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Fischer–Tropsch synthesis over iron-based catalysts in a slurry reactor. Reaction rates, selectivities and implications for improving hydrocarbon productivity

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Abstract

A promoted iron Fischer–Tropsch synthesis catalyst is used in a slurry reactor to evaluate and compare the selectivity and yields of total hydrocarbons, light alkenes (C_2–C_3) and intermediate range (C_6–C_{16}) linear-α-alkenes for syngas derived from natural gas and coal. The catalyst has a high hydrocarbon yield of 0.6 g (of hydrocarbon)/h-g Fe at high CO conversions (>85%). The syngas derived from coal produces a slightly higher total hydrocarbon yield than natural gas-derived syngas, due to a lower reactor partial pressure of water which inhibits the Fischer–Tropsch reaction rate. The natural gas-derived syngas produces a lighter and more paraffinic hydrocarbon product than coal-derived syngas. The selectivity and yields of light alkenes as well as the intermediate range linear-α-alkenes decrease considerably with reaction time and CO conversion for syngas derived from both sources. The yields of these valuable products can be considerably improved by a lower single-pass reactor CO conversion with recycle of unconverted syngas or by using reactors in series. The syngas derived from coal produces a slightly lower ethylene and propylene yield, but a higher intermediate-range linear-α-alkene yield than that of natural gas-derived syngas.

Keywords: Fischer–Tropsch synthesis (FTS); Catalyst, iron; FTS reaction rate; FTS product selectivity; FTS process

1. Introduction

The Fischer–Tropsch process converts synthesis gas (a mixture of carbon monoxide and hydrogen) to hydrocarbons. A wide hydrocarbon product slate is obtained with hydrocarbons containing 1–100, and even higher carbon atoms. The current focus of many of the studies on the Fischer–Tropsch synthesis (FTS) deals with the production of transportation fuels such as gasoline and diesel. However, just as in the case of crude petroleum refining, the production of chemicals and chemical feedstocks from the FTS is an important and significant element of the overall product slate.

Iron-based FTS catalysts produce a hydrocarbon mixture with a significant alkene content. These alkenes are potential feedstocks for the manufacture of chemicals. For example, light alkenes, such as ethene and propene, are primary feedstocks for the manufacture of polymers and petrochemicals. Due to the stepwise build-up of the hydrocarbon chains in the FTS, a high proportion of linear alkenes are produced and, even more importantly, contain the double bond in the terminal (or α) position. These linear α-alkenes can potentially be used for the manufacture of high-

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value chemicals. For example, the C_6–C_{16} linear-α-olefins can be used for the manufacture of biodegradable detergents and PVC plasticizers [1]. Thus, from the viewpoint of producing chemicals and chemical feedstocks, the FTS catalyst should have a high selectivity to alkenes and linear-α-alkenes.

Synthesis gas can be produced from both natural gas or coal. The H_2/CO ratio of the synthesis gas obtained from these two sources is different when advanced coal gasifiers are used. The synthesis gas produced from coal using advanced gasifiers has a much lower H_2/CO ratio than the synthesis gas produced from natural gas. It is expected that the FTS processing of the syngas from these two sources would lead to different selectivities and yields of the desired alkene products.

In this study, we have investigated the production of hydrocarbons and alkenes from the FTS over an iron-based catalyst in a slurry reactor. In addition, the catalyst selectivity has been compared for syngas feeds corresponding to two different sources: coal-derived with a low H_2/CO ratio and natural gas-derived with a high H_2/CO ratio. A high activity precipitated iron-based catalyst is used for this study.

2. Experimental

2.1. *Catalyst*

A precipitated iron catalyst containing silica and potassium was prepared by continuous co-precipitation in a stirred open tank. Tetraethyl *ortho*-silicate in excess water was added to an iron(III) nitrate solution to provide the molar ratio 100 $(Si/(Si + Fe))$ of 4.4. The resulting mixture and concentrated ammonium hydroxide were separately pumped to the precipitation tank at a rate to maintain a pH of about 9 and an average residence time of 6 min. The resulting slurry was continuously withdrawn and filtered using three rotary vacuum drum filters in parallel. After two washes with deionized water and re-filtering, the filter cake was dried in an air-flow oven at 100°C. Potassium was added to this catalyst as potassium tertiary-butoxide during the loading of the FTS reactor. The amount of potassium added is such as to obtain a K:Fe weight ratio of 0.005. The final composition of the catalyst was 61.8 wt% Fe, 0.897 wt% Si, 0.311 wt% K and the balance oxygen. The BET surface area of the dried catalyst was 284 $m^2 g^{-1}$.

2.2. *Reactor and product analysis*

The reactor used is a 1 l stirred tank slurry reactor. Details of the reaction system and the product analysis has been reported previously [2].

2.3. *Procedure*

A known amount of catalyst (5 g) is loaded in the reactor with 300 g of C_{28}-alkane as the start-up solvent. The catalyst is pre-treated with CO at 270°C, 175 psig (1.308 MPa) at a CO flow rate of 13.4 Nl/h for 24 h.

The reaction conditions are 270°C, 175 psig (1.308 MPa) and a stirring speed of 750 rpm. The H_2/CO feed ratio of syngas is maintained at either 0.67 or 1.7. About two days are required at the start of a run before the catalyst reaches steady state, as evidenced by a constant conversion of syngas. Subsequently, the space velocity of the syngas is varied between the limits of 5 and 70 Nl (of synthesis gas)/h-g Fe. The conversions of CO, H_2, and the formation of various products are measured with a period of $\approx$24 h at each space velocity. Periodically, during a run, the catalyst activity is measured at pre-set 'standard' conditions to check for catalyst deactivation.

3. Results and discussion

Preliminary experiments showed that syngas conversion did not change upon varying the stirrer speed between 650 and 1050 rpm. This indicates the absence of external transport limitations on catalyst activity at the stirrer speed used (750 rpm). Catalyst samples withdrawn from the reactor in a preliminary experiment showed that the particle size of the catalyst in the reactor is <3 μm. This is well below the particle sizes at which internal diffusion becomes significant [3]. Reaction runs lasted for $\approx$12 to 15 days. The catalyst activity measured at preset 'standard' conditions during the course of the reaction runs was practically constant indicating the absence of catalyst deactivation.

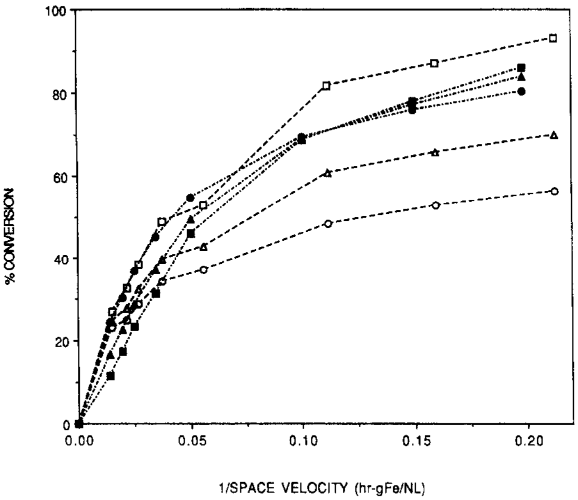

Fig. 1. Conversions of (△, ▲) syngas, (□, ■) carbon monoxide and (○, ●) hydrogen, with space time for two different feed ratios of H_2/CO (open symbols: H_2/CO feed ratio=1.7; filled symbols: H_2/CO feed ratio=0.67).

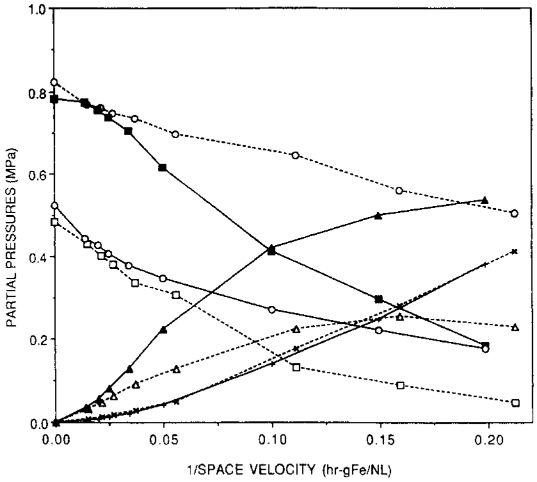

Fig. 2. Partial pressures of (□, ■) carbon monoxide, (○, ●) hydrogen, (△, ▲) carbon dioxide and (×, +) hydrocarbons, with space time for two different feed ratios of H_2/CO (open symbols and ×: H_2/CO feed ratio=1.7; filled symbols and +: H_2/CO feed ratio=0.67).

3.1. *Conversions*

The conversions of syngas, CO and H_2, with space time (or reaction time) for the two H_2/CO feed ratios are given in Fig. 1. The experimental data cover a wide range of conversions: for CO, the conversions range from 10 to 90%. The water gas shift reaction (WGS) occurs simultaneously with the FTS over iron-based catalysts,

$$\text{FTS}: \ CO+(1+(n/2))H_2 \rightarrow CH_n+H_2O$$

$$\text{WGS}: \ CO+H_2O \rightarrow CO_2+H_2$$

and leads to a variation in the usage of H_2 relative to that of CO during the FTS [4]. Hence, the conversions of H_2 and CO differ from each other as well as from the syngas conversion. As shown in Fig. 1, the syngas conversion is greater for the low H_2/CO feed ratio (0.67) than for the higher H_2/CO feed ratio (1.7) at the same space velocity, except at low reaction times. At low reaction times, the situation is reversed with the syngas conversion being slightly higher for the higher H_2/CO ratio. The conversion of CO, however, shows a different behavior. The CO conversion is higher at all the space velocities studied for the syngas with a higher H_2/CO ratio.

3.2. *Partial pressures*

The partial pressures of reactants and products (except water) at the reactor exit as a function of space time are shown in Fig. 2. Note that since the reactor used is equivalent to a continuous-flow stirred tank reactor, the partial pressures inside the reactor are the same as at the reactor exit. As expected, the partial pressure of hydrogen in the reactor is much higher for the high H_2/CO ratio than that for the low H_2/CO ratio. The partial pressure of CO in the reactor shows the opposite behavior. While the partial pressure of hydrocarbons in the reactor is not very different for the two H_2/CO ratios used, the partial pressure of CO_2 is much higher for the low H_2/CO ratio than that for the higher H_2/CO ratio.

The partial pressure of water for both H_2/CO ratios shows an initial increase with space time followed by a decrease, as shown in Fig. 3. This is in contradiction to the generally accepted view that the partial pressure of water continuously increases with space time [5]. However, from the FTS and WGS reactions shown above it can be seen that water formed by the FTS is subsequently consumed by the WGS reaction. Hence, it is an intermediate and should exhibit a maximum in partial pressure with space time, as shown in Fig. 3. In

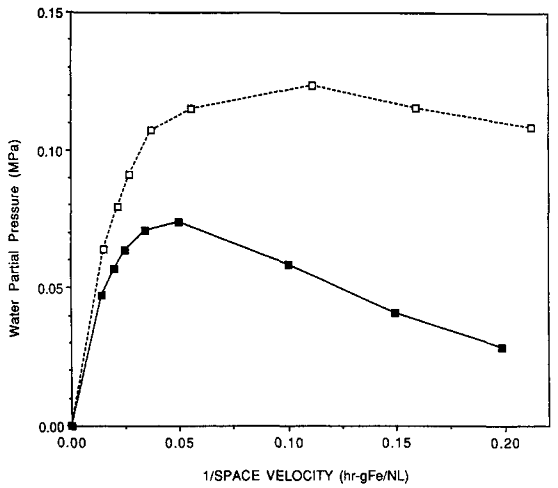

Fig. 3. Partial pressure of water (□, ■), with space time for two different feed ratios of H_2/CO (open symbols: H_2/CO feed ratio=1.7; filled symbols: H_2/CO feed ratio=0.67).

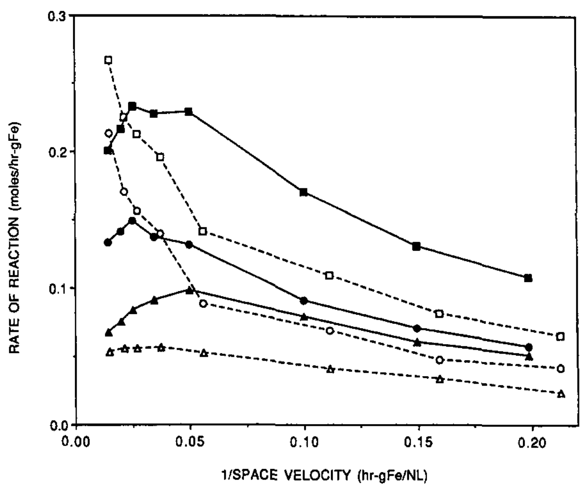

Fig. 4. Rates of (□, ■) carbon monoxide conversion, (△, ▲) carbon dioxide formation and (○, ●) Fischer–Tropsch reaction, with space time for two different feed ratios of H_2/CO (open symbols: H_2/CO feed ratio=1.7; filled symbols: H_2/CO feed ratio=0.67).

contrast to the CO_2 partial pressure, the water partial pressure in the reactor is higher for the high H_2/CO ratio than for the low H_2/CO ratio. This implies a higher rate for the WGS reaction (relative to the FTS reaction) for the low feed H_2/CO ratio.

3.3. *Reaction rates*

The rates of CO conversion, r_{CO}, CO_2 formation, r_{CO_2} , and FTS reaction, r_{FTS}, are shown in Fig. 4 for the two H_2/CO ratios used. Even though a higher CO conversion is exhibited by the syngas with a higher H_2/CO ratio, the actual number of moles of CO converted (i.e. r_{CO}) is less than the syngas with a lower H_2/CO ratio. This is because the inlet feed rate of CO is greater in the case of syngas with a low H_2/CO ratio.

The CO converted can either form hydrocarbons or CO_2 via the WGS reaction. The CO_2 formation rate is equal to the rate of the WGS, i.e.

$$r_{WGS} = r_{CO_2} \qquad (1)$$

The rate of the FTS is calculated from

$$r_{FTS} = (r_{CO} - r_{CO_2}) \qquad (2)$$

The rate of the FTS is always greater than the rate of the WGS as the FTS reaction supplies the water needed for the WGS. The difference between the two rates is greater at low space times, but it decreases as the space time increases for both H_2/CO ratios (Fig. 4). Both the rate of the FTS as well as that of the WGS are greater for the low H_2/CO ratio than for the high H_2/CO ratio.

3.4. *Carbon utilization*

A perceived disadvantage of using iron-based catalysts for the FTS is that a large proportion of the CO in the syngas is converted to CO_2 rather than the desired hydrocarbons. Hence, it is important to follow the fraction of CO converted to hydrocarbons for the two H_2/CO ratios. This can be calculated from

$$\text{Fraction of CO converted to hydrocarbons} = r_{FTS}/r_{CO} \qquad (3)$$

This fraction is usually considered to be 0.5 by assuming that the number of moles of CO taking part in the FTS is the same as that taking part in the WGS. However, this can only be the case if the rate of the WGS is always equal to the rate of the FTS. As shown in Fig. 4, these two rates are unequal for the catalyst studied and the difference between the two rates varies with space time. Hence, the fraction of CO converted to hydrocarbons is >0.5, as shown in Fig. 5. This fraction decreases with reaction time for both the inlet

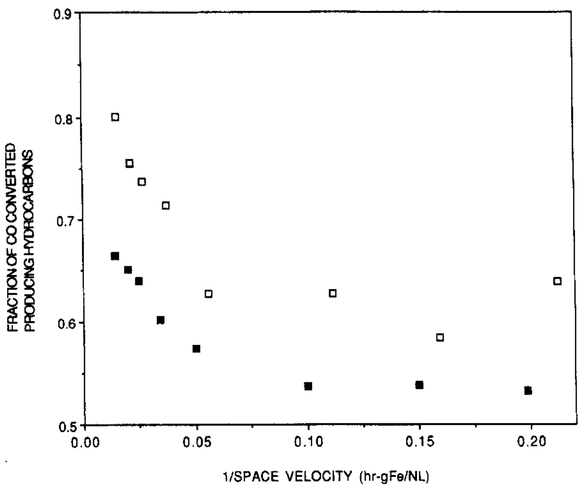

Fig. 5. Fraction of the CO converted to produce hydrocarbons with space time for two different feed ratios of H_2/CO (open symbols: H_2/CO feed ratio=1.7; filled symbols: H_2/CO feed ratio=0.67).

H_2/CO ratios used. Thus, at higher reaction times, an increasing fraction of the feed CO is converted to CO_2 rather than hydrocarbons.

Further, the fraction of CO converted that produces hydrocarbons is much greater for the syngas with a higher H_2/CO than that with a lower H_2/CO ratio. Hence, a more efficient utilization of the CO converted to produce hydrocarbons is obtained when using a syngas with a high H_2/CO ratio. For a low H_2/CO ratio, the extra hydrogen needed for high FTS conversions has to be produced by the WGS reaction. This leads to a greater conversion of CO to CO_2 rather than to hydrocarbons, especially at high conversions, and the fraction approaches the value of 0.5 at high reaction times.

3.5. Hydrocarbon yields

The rate of hydrocarbon formation, or hydrocarbon yield, is shown in Fig. 6 for the two H_2/CO ratios used. The hydrocarbon yield decreases drastically with reaction time for both the H_2/CO ratios used. The rate of CO conversion is lower for the high H_2/CO ratio, but a higher fraction of the CO converted is utilized to produce hydrocarbons. The net result is that the hydrocarbon yield for the high H_2/CO ratio syngas is only slightly less than the yield for the low H_2/CO syngas, as shown in Fig. 6. The hydrocarbon yield obtained at high CO conversions (86 to 93%) is about 0.6 g (of hydrocarbon)/h-g Fe which compares favorably with a yield of 0.57 g (of hydrocarbon)/h-g Fe at a CO conversion of 91% obtained in an early study at the same reaction conditions, but presumably operating with recycle to attain this high conversion [6].

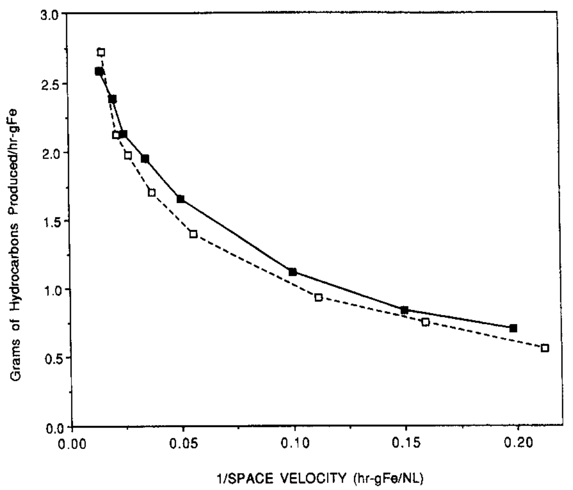

Fig. 6. Hydrocarbon yield per gram of Fe with space time for two different feed ratios of H_2/CO (open symbols: H_2/CO feed ratio=1.7; filled symbols: H_2/CO feed ratio=0.67).

It is surprising that higher hydrocarbon yields and a higher FTS reaction rate are obtained with a lower H_2/CO ratio. The syngas with a high H_2/CO ratio should have a higher partial pressure of hydrogen and should not depend on the WGS reaction to supply the extra hydrogen needed for the FTS. An explanation for this behavior can be discerned from a modified reaction-rate expression proposed for the FTS [7,8]:

$$r_{\mathrm{FTS}} = \frac{kP_{\mathrm{CO}}P_{\mathrm{H_2}}}{P_{\mathrm{CO}} + bP_{\mathrm{H_2O}}} \tag{4}$$

which shows that water inhibits the FTS rate. In the originally proposed rate expression [7,8], the syngas consumption rate was used instead of the FTS rate, assuming the two rates to be the same or proportional. However, it has been shown that these rates are not necessarily equal or proportional [9] and that the FTS rate should be used instead. A linearized version of this expression is

$$\frac{P_{\mathrm{H_2}}}{r_{\mathrm{FTS}}} = \frac{1}{k} + \frac{b}{k}\frac{P_{\mathrm{H_2O}}}{P_{\mathrm{CO}}} \tag{5}$$

The data obtained in this study are plotted according to the linearized rate expression in Fig. 7 and show a

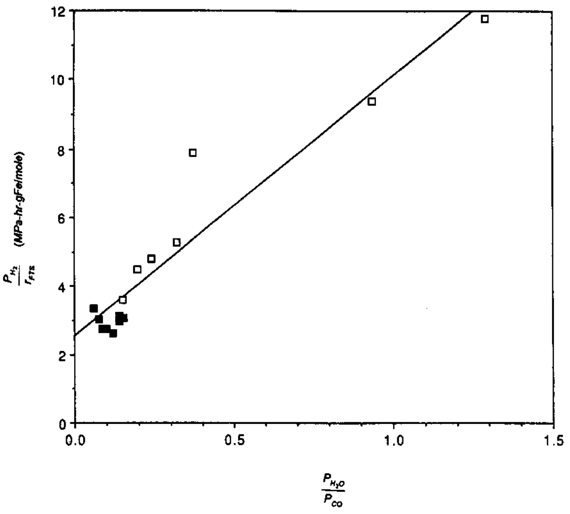

Fig. 7. Fischer–Tropsch linearized kinetic plot of Eq. (5) (□:H_2/CO feed ratio=1.7; ■:H_2/CO ratio=0.67).

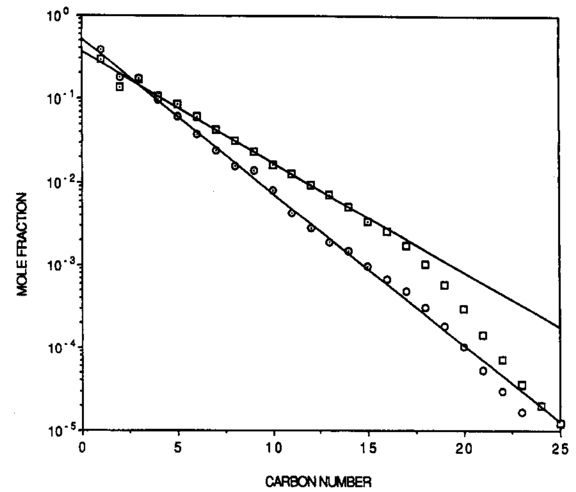

Fig. 8. Hydrocarbon selectivity plots for two different feed ratios of H_2/CO at similar CO conversion levels (O:H_2/CO feed ratio=1.7, CO conversion=82%; □:H_2/CO feed ratio=0.67, CO conversion=79%).

reasonably good fit. Similar to the partial pressure of water (Fig. 3), the ratio of the partial pressure of water to that of CO is greater for the high H_2/CO ratio than for the low H_2/CO ratio. Eq. (5) implies that the smaller FTS reaction rate and smaller hydrocarbon yields obtained for the high H_2/CO ratio are due to the greater value of the ratio of the partial pressure of water to that of CO.

The least-squares regression line fitted to the experimental data in Fig. 7 yields a value of the rate constant, k, as 0.398 mol/h-g Fe-MPa and a value of the adsorption parameter, b, as 3.016.

3.6. *Selectivity of hydrocarbons with carbon number*

Examples of hydrocarbon selectivity plots obtained at approximately the same CO conversion for the two H_2/CO ratios used are shown in Fig. 8. The selectivity plots are consistent with the Anderson–Shulz–Flory (ASF) reaction mechanism with a single value of the chain growth probability given by the slopes of the straight lines in Fig. 8. The deviation from the single value of the slope for hydrocarbons possessing >18 carbon atoms has been previously shown to be due to accumulation of these high-boiling hydrocarbons in the reactor slurry [10,11].

The syngas with a low H_2/CO ratio produces heavier hydrocarbons with a higher value of the chain-growth probability, α, of 0.74. The syngas with a high H_2/CO ratio exhibits a value of 0.67 for α, producing a significantly lighter hydrocarbon product. The value of the chain-growth probability shows a negligible dependence on the syngas space velocity or CO conversion.

The selectivity to alkanes as a function of carbon number is shown in Fig. 9 at similar values of CO conversion for the two H_2/CO feed ratios of the syngas. Unlike the chain-growth probability, the alkane selectivity is dependent on the number of carbon atoms in the hydrocarbon chain. For both the H_2/CO ratios, the minimum alkane selectivity is at a carbon number of three. The C_2 hydrocarbons exhibit a higher alkane selectivity than the C_3 hydrocarbons, while the alkane selectivity gradually increases for hydrocarbons possessing more than three carbon atoms, up to about C_{25}–C_{30}. Hydrocarbons possessing >30 carbon atoms consist almost exclusively of alkanes. Alkenes are considered to be primary products of the FTS and can be subsequently hydrogenated to alkanes. The dependence of the alkane selectivity on chain length has been previously attributed [12] to be a resultant of (i) a decreasing hydrogenation ability of alkenes with increasing carbon number, along with (ii) an increase in reactor hold up (or residence time) of the alkenes with increasing

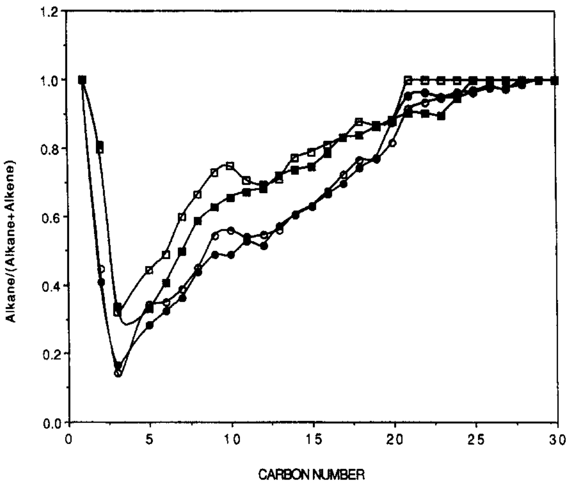

Fig. 9. Alkane fraction in total hydrocarbon product with carbon number for two different feed ratios of H_2/CO at low and high CO conversions (□:H_2/CO feed ratio=1.7, CO conversion=82%; ○:H_2/CO feed ratio=1.7, CO conversion=27%; ■:H_2/CO feed ratio=0.67, CO conversion=79%; ●:H_2/CO feed ratio=0.67, CO conversion=24%).

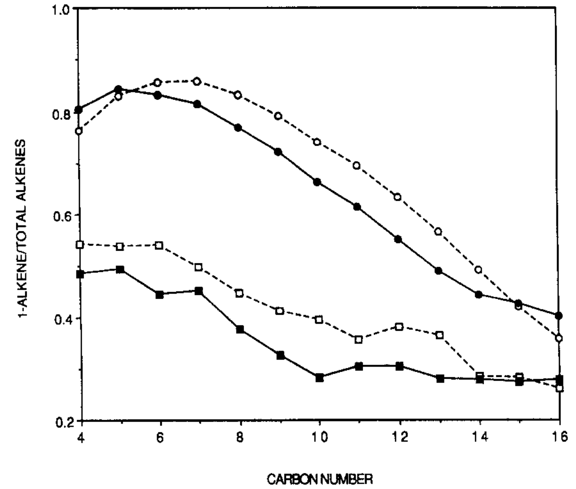

Fig. 10. Fraction of linear-α-alkenes in total alkene product with carbon number for two different feed ratios of H_2/CO at low and high CO conversions (□:H_2/CO feed ratio=1.7, CO conversion=82%; ○:H_2/CO feed ratio=1.7, CO conversion=27%; ■:H_2/CO feed ratio=0.67, CO conversion=79%; ●:H_2/CO feed ratio=0.67, CO conversion=24%).

carbon number. Fig. 9 shows that a significant quantity of alkenes are obtained in the hydrocarbon product range of C_2–C_{15}.

The alkane selectivity depends on the CO conversion. At high CO conversion, the alkane selectivity is greater at all carbon numbers, while the alkene selectivity is greater at low CO conversions. As expected, the syngas with a higher H_2/CO ratio exhibits a slightly higher selectivity toward alkanes. This difference in alkane selectivity is especially higher in the range of C_5–C_{12}.

The fraction of linear-α-alkenes in the total alkenes formed with carbon number is shown in Fig. 10 at similar values of CO conversion. In general, the selectivity toward linear-α-alkenes depends on and decreases with carbon number. This is, perhaps, due to the linear-α-alkenes being intermediates in the formation of internal alkenes. As the reactor residence time of linear-α-alkenes increases with carbon number, the linear-α-alkenes with higher carbon numbers have a greater chance to isomerize. Hence, the selectivity of linear-α-alkenes decreases with carbon number.

Further, the decrease in selectivity of the linear-α-alkenes is more drastic at low CO than at high CO conversions. Note, however, that at low CO conversions a maximum in the linear-α-alkene selectivity at C_5–C_7 is observed. The fraction of linear-α-alkenes is much greater at low CO conversions (0.5 to 0.8 between C_4 and C_{12}; upper curves in Fig. 10) than at higher values of the CO conversion (0.3 to 0.5 between C_4 and C_{12}). The syngas with a higher feed H_2/CO ratio exhibits a significantly greater selectivity toward the linear-α-alkenes than the syngas with a low H_2/CO ratio at similar CO conversion.

3.7. *Alkene selectivities and yields*

The selectivity toward alkenes in the C_2 and C_3 hydrocarbons as a function of CO conversion is shown in Fig. 11. This figure clearly shows a large decrease in the fraction of alkenes for C_2 hydrocarbons (0.6 to 0.1) with increasing CO conversion. The decrease in the alkene fraction is also observed for the C_3 hydrocarbon with CO conversion, though it is considerably smaller (0.8 to 0.6). This decrease in alkene selectivity at high conversions is consistent with the alkenes being intermediates in the formation of alkanes of the same carbon number.

Further, the alkene selectivity is higher for the C_3 hydrocarbon than that for the C_2 hydrocarbon. Up to about 70% CO conversion, the syngas with a low H_2/

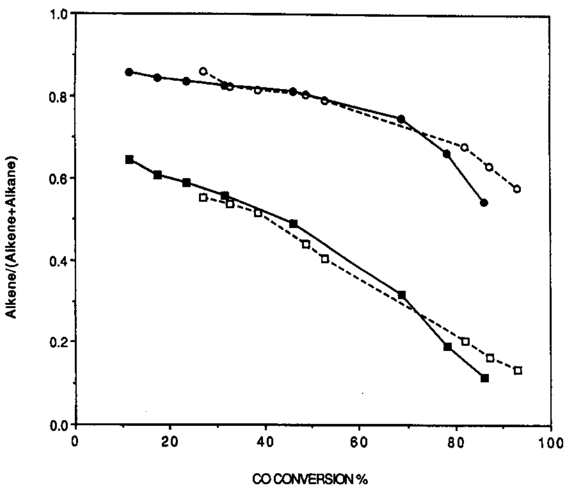

Fig. 11. Alkene selectivity for (□, ■) C_2 and (○, ●) C_3 hydrocarbons with carbon monoxide conversion for two different feed ratios of H_2/CO (open symbols: H_2/CO feed ratio=1.7; filled symbols: H_2/CO feed ratio=0.67).

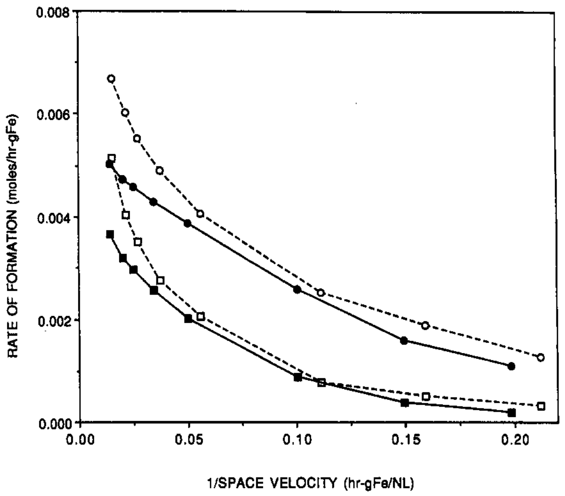

Fig. 12. Yields of (□, ■) ethylene and (○, ●) propylene, per gram of Fe with space time for two different feed ratios of H_2/CO (open symbols: H_2/CO feed ratio=1.7; filled symbols: H_2/CO feed ratio=0.67).

CO ratio has similar or slightly higher selectivity to ethylene and propylene. However, at higher CO conversions greater selectivity to ethene and propene is shown by the syngas with a higher H_2/CO ratio.

As shown in Fig. 8, the syngas with a higher H_2/CO ratio produces a lighter hydrocarbon product. Hence, even though the syngas with a lower H_2/CO ratio has a slightly higher alkene selectivity for C_2 and C_3 hydrocarbons, the yields of ethene and propene are greater for the syngas with a higher H_2/CO ratio (Fig. 12). Consistent with Fig. 11, the yield of propene is considerably greater than the yield of ethene for both the H_2/CO ratios. The yields of both ethene and propene decrease considerably with reaction time or conversion, as shown in Fig. 12.

The selectivity toward linear-α-alkenes is shown for three representative hydrocarbons (C_6, C_{10} and C_{14}) as a function of CO conversion in Fig. 13. The selectivity to linear-α-alkenes decreases with increasing CO conversion for all the hydrocarbons shown. This decrease in selectivity suggests that the linear-α-alkenes are intermediates in the formation of isomerized alkenes, as mentioned previously. The syngas with a higher H_2/CO ratio exhibits a slightly higher selectivity to linear-α-alkenes than the syngas with a low H_2/CO ratio. The difference in selectivity is greater at higher values of the CO conversion.

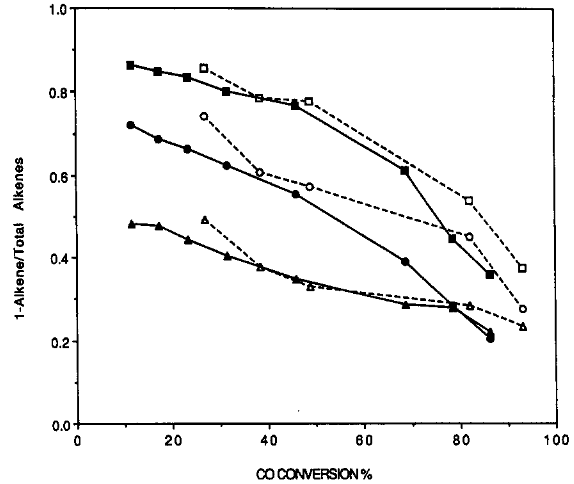

Fig. 13. Linear-α-alkene selectivity for (□, ■) C_6 , (○, ●) C_{10} and (△, ▲) C_{14} alkenes with carbon monoxide conversion for two different feed ratios of H_2/CO (open symbols: H_2/CO feed ratio=1.7; filled symbols: H_2/CO feed ratio=0.67).

The yields of representative linear-α-alkenes (C_6, C_{10} and C_{14}) are shown in Fig. 14. Consistent with the indication that linear-α-alkenes are intermediates (Fig. 13), a maximum in the yield is exhibited for several of the linear-α-alkenes at low reaction times. At higher values of the reaction time, the yields for the

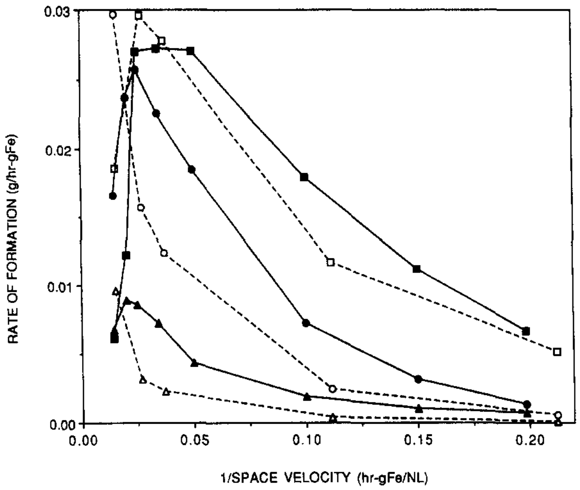

Fig. 14. Yields (per gram of Fe) of (□, ■) C_6, (○, ●) C_{10} and (△, ▲) C_{14} linear-α-alkenes with space time for two different feed ratios of H_2/CO (open symbols: H_2/CO feed ratio=1.7; filled symbols: H_2/CO feed ratio=0.67).

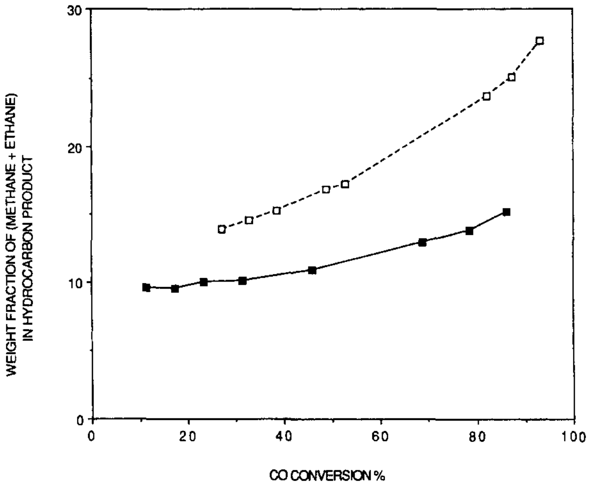

Fig. 15. Selectivity to methane and ethane expressed as wt% of total hydrocarbon product with space time. (□:H_2/CO ratio = 1.7; ■:H_2/CO ratio = 0.67).

linear-α-alkenes decrease considerably. The syngas with a low H_2/CO ratio exhibits greater yields of the linear-α-alkenes at higher reaction times. This is probably due to the higher amounts of the intermediate-range C_6–C_{15} hydrocarbons produced from the low H_2/CO ratio syngas.

3.8. *Methane and ethane selectivities*

The light, saturated hydrocarbon product gases such as methane and ethane can neither be used as chemical feedstocks nor as transportation fuels. Hence, the selectivity of these gases in the hydrocarbon products should be minimized. As shown in Fig. 15, the selectivity to methane and ethane increases significantly with reaction time for both the H_2/CO ratios. The feed gas with a high H_2/CO ratio exhibits a higher selectivity toward methane and ethane in the product hydrocarbons. This is consistent with the smaller value of the chain-growth probability, α, exhibited by the high H_2/CO ratio.

3.9. *Productivity of chemical feedstocks*

Lighter alkenes (ethene and propene) and intermediate-range linear-α-alkenes produced from the FTS are potentially valuable chemical feedstocks. However, as mentioned earlier, the selectivity for, and yields of, light alkenes and linear-α-alkenes decrease rapidly with increasing reaction time and higher conversion. Simultaneously, the fraction of CO converted, producing hydrocarbons, and the total hydrocarbon yield decreases with increasing reaction time and conversion. Further, the selectivity to undesired methane and ethane in the hydrocarbon products increases with reaction time and conversion. Hence, operating an FTS reactor at high syngas conversions (>85%) would lead to lower yields of total hydrocarbons and chemicals and higher yields of methane and ethane. It is thus preferable to limit the syngas conversion in the reactor to a lower value. Higher overall syngas conversions can be achieved by recycling unconverted syngas or by having two or more reactors in series. It is recognized that recycle or extra reactors lead to an increase in process cost. However, depending on the lower single-pass reactor conversion, large increases in the yields of alkenes and linear-α-alkenes can be obtained, as indicated in this study.

An example is provided below for the low H_2/CO ratio syngas to illustrate the benefit of low single-pass conversion with recycle. Let us consider two reactors with equal sizes and catalyst loadings. The first reactor is a single-pass reactor with a CO conversion of 90%

Table 1
Comparison of a single-pass reactor with a recycle reactor

	Single pass reactor	Recycle reactor
Single pass CO conversion	90%	67%
Fresh feed:Recycle ratio	—	2:1
Space velocity through reactor	3.1 Nl/h-g Fe	10 Nl/h-g Fe
Syngas throughput	3.1 Nl/h-g Fe	6.7 Nl/h-g Fe
Total hydrocarbon yield	0.55 g/h-g Fe	1.1 g/h-g Fe
C_2 and C_3 alkene yield	0.06 g/h-g Fe	0.15 g/h-g Fe
Linear C_6 α-alkene yield	0.006 g/h-g Fe	0.018 g/h-g Fe
Linear C_{10} α-alkene yield	0.0015 g/h-g Fe	0.007 g/h-g Fe
Linear C_{14} α-alkene yield	0.0005 g/h-g Fe	0.002 g/h-g Fe

and, hence, a space velocity of 3.1 Nl/h-g Fe (from Fig. 1) while the second reactor operates with recycle and a single pass CO conversion of 67%. Incidentally, at 67% CO conversion, the H_2/CO ratio of the unconverted recycle syngas and the fresh feed syngas is the same for the low H_2/CO ratio. Thus, the H_2/CO ratio of the recycle gas need not be adjusted. Table 1 compares the yields and syngas throughputs for the two reactors. The recycle reactor can process more than double the volume of syngas per weight of iron and produces twice as much hydrocarbons as the single-pass reactor. Further, the use of recycle increases the C_2 and C_3 alkene yield by a factor of 2.5 and triples, or further enhances, the yields of intermediate range linear-α-alkenes. These larger yields may possibly offset the increased cost of recycle and separation of CO_2, water and lighter hydrocarbons from the unconverted syngas before recycle.

The selectivities and yields of light alkenes and linear-α-alkenes have been compared for syngas derived from two fossil-energy sources (natural gas and coal). The hydrocarbon products from natural gas-derived syngas (high H_2/CO ratio) are lighter, implying a greater selectivity to C_2 and C_3 hydrocarbons, but are slightly more paraffinic. The resultant yields of ethene and propene are only slightly higher for the natural gas-derived syngas. The selectivity to intermediate-range linear-α-alkenes (C_6–C_{14}) of the natural gas-derived syngas is higher, but the amounts produced are much lower due to a smaller value of the chain-growth probability. The result is that lower yields for the linear-α-alkenes are obtained from the natural gas-derived syngas than that from the coal-derived syngas (low H_2/CO ratio). Thus, from the viewpoint of the productivity of valuable chemical feedstocks, the use of coal-derived syngas compares favorably with syngas derived from natural gas for the catalyst used in this study.

4. Conclusion

Iron-based FTS catalysts produce appreciable quantities of light alkenes (ethene and propene) and intermediate range (C_6–C_{14}) linear-α-alkenes. These products are potentially valuable and useful feedstocks for the organic chemical industry. The selectivities and yields of these chemical feedstocks have been evaluated and compared for syngas derived from two fossil-energy resources: natural gas (high H_2/CO ratio) and coal (low H_2/CO ratio).

A promoted iron catalyst which has a high hydrocarbon yield is used for both sources of syngas (0.6 g (of hydrocarbon)/h-g Fe) at CO conversions >85%. The syngas derived from coal produces a slightly higher yield of total hydrocarbons as compared to the natural gas-derived syngas. This is due to the higher ratio of the partial pressure of water to that of CO in the reactor for the natural gas-derived syngas which inhibits the Fischer–Tropsch reaction rate. The natural gas-derived syngas produces a lighter hydrocarbon product with a smaller value of the chain-growth probability. Alkene selectivity of the hydrocarbon products is appreciable in the C_2–C_{15} hydrocarbon range. The selectivity to linear-α-alkenes is high at low CO conversions.

The selectivity and yields of total hydrocarbons, light alkenes and linear-α-alkenes decrease considerably with increasing reaction times and higher CO conversions for syngas derived from both sources. This implies that it is preferable to limit the single-pass reactor CO conversion to a lower value, thereby increasing the selectivity to valuable hydrocarbons and chemical feedstocks. Higher overall conversions and yields can be achieved by recycle of unconverted syngas or use of two or more reactors in series. The use of a recycle reactor can increase the total hydrocarbon, light alkene and linear-α-alkene yields by a factor of two or more as compared to a single pass reactor.

The syngas derived from coal produces a slightly lower yield of lighter alkenes such as ethene and propene. However, substantially higher yields of intermediate-range linear-α-alkenes are produced from the coal-derived syngas.

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