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Activity and selectivity of precipitated iron Fischer–Tropsch catalysts

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Abstract

Low-temperature (230°C), slurry phase Fischer–Tropsch synthesis (FTS) was conducted with precipitated iron-silicon catalysts under industrially relevant conditions (flow=3.1 Nl h^{-1} g-Fe^{-1}, H_2:CO=0.7, P=1.31 MPa). The effects of activation gas (hydrogen, carbon monoxide, or syngas) and promoters (potassium and copper) on activity and selectivity were explored. Optimum potassium promotion was 4–5 at%, relative to iron. Promotion with copper lowered the reduction temperature and increased FTS activity, regardless of the activation gas used. Carbon monoxide activation gave the highest activity for a 100Fe/4.4Si/5.2K catalyst (atomic percent, relative to iron) while syngas activation was superior for a 100Fe/4.4Si/2.6Cu/5.2K catalyst. Selectivity of the FTS product was not affected by the activation gas employed or copper promotion; however, potassium promotion increased wax and alkene selectivity. A syngas activated 100Fe/4.4Si/2.6Cu/5.2K catalyst gave the best overall performance at 230°C. Alkene selectivity was >75% for the C_2–C_{11} fraction, methane selectivity was <3 wt% and C_{12}^+ selectivity was >70 wt%.

Keywords: Fischer–Trposch synthesis (FTS); FTS catalyst activity; FTS product selectivity; Copper; FTS promoter; Potassium

1. Introduction

The Fischer–Tropsch synthesis (FTS) offers the potential of converting syngas into high value chemicals [1–3]. Although several metals are active for the FTS, only iron and cobalt catalysts appear economically feasible on an industrial scale [4]. The high water-gas shift activity of iron makes it an ideal catalyst for converting hydrogen-lean syngas derived from coal [4,5]. Controlling selectivity is an important aspect of FTS catalyst development. Cobalt catalysts have a high activity for hydrogenation [1] and tend to produce linear alkanes. Iron catalysts are more versatile than cobalt catalysts, produce less methane and can be geared for the production of alkenes, oxygenates and branched hydrocarbons, depending on promoters and the process conditions employed [1–3]. Sasol is currently using an iron-based catalyst in a commercial slurry reactor; high alkene selectivity relative to fixed bed reactors is reported [6].

Several factors influence the selectivity and activity of FTS catalysts. Product selectivity of iron catalysts is generally controlled by promoting with one or more alkali metals [2]. Potassium has been known to increase wax and alkene yields while decreasing the production of undesirable methane [2,7]. Potassium also has been implicated in increasing FTS and water-gas shift activity [8]. Activation procedures

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can largely affect selectivity and activity of iron catalysts [9,10]. Precipitated iron catalysts are generally activated with hydrogen, carbon monoxide, or syngas. Catalysts activated with carbon monoxide have been reported to produce a higher molecular weight product than syngas or hydrogen activated catalysts; however, several factors such as temperature, pressure and duration of the activation step determine the ultimate activity and stability of iron catalysts [10,11]; therefore, it is difficult to state which activation procedure is superior.

Copper has traditionally been added to precipitated iron catalysts to facilitate reduction of iron oxide to metallic iron during hydrogen activations [7]. Copper has been shown to minimize sintering of iron catalysts when activating with hydrogen by lowering the reduction temperature [2]. The effect of copper promotion on iron catalysts activated with carbon monoxide or syngas is not as well documented although Kölbel and Ralek have reported that only 0.1 wt% of copper is necessary for successful activation of Fe/Cu/K catalysts with syngas [5].

Throughout our FTS studies, it has been found that syngas activation at an elevated pressure (>0.80 MPa) requires the catalyst to be promoted with copper in order to achieve reasonable activity. Previous work in our laboratory has shown that the activity of syngas activated Fe/Si/K catalysts is related to the hydrogen partial pressure of the activation gas [10]. Low hydrogen partial pressure inhibits the formation of oxidizing water which enables active iron carbides to be formed. Likewise, we have found that copper promotion has a similar effect. Treatment of a 100Fe/3.6Si/0.71K catalyst with syngas (H_2:CO=0.7) for 24 h at high pressure (1.31 MPa) and 270°C resulted in <18% syngas conversion [12]. When a 100Fe/3.6Si/2.6Cu/0.71K catalyst was treated similarly, it was found to undergo an induction period in which the syngas conversion increased to over 50% [12]. Mössbauer spectroscopy [12] analysis showed that the 100Fe/3.6Si/0.71K catalyst was composed of only Fe_3O_4, while the 100Fe/3.6Si/2.6Cu/0.71K catalyst had been partially carbided. The active species of iron-based Fischer–Tropsch catalysts has been debated since Fischer initially proposed that bulk carbides were responsible for catalyst activity [13]. Emmet later demonstrated that an iron catalyst carbided with ^{14}C labeled carbon monoxide, produced hydrocarbons with a lower radioactivity than the catalyst, thereby indicating that the bulk carbide was not responsible for the activity; however, he did not rule out the possibility that a surface carbide could be responsible for FTS activity [14]. Biloen et al., using ^{13}C tracers, have proposed that a surface carbide species is responsible for FTS activity on nickel, cobalt and ruthenium catalysts [15]. Similarly, Stockwell et al. have proposed that a CH species derived from surface carbon is the active species on a supported iron catalyst [16]. Amelse et al., using Mössbauer spectroscopy [17], and more recently Shroff et al., using high resolution transmission electron microscopy [18], have proposed that the activity of iron catalysts is related directly to the extent of bulk carbide formation; however, these studies were conducted in fixed bed differential reactors at atmospheric pressure under low conversions and activity was based on the rate of methane formation. At low conversions, the H_2:H_2O and CO:CO_2 ratios are high enough such that the reactor atmosphere is reducing and iron carbides are the thermodynamically stable phases [19]. At industrially relevant conditions, that is high conversion, enough water and carbon dioxide are present to oxidize the catalyst. Mössbauer spectroscopy and X-ray diffraction of activated and used iron catalyst samples clearly indicate that iron carbides are oxidized to magnetite at high conversion at the bottom of fixed bed reactors [20]; however, fixed bed reactors are not ideal for conducting catalyst characterization studies, because at high conversion a reducing atmosphere exists at the entrance of the reactor, while an oxidizing atmosphere (high H_2O and CO_2 partial pressure) may exist at the reactor outlet. We have conducted catalyst characterization studies in the slurry phase using continuous stirred tank reactors (CSTRs) [21,22]. In CSTRs, the total amount of the catalyst is exposed to the same reaction environment which allows for better correlation between catalyst composition and activity. We have found that a correlation between the amount of iron carbide and activity cannot always be made [22]; in some cases, peak catalyst activity is obtained when the entire bulk of the iron carbide appears to be oxidized to Fe_3O_4 [21].

Our research is currently directed at developing iron-based catalysts for the production of wax and 1-alkenes from hydrogen-lean syngas. Herein we report results of the effect of activation gas (hydrogen, carbon monoxide or syngas) and promoters (potassium and copper) on the activity and selectivity of precipitated iron-silicon catalysts.

2. Experimental

Catalyst compositions are expressed as atomic percent relative to iron:

$$\frac{M}{M+\mathrm{Fe}} \times 100$$

All catalysts used in this study were derived from a precipitated 100Fe/4.4Si/1.0K catalyst, unless otherwise noted. Preparation details of this catalyst are presented elsewhere [10]. Copper promotion was accomplished by impregnation with aqueous copper(II) nitrate hemipentahydrate. Additional potassium was added as potassium *tert*-butoxide during reactor loading. All FTS runs were conducted in a one liter autoclave, operating as a CSTR [10]. Catalysts were suspended in Ethylflo 164 hydrocarbon oil (Ethyl Corporation) which consists of a mixture of C_{30} isomers. All catalyst loadings were 10 or 5 wt%. Hydrogen and carbon monoxide flow rates were controlled by two mass flow controllers (Brooks Instruments) with the resulting synthesis gas composition regulated by adjusting the flow rate of the appropriate gas. The synthesis gas, after passing through a 2 l mixing vessel, was delivered to the catalyst slurry through a dip tube that extended below the impeller blade. The effluent exited the reactor and passed sequentially through two traps maintained at 60 and 0°C. Accumulated reactor wax was removed daily through a tube fitted with a sintered metal filter (0.5–2.0 μm). Uncondensed effluent was sent to an on-line Carle gas analyzer for determination of carbon monoxide, hydrogen, carbon dioxide, methane and C_2–C_4 alkanes, and alkenes. An on-line Hewlett-Packard 5790 GC equipped with a Porpack-Q column was utilized for C_4–C_9 quantification. Liquid samples were analyzed with a Hewlett-Packard 5890 GC equipped with a 60 m DB-5 capillary column. The reactor was also equipped with a tube that extended below the liquid level which permitted catalyst slurry samples to be withdrawn periodically.

Catalysts were activated with carbon monoxide, hydrogen or synthesis gas (H_2:CO=0.7). In general, the activation gas flow was started at ambient conditions, the necessary reactor pressure was set, and the reactor was ramped to the appropriate temperature at 2°C min^{-1}. After reaching the activation temperature, the conditions were maintained for 24 h. Carbon monoxide (2.0 Nl h^{-1} g-Fe^{-1}) and syngas (3.4 Nl h^{-1} g-Fe^{-1}) activations were conducted at 0.10 MPa and 270°C while hydrogen (12 Nl h^{-1} g-Fe^{-1}) activations were conducted at 0.10 MPa and 220°C. The lower temperature and higher flow rate were chosen for hydrogen activations in order to prevent sintering of the metallic iron that is formed [2]. Immediately following the activation procedure, reactors were brought to synthesis conditions – hydrogen:carbon monoxide ratio of 0.7, 3.1 Nl h^{-1} g-Fe^{-1}(STP – 0°C, 0.10 MPa), 230 or 270°C, 1.31 MPa.

Thermogravimetric analyses (TGA) were performed with a Seiko SSC/5200 instrument. Each experiment was run with 20–30 mg of sample and a calcined alumina reference. Three different reducing gases were employed – 49% hydrogen in helium (195 ml min^{-1}), 39% carbon monoxide in helium (165 ml min^{-1}) and 47% syngas (H_2:CO=0.7) in helium (190 ml min^{-1}). Samples were treated with the reducing gas at ambient conditions for 10 min and then the temperature was ramped to 600°C (20°C min^{-1}) and held for 5 min.

3. Results and discussion

3.1. Catalyst activation

Previously reported results with 100Fe/3.6Si/0.73K and 100Fe/3.6Si/2.6Cu/0.73K catalysts clearly indicate that the formation of bulk carbide is necessary to obtain substantial activity and that copper plays a role in the carbide formation [12]. Thermogravimetric experiments have been performed to understand the effects of copper on hydrogen, carbon monoxide and syngas activation of precipitated iron catalysts. Experiments were performed on a series of catalysts containing different quantities of copper (100Fe/4.4Si/5.2K, 100Fe/4.4Si/0.5Cu/5.2K, 100Fe/4.4Si/2.6Cu/5.2K and 100Fe/4.4Si/5.0Cu/5.2K). Hydrogen reduction resulted in substantial weight loss with two inflections (Fig. 1) that have been shown by Mössbauer spectroscopy and XRD [22] to correspond to the

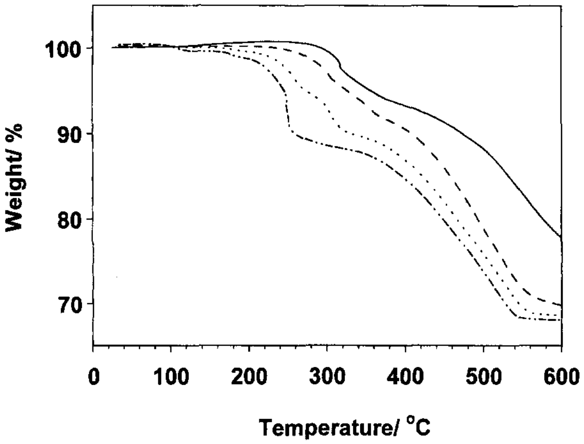

Fig. 1. Weight change measured by TGA of (–) 100Fe/4.4Si/5.2K, (- - -) 100Fe/4.4Si/0.5Cu/5.2K, (· · ·) 100Fe/4.4Si/2.6Cu/5.2K and (-·-·) 100Fe/4.4Si/5.0Cu/5.2K catalysts reduced with hydrogen.

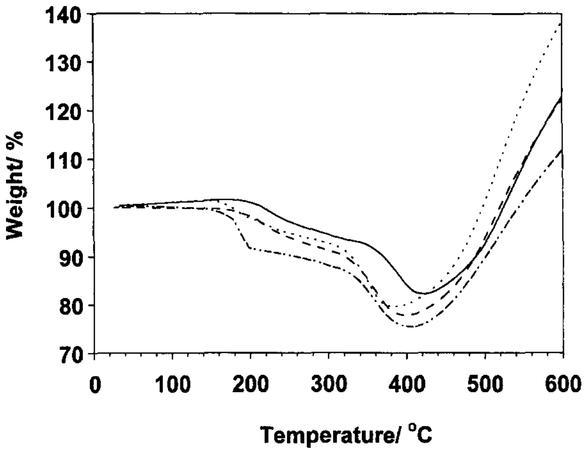

Fig. 2. Weight change measured by TGA of (–) 100Fe/4.4Si/5.2K, (- - -) 100Fe/4.4Si/0.5Cu/5.2K, (· · ·) 100Fe/4.4Si/2.6Cu/5.2K and (-·-·) 100Fe/4.4Si/5.0Cu/5.2K catalysts reduced with CO.

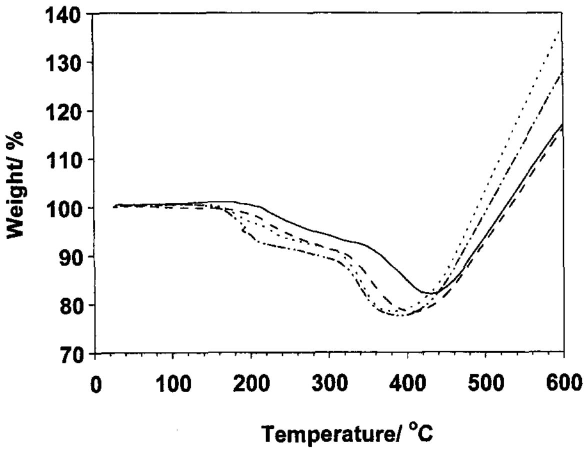

Fig. 3. Weight change measured by TGA of (–) 100Fe/4.4Si/5.2K, (- - -) 100Fe/4.4Si/0.5Cu/5.2K, (· · ·) 100Fe/4.4Si/2.6Cu/5.2K and (-·-·) 100Fe/4.4Si/5.0Cu/5.2K catalysts reduced with syngas (H_2:CO=0.7).

reduction sequence: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$. Richard et al. [23] have reported similar findings with unpromoted and promoted Fe_2O_3 catalysts. Our results show that the temperature at which both reduction steps occur is dependent on the level of copper promotion. The onset of the reduction sequences shifted from about 250°C and about 330°C for the 100Fe/4.4Si/5.2K catalyst to about 200°C and about 250°C for the 100Fe/4.4Si/5.0Cu/5.2K catalyst (Fig. 1).

Reduction with carbon monoxide produced two weight losses (Fig. 2) corresponding to the sequential reduction of Fe_2O_3 to Fe_3O_4 and Fe_3O_4 to iron carbide(s) [22]. After the formation of iron carbide(s), a rapid weight gain corresponding to the deposition of Boudouard carbon was seen ($2CO \rightarrow C + CO_2$). Reduction with syngas (H_2:CO=0.7) gave results nearly identical to those found for carbon monoxide reduction (Fig. 3). The similarity between carbon monoxide and syngas reduction is supported by Richard et al. who have reported that reduction of α-Fe_2O_3 with syngas (H_2:CO=1.0) is analogous to reduction with diluted carbon monoxide [23]. As was found with hydrogen reduction, the reduction steps for the carbon monoxide and syngas treated catalysts generally occurred at lower temperatures with increasing levels of copper.

It has been proposed that reduction of metal oxides by hydrogen to the zero valence state can be described by either a nucleation model or a contracting sphere model [24]. Only metal oxides that are reduced according to the nucleation mechanism have the reduction temperature affected by promoters, that is iron oxide promoted with copper. In the nucleation model, metal nuclei are formed by the removal of oxide ions from the lattice and the reduction process accelerates as previously formed nuclei grow and new nuclei are formed [24]. The reduction temperature of copper(II) oxide is ≈150–200°C lower than the reduction temperature of iron oxide. During the reduction of iron oxide promoted with copper oxide, the copper oxide will reduce to the metallic state first and will form sites of nucleation that accelerate the reduction of iron oxide [24]. Wachs et al. have studied the effects of copper and silver on the hydrogen reduction of low surface area α-Fe_2O_3 [25]. Copper was found to lower the temperature where reduction is initiated from about 300 to about 150°C; however, promotion with silver had no effect on the catalyst reduction. Copper was found to be much more dispersed on the catalyst surface than silver and was concluded to provide more sites of nucleation for reduction to occur. A similar process may occur for reduction with carbon monoxide or syngas. Shroff et al. have shown by transmission electron microscopy (TEM) that reduction of a commercial iron oxide catalyst ($Fe_2O_3/CuO/K_2O$) with carbon monoxide proceeds by first reducing rapidly to Fe_3O_4 and then slowly to iron carbide(s) [18]. The iron carbide(s) were clearly shown to form as small nuclei on the surface of the Fe_3O_4 crystallites. Kölbel and Ralek report that only a small amount of copper is necessary to promote the reduction of iron oxide [5]. The results presented here show that reduction with hydrogen, carbon monoxide, or syngas is accelerated with increasing levels of copper promotion. This is in agreement with more nucleation sites being available with an increasing amount of copper.

3.2. *Activity and selectivity*

We have developed a precipitated FT catalyst, 100Fe/4.4Si/1.0K, that shows high activity and stability [10]. With the proper activation, this catalyst has an initial carbon monoxide conversion >90% and deactivates at a rate of 0.6% (CO conversion) per week when operating at 270°C, 1.31 MPa and a space velocity of 3.1 Nl h^{-1} g-Fe^{-1} [10]. Activation with carbon monoxide (0.10 or 1.31 MPa) or syngas (H_2:CO=0.7, 0.10 MPa) at 270°C results in carbon monoxide conversion >90%; however, activations with hydrogen are only successful when the catalyst is promoted with copper (Fig. 4). Carbon monoxide conversion of the 100Fe/4.4Si/1.0K catalyst activated with hydrogen started at 20% and gradually increased to about 60% during the first 600 h at synthesis conditions. In contrast, hydrogen activation of the same catalyst with the copper promoter (100Fe/4.4Si/2.6Cu/1.0K) resulted in an initial carbon monoxide conversion >80%. This hydrogen activated catalyst showed stability equal to that of the carbon monoxide or syngas activated 100Fe/4.4Si/1.0K catalyst; a deactivation rate of <0.9% per week was achieved for over 3500 h. Bukur et al. have shown by XPS that carbon monoxide is more effective at reducing the surface of a commercial iron oxide catalyst promoted with copper, potassium and silica [26]. Richard et al. have shown that reduction of Fe_3O_4 to Fe_5C_2 by carbon monoxide is more thermodynamically favored than reduction of Fe_3O_4 to α-Fe by hydrogen [23]. As a result, copper promotion is necessary to ensure the formation of metallic iron when activating with hydrogen; high activity is obtained when the metallic iron is converted to iron carbide(s) during synthesis.

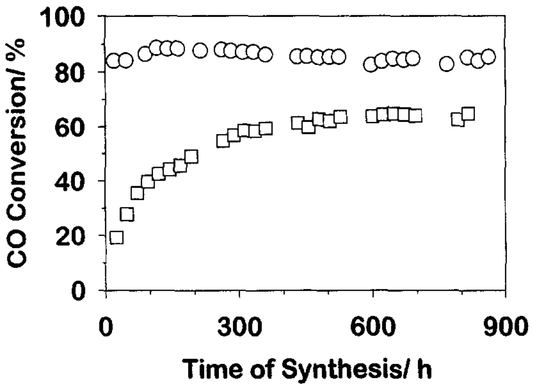

Fig. 4. Carbon monoxide conversion as a function of time on stream for a (□) 100Fe/4.4Si/1.0K catalyst and a (○) 100Fe/4.4Si/2.6Cu/1.0K catalyst. Activation conditions: H_2 flow rate=12 Nl h^{-1} g-Fe^{-1}, 220°C, 0.10 MPa, 24 h. Synthesis conditions: H_2:CO=0.7, 3.1 Nl h^{-1}g-Fe^{-1}, 270°C, 1.31 MPa.

We have generally found that catalysts activated with carbon monoxide have a higher selectivity for high molecular weight products than catalysts activated with syngas or hydrogen [10]. Bukur et al. report that carbon monoxide and syngas activations result in a heavier product distribution when a fixed bed reactor is used [21], while carbon monoxide activation results in lower methane selectivity than hydrogen or syngas activations in a slurry reactor [9]. However, all activation procedures using the 100Fe/4.4Si/1.0K catalyst resulted in an optimized product distribution for gasoline and light gases, and not in high value chemicals

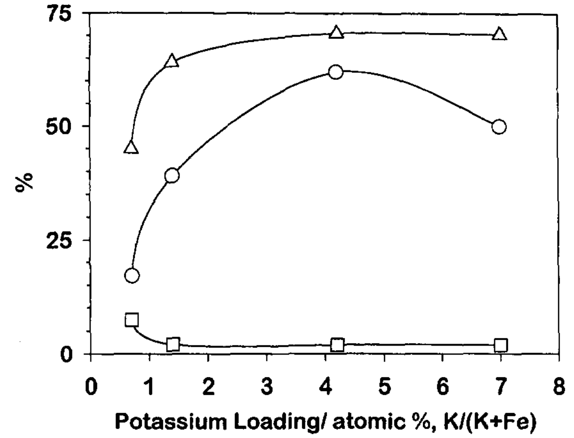

Fig. 5. (○) Syngas conversion, (△) C_2-ethylene selectivity and methane selectivity, (□) wt% of hydrocarbon product, as a function of potassium loading for a 100Fe/4.4Si catalyst. Synthesis conditions: H_2:CO=0.7, 1.0 Nl h^{-1} g-Fe^{-1}, 230°C and 1.31 MPa.

like wax and alkenes, when FTS was conducted at 270°C. Several factors are known to affect the selectivity of iron-based catalysts in addition to the activation procedure. Alkali promotion, that is potassium, has been well established as being critical for increasing alkene and wax yields, while lowering of the reaction temperature has been shown to decrease methane and increase wax production [2]. Increasing reaction pressure will also increase wax selectivity; however, it has been reported that catalyst stability decreases [9].

Since it is well known that decreasing FTS temperature and optimizing alkali promotion are effective at increasing wax and alkene yields, four low-temperature runs were conducted at 230°C on a 100Fe/4.4Si catalyst in which the potassium content was varied. The highest syngas conversion, after carbon monoxide activation, was obtained with a potassium loading between 4 and 5 at% (Fig. 5). Interestingly, at 270°C the maximum conversion for a similar catalyst was obtained with a potassium loading of about 1.0 at%. Potassium is a FTS promoter because it increases the rate of dissociation of the C–O bond of carbon monoxide [27,28]. As the temperature is decreased it becomes harder to dissociate the C–O bond, hence a higher potassium loading is required. This is fortuitous because the high potassium content required at 230°C also decreased methane and ethane production (Fig. 5).

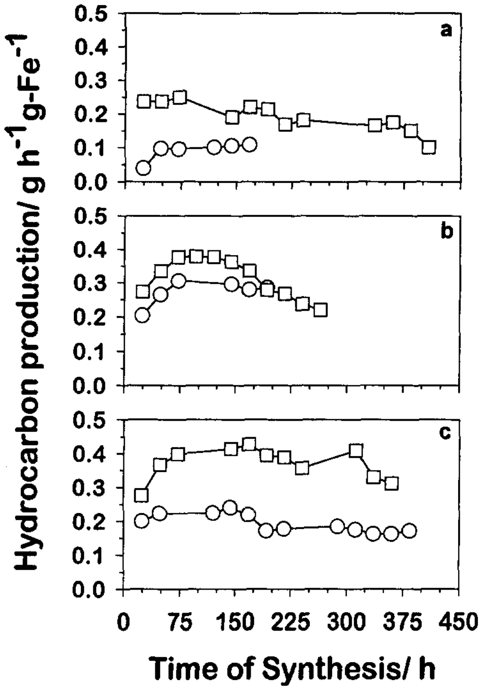

Fig. 6. Hydrocarbon production rate for (○) 100Fe/4.4Si/5.2K and (□) 100Fe/4.4Si/2.6Cu/5.2K catalysts. Activation conditions: (a) hydrogen flow rate=12 Nl h^{-1} g-Fe^{-1}, 220°C, 0.10 MPa for 24 h, (b) carbon monoxide flow rate=2.0 Nl h^{-1} g-Fe^{-1}, 270°C, 0.10 MPa for 24 h, (c) H_2:CO=0.7 at 3.1 Nl h^{-1} g-Fe^{-1}, 270°C, 0.10 MPa for 24 h. Synthesis conditions: H_2:CO=0.7, 3.1 Nl h^{-1} g-Fe^{-1}, 230°C and 1.31 MPa.

Despite the improved selectivity, the activities of all of the 100Fe/4.4Si/*x*K catalysts were unacceptably low at 230°C. The rate of hydrocarbon production relative to the amount of iron is a good measure of FTS activity. The rate of hydrocarbon production for a 100Fe/4.4Si/5.2K catalyst increased with respect to activation gas according to the order: hydrogen<syngas<carbon monoxide. The activity of the carbon monoxide activated catalyst underwent an induction period in which the rate of hydrocarbon production reached 0.30 g h^{-1} g-Fe^{-1} after 72 h (Fig. 6). The hydrogen activated catalyst also went through an induction period; however, the activity was less than half that obtained when activation was conducted with carbon monoxide (Fig. 6). The syngas activated catalyst deactivated slowly from a maximum rate of 0.24 g h^{-1} g-Fe^{-1} (Fig. 6).

Bukur et al. have reported that copper promotion increases FTS activity of precipitated iron catalysts

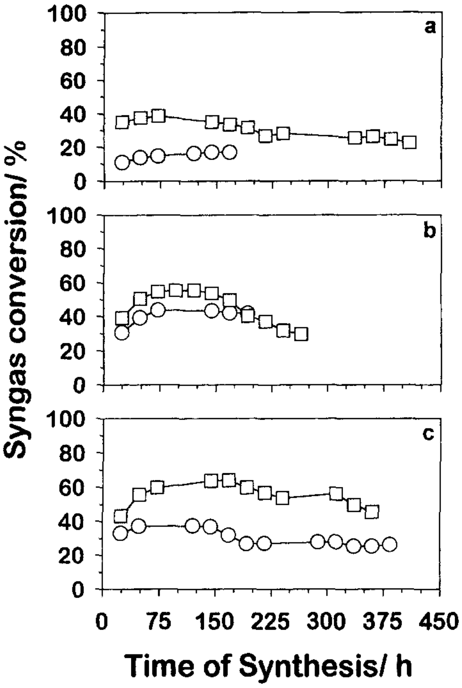

Fig. 7. Syngas conversion for (○) 100Fe/4.4Si/5.2K and (□) 100Fe/4.4Si/2.6Cu/5.2K catalysts. Activation conditions: (a) hydrogen flow rate=12 Nl h^{-1} g-Fe^{-1}, 220°C, 0.10 MPa for 24 h, (b) carbon monoxide flow rate=2.0 Nl h^{-1} g-Fe^{-1}, 270°C, 0.10 MPa for 24 h, (c) H_2:CO=0.7 at 3.1 Nl h^{-1} g-Fe^{-1}, 270°C, 0.10 MPa for 24 h. Synthesis conditions: H_2:CO=0.7, 3.1 Nl h^{-1} g-Fe^{-1}, 230°C and 1.31 MPa.

and that there is a synergistic effect when both potassium and copper are used [8]. Soled et al. [29] have claimed that promotion with both potassium and copper is essential in order to obtain the highest activity, lowest methane selectivity and highest alkene selectivity with a precipitate iron-zinc catalyst. In an effort to improve FTS activity at 230°C, the 100Fe/4.4Si/5.2K catalyst was promoted with copper to give a composition of 100Fe/4.4Si/2.6Cu/5.2K. It was found that copper promotion significantly increased FTS activity for the carbon monoxide, syngas and hydrogen activated catalysts (Fig. 6). The maximum rate of hydrocarbon production achieved with the different activation gases increased in the order: hydrogen (0.25)<carbon monoxide (0.38)<syngas (0.43 g h^{-1} g-Fe^{-1}). Maximum syngas conversion followed a similar trend; hydrogen (38%)<carbon monoxide (56%)<syngas (64%) (Fig. 7).

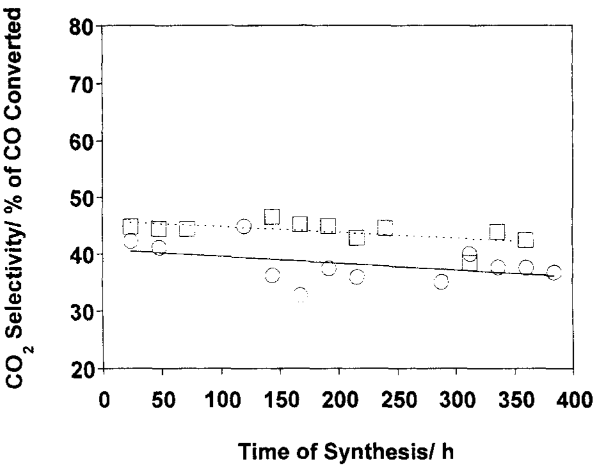

Fig. 8. Carbon dioxide selectivity for (○) 100Fe/4.4Si/5.2K and (□) 100Fe/4.4Si/2.6Cu/5.2K catalysts. Activation conditions: H_2:CO=0.7 at 3.1 Nl h^{-1} g-Fe^{-1}, 270°C, 0.10 MPa for 24 h. Synthesis conditions: H_2:CO=0.7, 3.1 Nl h^{-1} g-Fe^{-1}, 230°C and 1.31 MPa.

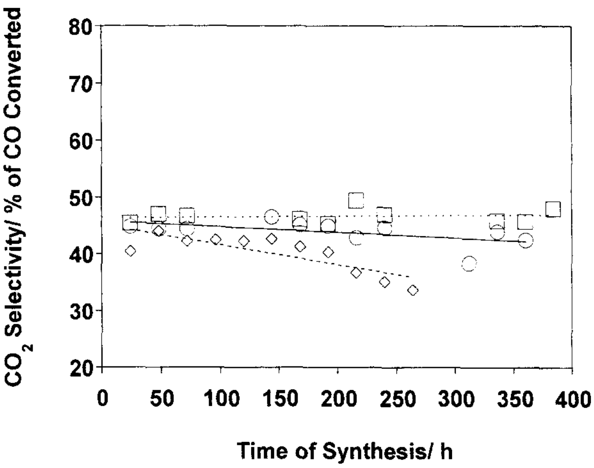

Fig. 9. Carbon dioxide selectivity for (□) 100Fe/4.4Si/2.6Cu/5.2K catalyst activated with hydrogen, (○) syngas (H_2:CO=0.7) and (◇) carbon monoxide. Synthesis conditions: H_2:CO=0.7, 3.1 Nl h^{-1} g-Fe^{-1}, 230°C and 1.31 MPa.

Carbon dioxide selectivity was found to be higher for the catalyst with copper (Fig. 8) which indicates that copper is a promoter for the water-gas shift reaction. Carbon dioxide selectivity obtained for the 100Fe/4.4Si/2.6Cu/5.2K catalyst varied according to the activation gas as follows: carbon monoxide<syngas<hydrogen (Fig. 9). Bukur et al. also report that

Table 1
Selectivity of 230°C FTS runs

Activation gas	H_2		CO		H_2:CO=0.7	
Catalyst [a]	I	II	I	II	I	II
TOS, h	168	168	168	192	624	192
Conversion, mol%						
CO	17	35	40	39	25	68
H_2	17	31	42	38	22	58
CO+H_2	17	34	41	39	24	64
Water-gas shift						
H_2:CO usage	0.69	0.60	0.73	0.68	0.64	0.60
K_p [b]	4	9	3	4	4	11
CO_2 selectivity, %, C basis	44	42	43	42	44	45
Productivity						
Total HC g^{-3} feed	35	71	83	84	51	138
C_3+HC g^{-3} feed	33	65	78	79	45	130
C_3+HC g^{-3} converted	194	191	190	202	188	203
Total HC g h^{-1} g-Fe^{-1}	0.10	0.22	0.25	0.26	0.15	0.42
Selectivity, wt% [c]						
C_1	2.6	3.8	2.9	2.2	5.7	2.2
C_2–C_4 (alkene) [d]	10	14(72)	15(82)	12(80)	21(79)	11(77)
C_5–C_{11} (alkene) [d]	20	37(66)	27(78)	25(76)	34(75)	15(78)
C_{12}^+	67	44	55	60	39	72
1-alkene, wt% [c]						
C_2	2.0	2.9	3.4	2.6	5.2	2.5
C_3	2.8	4.1	4.9	3.9	6.4	3.4
C_4	2.2	3.2	3.8	3.2	4.4	2.1
C_5	1.8	4.2	3.1	2.6	4.8	2.3
C_6	2.1	3.2	3.0	2.6	3.9	1.4
C_7	1.4	2.4	2.9	2.1	4.1	1.3
C_8	1.3	2.2	2.3	2.2	2.8	1.2
C_9	0.96	2.5	1.9	1.9	2.8	1.2
C_{10}	1.2	2.2	1.6	1.6	2.0	1.1
C_{11}	1.2	2.1	1.4	1.6	1.9	1.1

[a] I – 100Fe/4.4 Si/5.2K; II – 100Fe/4.4Si/2.6Cu/5.2K.
[b] $K_p = (p_{CO_2} p_{H_2})/(p_{CO} p_{H_2O})$.
[c] Based on total hydrocarbon product.
[d] Wt% of hydrocarbon fraction.

hydrogen activation leads to higher water-gas shift activity when operating at 260°C [9].

Product selectivities for the 100Fe/4.4Si/5.2K and 100Fe/4.4Si/2.6Cu/5.2K catalysts are shown in Table 1. Methane selectivity was low and wax selectivity was high for all runs. The best overall performance, based on syngas conversion and selectivity, was achieved by the syngas activated 100Fe/4.4Si/2.6Cu/5.2K catalyst. This is unlike the runs made at 270°C with the 100Fe/4.4Si/1.0K catalyst which had similar activity when activated with carbon monoxide or syngas. Methane selectivity <3 wt% (based on total hydrocarbon product), wax selectivity >70 wt% and high alkene yields were obtained at moderately high carbon monoxide conversion (>60%). The syngas activated 100Fe/4.4Si/2.6Cu/5.2K catalyst showed reasonable stability with total conversion >50% maintained for over 300 h. Contrary to FTS activity, alkene selectivity is not appreciably affected by the activation gas or the presence of copper. Alkene selectivity for the C_2–C_{11} product fraction was typically >70 wt%. As far as the commercial viability of iron-based FTS catalysts is concerned, most of the interest has focused on their ability to produce 1-alkenes for chemical feedstocks. We have found that >95% of the alkene fraction is composed of 1-alkenes for the 100Fe/4.4Si/*x*Cu/5.2K catalysts (x=0 or 2.6) when FTS is conducted at 230°C. Table 1 shows the selectivity of the C_2–C_{11} 1-alkenes relative to the total FTS product. Although geared for the production of wax and transportation fuels, the 100Fe/4.4Si/2.6Cu/5.2K catalyst also produces significant amounts of light alkenes, in fact, ethylene, propylene and 1-butene are the most abundant of all products by mass.

4. Conclusions

Moderately high FTS activity has been achieved in the slurry phase under industrially relevant conditions with a precipitated iron-silicon catalyst at 230°C. Optimum potassium promotion for a 100Fe/4.4Si/*x*K catalyst is in the range of 4–5 at%, relative to iron. In general, syngas and carbon monoxide activations at 270°C and 0.10 MPa result in better catalyst performance than hydrogen activation at 220°C. Low methane and high wax and alkene selectivities have been achieved for 100Fe/4.4Si/*x*Cu/5.2K catalysts (x=0 or 2.6).

The major difference between running at 270 and 230°C has been a rapid deactivation after ≈300 h on stream for the 230°C runs. Work in progress suggests that the deactivation is linked to the difficulty of separating the catalyst from the heavy wax that accumulates in the reactor. Eventually, all the runs reported here were stopped because the reactors had filled with wax soon after plugging of the internal filter. Work in progress has shown that a lower catalyst loading (<5 wt%), to reduce wax production, has enabled us to run for longer times and verify that the 100Fe/4.4Si/2.6Cu/5.2K catalyst is stable for >500 h. A study of catalyst deactivation will be reported elsewhere.

Copper promotion has been found to be imperative for low-temperature FTS or when hydrogen activations are utilized. Hydrocarbon productivity increased by as much as a factor of two with copper promotion. Copper has been found to increase the activity of hydrogen activated catalysts by lowering the reduction temperature which, in turn, reduces sintering of the metallic iron that is formed [2]. However, this does not explain why FTS activity of carbon monoxide and syngas activated catalysts is increased dramatically by copper promotion. Carbon monoxide and syngas activation generally reduce iron oxide catalysts to a mixture of iron carbides which are not as susceptible to sintering as metallic iron. TGAs clearly show that copper lowers the reduction temperature of hydrogen, carbon monoxide and syngas-treated catalysts. In addition, it has been found that the temperature of the reduction onset is correlated with the amount of copper. Based on previous reports, it can be speculated that increasing copper content increases the number of nucleation sites for the reduction process [25].

The FTS reaction requires a 2:1 hydrogen:carbon monoxide ratio, so catalysts must have good water-gas shift activity if syngas with low levels of hydrogen is used, that is H_2:CO=0.7. One possibility for the increase in FTS activity with copper promotion is that copper increases the water-gas shift activity. This is consistent with copper being used in commercial low-temperature water-gas shift catalysts. We have also found that copper promotion appears to favor the formation of iron carbides [12]. It may be possible that copper increases the activity of iron catalysts by increasing the number of active sites that are formed. Assuming that the active site(s) is a zero valence surface species, copper may serve as a means of preventing oxidation of the active metallic iron or iron carbide.

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