competing reactions for CO conversion:

$$CO + 2H_2 \rightarrow H_2O + -CH_2- \quad (3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (4)$$

At high CO conversion levels (about 90%), CO_2 production accounts for about 42% of the total CO conversion. After accounting for the CO_2 production, the synthesis with these catalysts at the conditions employed will therefore produce 208 g of hydrocarbons and oxygenates/m^3 of synthesis gas converted. The total oxygenates are based upon this yield of liquid and gaseous hydrocarbon plus oxygenate products.

3. Results and discussion

The conversion data during the run are illustrated in Fig. 1. During the period when equal molar amounts of CO and CO_2 were added (0–480 h), a portion of the CO was converted to CO_2 and the CO_2 conversion therefore appears to be negative. During the period when only H_2 and CO_2 were fed (504–720 h), the CO_2 conversion was about 25%. The conversion of CO_2 decreased when the amount of CO was increased (CO_2/CO=3) during the third period of the run (>720 h) and, as expected, the lower partial pressure of CO led to a lower percentage conversion of CO.

During the period of $^{14}CO_2$ addition (indicated in Fig. 1), the conversion of H_2 was about 32% while that of CO was about 74% and of CO_2 was about 9%. During this period, CO_2 was converted to CO so that these two gases exiting the reactor had essentially the same radioactivity/mol (1.7×10^2 for CO and 1.3×10^2 for CO_2). Thus, it is certain that there was interchange between these two compounds towards a similar specific radioisotope label.

The analysis of the C_4–C_{10} hydrocarbons indicates that all hydrocarbons have radioactivity (Fig. 2). This is a not a surprising result. A similar result (Fig. 3) was obtained when the $^{14}CO_2$ was added as a tracer but at a low chemical composition (0.2 mol% of the CO). The result that was obtained with low concentration of CO_2 is the one expected when the $^{14}CO_2$ serves to initiate and the chain growth is due to the unlabeled CO. The surprising result is the shape of the curve in Fig. 2.

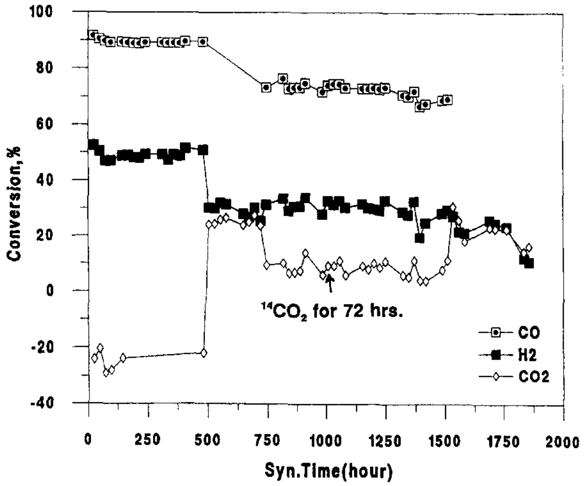

Fig. 1. Conversion of CO_2 and CO during FTS at 270°C, 8 atm, and the flows indicated in the text.

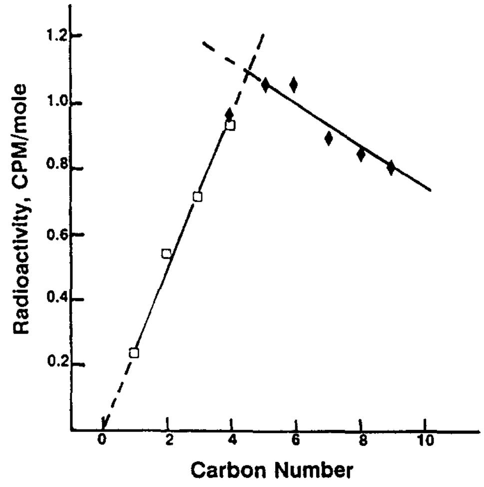

Fig. 2. Radioactivity/mol for products generated while adding $^{14}CO_2$ (see text for conditions).

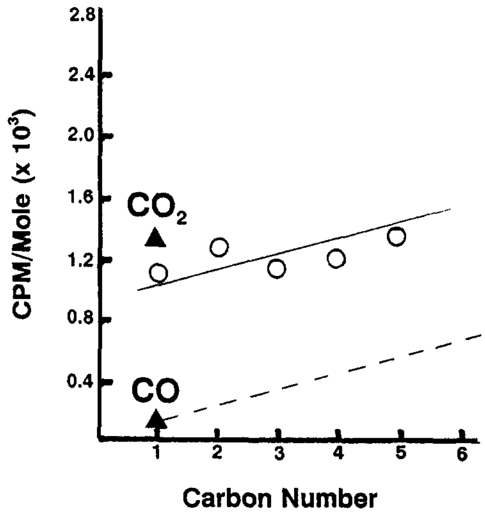

Fig. 3. The counts/min/mol vs. carbon number for (○) hydrocarbons; (■) CO_2; and (▲) CO in the exit gas.

If there was significant WGS conversion and it occurred at a rate that was similar to or exceeded that of the hydrocarbon synthesis, one would expect the CO as well as the CO_2 to contain significant ^{14}C. If the CO and CO_2 served to initiate chain growth and the CO to cause chain growth, the radioactivity/mol should increase with carbon number. Furthermore, the slope of the line should be equal to the ^{14}C content of the CO. Thus, if the WGS reaction had attained equilibrium prior to the beginning of the FTS, the radioactivity of C_1 should be the same as that of the CO_2 (and, in this case, the same as CO); this amount initiates the reaction and the slope of the line, defining the radioactivity/mol vs. the carbon number, should be defined by the radioactivity of the CO. This is exactly the result obtained for the hydrocarbons in the carbon number C_1–C_4 range, but the trend does not apply for carbon numbers >4.

One of the puzzling features of the earlier tracer studies was the result that the low isotopic distribution for the lower carbon number compounds was consistent with chain initiation by either an added alcohol or alkene; however, the ^{14}C/mol for the higher carbon number compounds decreased with increasing carbon number (Fig. 4). The slopes of the lines for the higher carbon number compounds for many runs that utilized different alcohols and alkenes were in the range −0.06 to −0.24 and appeared to depend upon the operating conditions [9]. Originally, the reason advanced for the decrease in the radioactivity/mol for the higher hydrocarbons was that two independent FTS chains contributed to the FTS reaction mechanism. However, a more recent work indicates that the accumulation of hydrocarbons may also impact the Anderson–Schulz–Flory (ASF) plot and even give the appearance of a two-alpha mechanism where the data fit two straight lines rather than one for a single ASF plot [10].

The slope of the line, based on the log (radioactivity/mol) as was done in Fig. 3, is −0.06, in agreement with the lower values obtained earlier [9]. Thus, it appears that the accumulation of hydrocarbons in the CSTR prior to the addition of the $^{14}CO_2$ dilutes the products in the C_4–C_9 hydrocarbon range sufficiently to cause the apparent decline in the radioactivity mol.

The present data, together with our earlier data, are consistent with the high partial pressure of CO inhibiting the adsorption of CO_2 and this, combined with the low H_2/CO ratio, caused CO_2 to only initiate chain growth. However, the lower CO partial pressure in the present study together with the higher H_2/CO ratio caused significant WGS to occur. Thus, the synthesis was conducted with the added ^{14}C distributed about equally between the CO and the CO_2, and this caused a linear increase in the radioactivity/mol for the C_1–C_4 hydrocarbons, as seen in Fig. 2. The accumulation of unlabeled hydrocarbons causes the radioactivity to be diluted for the higher carbon number hydrocarbons and the observed decline in the radioactivity/mol vs. carbon number plot.

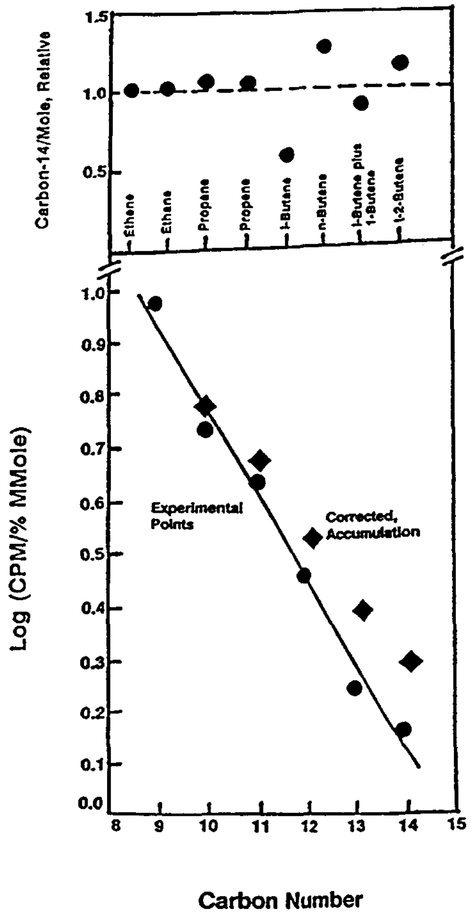

Fig. 4. Composite figure showing: (●) relative radioactivity for the lower carbon number compounds; (●) the measured values for the higher carbon number compounds; and (◆) the values for the higher carbon number compounds after correcting for reactor accumulation effects (from Ref. [8]).

The amount of oxygenates that are present in the aqueous layer depends upon the level of alkali in the catalyst (Fig. 5). In general, the alumina containing catalysts produce as much or more oxygenates than the silica containing catalyst. This is a surprising observation since alumina is known to be a much more active catalyst for the dehydration of alcohols than silica is. For an iron ammonia synthesis catalyst, it is generally accepted that the aluminium is present predominantly, or completely, as islands of alumina

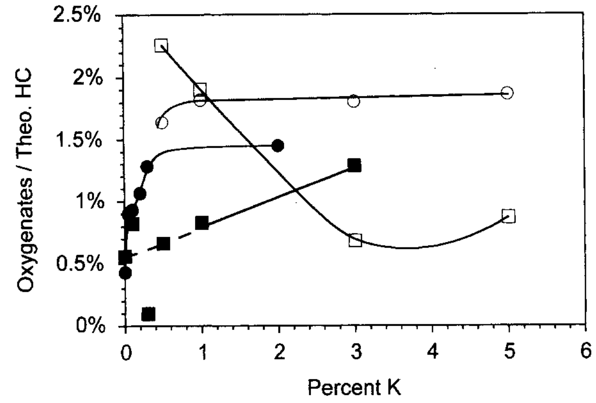

Fig. 5. The percentage of oxygenates in the hydrocarbonate plus oxygenate fraction from the conversion of synthesis gas (H_2/CO=0.7; T=230 or 270°C; P=170 psig; 3.1 Nl/h-g Fe with iron catalysts containing silica or alumina (Si or Al/Fe=0.044) with varying amounts of potassium (○ – alumina at 230°C; ● – alumina at 270°C; □ – silica at 230°C; and ■ – silica at 270°C).

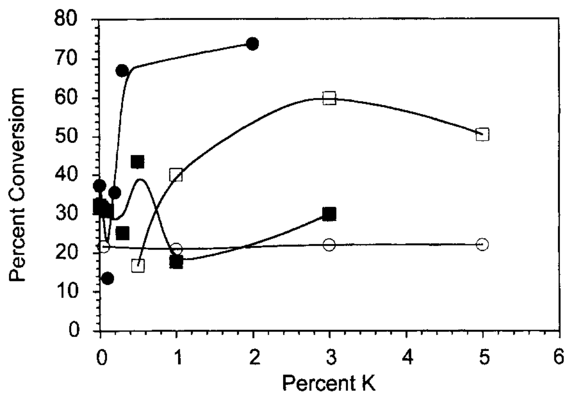

Fig. 6. The conversion of CO during the conversion of synthesis gas (H_2/CO=0.7; T=230 or 270°C; P=170 psig; 3.1 Nl/h-g Fe with iron catalysts containing silica or alumina (Si or Al/Fe=0.044) with varying amounts of potassium (○ – alumina at 230°C; ■ – silica at 270°C; □ – silica at 230°C; and ● – alumina at 270°C).

that cover a significant fraction of the iron surface [11]. Thus, if the aluminium in the Fischer–Tropsch catalysts was present as alumina islands on the surface, it is anticipated that it should function as an alcohol dehydration catalyst [12–14]. However, the experimental data differ from this expectation. This implies that the aluminium is present in Fischer–Tropsch catalysts in a form that differs from that of three-dimensional islands of alumina supported on the iron/iron oxide/iron carbide catalyst surface.

For the catalyst that contains 4.4 atomic ratio of Al, there is a dramatic increase in the oxygenate fraction of the products that are formed as small amounts of potassium are incorporated into the catalyst; however, increasing the potassium content above about 0.5 wt% produces only a slight, if any, increase in the fraction of oxygenates that are formed. For a given potassium content in the alumina containing catalyst, it appears that the products contain about 0.5 wt.% more oxygenates for the conversion at 230°C than at 270°C.

For the same potassium content, the catalyst containing silica produces a product that contains about half as much oxygenates at 270°C as the alumina containing catalyst at the same reaction conditions (Fig. 5). At 230°C, the oxygenate fraction of the products for the silica containing catalyst presents a different dependence on potassium content than for the alumina containing catalyst. Thus, the maximum fraction of oxygenates are obtained for the catalyst containing 0.5 wt% potassium, and the fraction of oxygenates decline to a low value as the potassium loading is increased beyond 0.5 wt%.

The CO conversions for the runs that produced the data shown in Fig. 5 are indicated in Fig. 6. For the alumina containing catalyst, the shapes of the CO conversion curves resemble in general those of the oxygenates production that were obtained at the same reaction temperature. The data for the alumina containing catalyst without alkali were obtained at an earlier reaction time than for the other catalysts and may therefore be somewhat higher than it would have been obtained at later times on-stream. For the particular silica containing catalysts utilized for generating the data shown in Figs. 5 and 6 at 270°C, the CO conversion pattern is just opposite that of the curve for the fraction of oxygenates in the products. These silica containing catalysts are not the ones that produce the optimum CO conversion, and the results for the high activity silica containing catalysts are discussed below. For the silica catalysts, the maximum CO conversion at 230°C is obtained for a catalyst that contains about 3 wt% potassium; the shape of the curve shown in Fig. 6 for the silica containing catalyst has been verified by repeat runs at 230°C. Again, it is noted that the CO conversion–potassium content curve is essentially the mirror image of the oxygenates production–potassium content curve.

The relative amount of oxygenates in the products usually increases as the catalyst remains on stream.

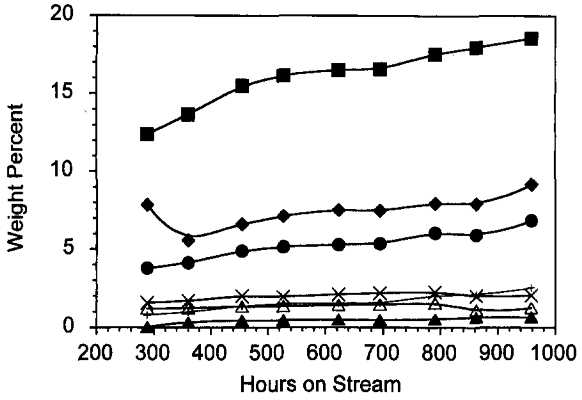

Fig. 7. The weight percent of oxygenate compounds in the aqueous phase formed during the conversion of synthesis gas with an alumina (Al/Fe=0.044) containing iron catalyst and 0.5 wt% potassium (H_2/CO=0.7; T=230 or 270°C; P=170 psig; 3.1 Nl/h-g Fe; ◆ – methanol; ■ – ethanol; ▲ – ethanal; × – acetone; Δ – 2-propanol; ● – 1-propanol; and + – 1-butanol).

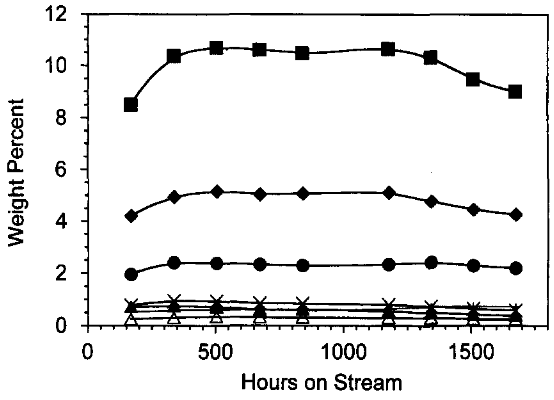

Fig. 8. The weight percent of oxygenate compounds in the aqueous phase formed during the conversion of synthesis gas with a silica (Si/Fe=0.044) containing iron catalyst and 0.5 wt% potassium (H_2/CO=0.7; T=230° or 270°C; P=170 psig; 3.1 Nl/h-g Fe; ◆ – methanol; ■ – ethanol; ▲ – ethanal; × – acetone; Δ – 2-propanol; ● – 1-propanol; and + – 1-butanol).

This is illustrated by the data in Fig. 7, and indicates that the fraction of each oxygenate increases as the catalyst ages to provide a gradual decrease in CO conversion.

In general, the WGS reaction occurs to a greater extent with the alumina containing catalyst than with the silica containing catalyst. This, combined with the higher relative production of oxygenates with the alumina containing catalyst, causes the weight percent of oxygenates to be much higher in the water fraction for the alumina containing catalyst (Figs. 7 and 8).

The amount of potassium in the catalyst affects the oxygenate distribution as well as the total amount of oxygenates formed. Thus, for the alumina containing catalyst, the percentage of methanol in the water soluble oxygenates declines continuously from about 30% to <10% as the potassium level is increased from 0 to 5 wt% (Fig. 9). (Note that the wt% K was varied from 0 to 5 wt% but not each catalyst within a series was tested.) As the potassium loading is increased the amount of ethanol and propanol increases up to a loading of about 1 wt% potassium and then declines with further increases in potassium content. The dominant change in the oxygenate composition in going from 1 to 3 wt% potassium is the dramatic increase in the amount of propanal that is formed. Whereas the propanal concentration dramatically increased to become the dominant oxygenate in the aqueous phase for the 3 wt% potassium catalyst, the amount of ethanal (acetaldehyde) did not increase significantly. A partial explanation for this is that the ethanal undergoes condensation reactions to produce higher carbon number components that have been identified as components in the oil fraction (A.W. Fort, D.J. Houpt and B.W. Davis, unpublished results). The oxygenates distribution for the alumina (4.4 atomic fraction) containing catalyst was very similar to that shown in Fig. 10 for the silica catalyst,

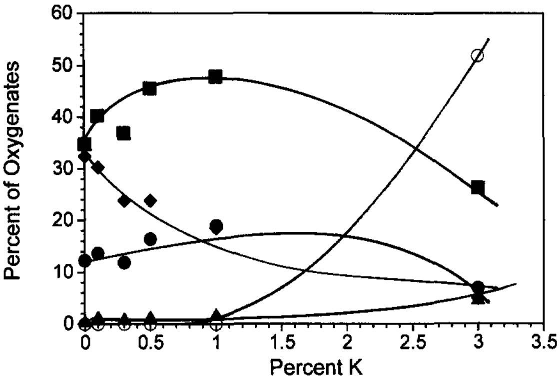

Fig. 9. The percentage of the oxygenate fraction made up by individual compounds (◆ – methanol; ■ – ethanol; ▲ – ethanal; ● – 1-propanol; and ○ – propanal) from the conversion of syngas with a silica (Si/Fe=0.044) containing iron catalyst and 0.5 wt% potassium (H_2/CO=0.7; T=270°C; P=170 psig; 3.1 Nl/h-g Fe).

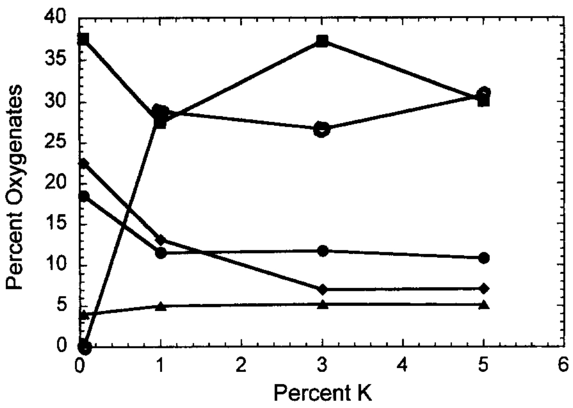

Fig. 10. The percentage of the oxygenate fraction made up by individual compounds (◆ – methanol; ■ – ethanol; ▲ – ethanal; ● – 1- propanol; and ○ – propanal) from the conversion of syngas with a silica (Si/Fe=0.044) containing iron catalyst and 0.5 wt% potassium ($H_2/CO=0.7$; $T=230°C$; $P=170$ psig; 3.1 Nl/h-g Fe).

except that the maximum for the fraction represented by ethanol and 1-propanol was attained at about 0.5 wt% alkali, a lower basic promoter level than was needed to obtain the maximum for the silica containing catalyst. The dependence of the oxygenates distribution, as well as the maximum for ethanol and 1-propanol, was essentially the same at 230°C and 270°C for the alumina containing catalyst. However, it appears that there are differences in the patterns obtained for the silica containing catalyst at 230°C and 270°C. At 230°C, the fractions of ethanol and 1-propanol are essentially constant as the potassium content varies from 1 to 5 wt% (Fig. 10). Again, the amount of ethanal is small compared to that of ethanol (about 20 times more ethanol). Ethanol is present at about 4 times the weight fraction of 1-propanol; however, the weight fraction of ethanol plus ethanal is about equal to that of 1-propanol plus propanal. Propanal is a dominant oxygenate product in the aqueous phase, and the amount of propanal remains essentially constant over the potassium range of 1–5 wt%.

A number of repeat preparations of the catalyst that contains Si/Fe=0.044 and K/Fe=0.71 (0.5 wt% K) has been carried out and these have been utilized in longterm activity/selectivity studies. A representative conversion vs. time curve is shown in Fig. 11 for a catalyst that was activated in synthesis gas for 24 h at 270°C and at 14.7 psia total pressure. The catalyst exhibits longterm stability of activity, declining at a rate that is <1% CO conversion/week. Also included in Fig. 11 is the fraction of oxygenates (based on total oxygenates plus hydrocarbons) that are formed during the >2 500 h of run time. It is apparent that at this higher conversion level, the oxygenates are present at only about one-hundredth the fraction that they are for lower conversion levels with a similar catalyst. It therefore appears that, with the silica containing catalyst, alcohol reincorporation and/or alcohol conversion (such as dehydration) occurs at high conversion levels to reduce the total oxygenate fraction to a very low level. This observation with silica for the high conversion data does not appear to apply for a similar catalyst where alumina has been incorporated in place of silica. Even though the oxygenates in Fig. 11 are present in low concentrations, the distribution of the oxygenate compounds are essentially the same as shown in Figs. 9 and 10 for the lower CO conversion and higher oxygenates concentration.

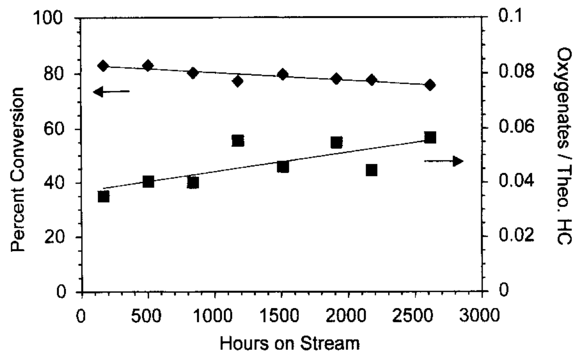

Fig. 11. The conversion and oxygenates production during longterm testing of a precipitated iron catalyst containing silica (Si/Fe=0.044) and potassium (0.5 wt%).

The impact of the potassium content upon the carbon number distribution of the oxygenates present in the aqueous phase is illustrated in Fig. 12. While the carbon number (*N*) is plotted vs. the ln (wt%/*N*), this is not intended to be a typical ASF plot since only the oxygenates present in the aqueous phase are included in the figure. The data make it clear that, as the potassium content of the catalyst is increased, the amount of methanol declines while there is a corresponding increase in the C_2 and C_3 fractions; furthermore, the increase in the C_3 fraction is greater than that for the C_2 fraction.

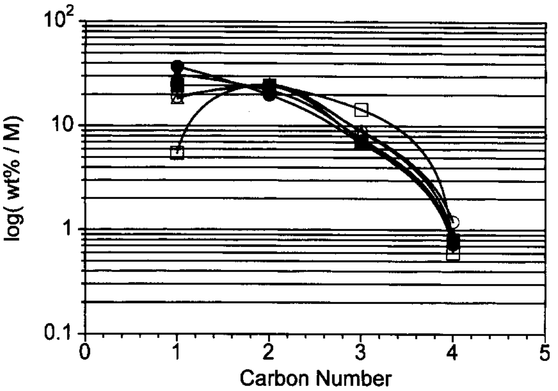

Fig. 12. The ln ((wt% N)/N) vs. the carbon number, N, of the oxygenates formed from the conversion of syngas with an alumina (Al/Fe=0.044) containing iron catalyst and various wt% potassium (● - 0% K/Fe; ▲ - 0.05% K/Fe; ■ - 0.1% K/Fe, ○ - 0.3% K; △ - 0.5% K/Fe; □ - 2.0% K/Fe) (H_2/CO=0.7; T=270°C; P=170 psig; 3.1 Nl/h-g Fe).

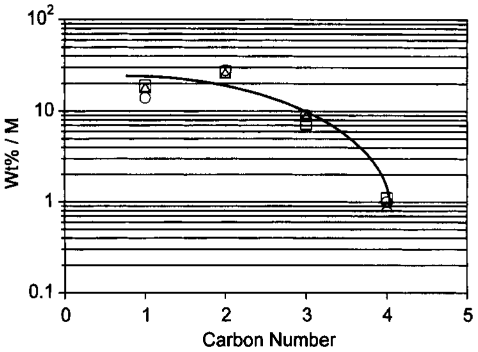

Fig. 13. The ln ((wt% N)/N) vs. the carbon number, N, of the oxygenates formed from the conversion of syngas with an alumina (△ - Al/Fe=0.044; ○ - Al/Fe=0.06; and □ - Al/Fe=0.08) containing iron catalyst with 0.5 wt% potassium (H_2/CO=0.7; T=270°C; P=170 psig; 3.1 Nl/h-g Fe).

The carbon number distribution of the oxygenate products does not depend to a measurable extent upon the content of either silica or alumina over the ranges (4–8 atomic% of the iron) examined in this study; this is illustrated in Fig. 13 for the data pertaining to the alumina containing catalyst.

4. Conclusions

The water soluble C_1–C_4 oxygenates represent a significant fraction of the products formed during the FTS. Thus, this water soluble oxygenate fraction represents about 1.5–2 wt% of the hydrocarbon plus oxygenate products; the alumina containing catalyst produces about 0.5 wt% more oxygenates than the silica containing catalyst with a similar potassium content. In general, as the catalyst ages, the amount of oxygenates produced per unit of syngas converted gradually increases. The oxygenates production, in general, mirrors that of the CO conversion; that is, the higher the conversion the lower the oxygenates production.

The distribution of the compounds within the oxygenates is primarily determined by the amount of potassium in the catalyst but is essentially independent of the alumina or silica content. Thus, for a given alkali loading, the carbon number distribution of the catalyst is independent of the amount of either alumina or silica in the catalyst in the 4 to 8 wt% loading.

As the alkali loading of the catalyst is increased the normal alcohol fractions decrease. The oxygenate that increases most dramatically with an increase in potassium loading is the aldehyde class of compounds. The increase in ethanal is much less, relative to ethanol, than the increase in propanal relative to 1-propanol. At least some fraction of the ethanal is converted to products consistent with aldol condensation reactions to produce higher carbon number compounds that are not soluble in the aqueous phase. The ethanol–ethanal is essentially in equilibrium during synthesis using a C-73 catalyst manufactured by United Catalyst [15]. This was not the case in the present study. For the high potassium loadings, the formation of the high concentration of aldehyde implies that the aldehyde, and not the primary normal alcohol, is a primary product of the FTS. It seems likely that the direct formation of the aldehyde occurs by a reaction pathway that competes with the FTS and which is similar to or is a hydrocarbonylation reaction.

The conversion of CO_2 with an iron catalyst is much slower than the conversion of CO. However, it has been shown that when CO_2 is present at low concentrations (0.2 mol% of CO), it can act to initiate chain growth but does not contribute to a measurable extent to chain propagation [5,8,16]. However, when CO_2 is present in a larger amount relative to CO (CO_2/CO=3; ratio of H_2/CO_x=1.5), the WGS reaction was rapid relative to that of the FTS. This permitted equilibration of the ^{14}C between CO and CO_2 so that mechanistic data cannot be discussed from the ^{14}C content of the products.

In brief, it appears that a Fischer–Tropsch plant that has the objective of developing a chemical component based on oxygenates would want to use alumina as the structural promoter. Furthermore, the operator could have some control over the amount and distribution of the oxygenate products by controlling the level of potassium that is present in the catalyst.

Acknowledgements

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