Investigations on the effect of reaction parameters over Fe/Cu/K catalyst for the production of selective range of liquid hydrocarbon

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Abstract. Effect of reaction conditions were investigated for Fischer-Tropsch (FT) synthesis process over Fe/Cu/K/SiO₂ catalyst for maximization of a selective range of liquid hydrocarbon (C_{5–20}). Operating conditions of the reaction have a strong impact on the activity and selectivity of the process. The parameters that influence the FT synthesis reaction and product distribution include the reactor temperature, pressure, space velocity, the H₂/CO molar ratio in the feed syngas and the catalyst. Experiments were performed at varying range of temperature, pressure, Space velocity and H₂/CO molar ratio. Variation in C₅₊ selectivity and (olefin/paraffin) O/P ratio were observed and analyzed to select the optimum values. Reaction conditions affect the H₂ and CO surface coverage and re-adsorption of olefins which play a crucial role in altering overall product selectivity. Reaction rates for FT and water gas shift (WGS) reactions were compared at different conditions. At optimum conditions, CO conversion and C₅₊ selectivity were 45.9% and 77.4%, respectively.

Keywords. Syngas; CO-hydrogenation; product selectivity; Fischer-Tropsch Synthesis.

1. Introduction

Hydrogenation of CO is a key step of Fischer-Tropsch (FT) Process which produces a spectrum of products in the form of liquid hydrocarbons. The crucial step of the process is optimization of the operating conditions with the proper catalyst selection. Selection and the screening of catalysts were already accomplished in our earlier work.^{1,2} Effect of Cu and K promoters has been investigated over the Fe/SiO₂ catalyst, and it was shown that along with textural and morphological properties, promoters also influenced the activity and product selectivity of catalyst.

Reaction parameters had a strong impact on the catalyst performance which eventually affects the product distribution. Effect of operating condition and the consequences of the variation of the parameters were investigated by various authors.^{3–7} Bukur *et al.*,⁴ investigated the effect of reaction parameter on the activity and product selectivity of commercial silica-based Fe catalyst. While investigating the effect of process variables on the reaction rates and the performance of Fe–Co–Mn catalyst. Arsalanfar *et al.*,⁵ observed that the parameters such as temperature, pressure, and the H₂/CO ratio had

a marked impact on the rates of CO consumption, CH₄ formation, and hydrocarbon formation. Ozkara-Aydinoglu *et al.*,⁶ studied the effect of reaction conditions and catalyst loading on the carbon number distribution in the product using precipitated Fe catalysts promoted with K and Cu. They also observed that the change in process conditions had a significant effect on hydrocarbon product distribution. Product distribution shifted towards higher molecular weight products (C₁₉₊ range) with the decrease in space velocity, but in case of temperature, an opposite trend was observed.

Product distribution, especially the nature of the liquid product strongly depends on the operating condition. Anderson *et al.*, introduced the first product distribution model in terms of Anderson–Schulz–Flory (ASF) equation.^{8,9} In the long history of FT, researchers have followed both classical ASF non-ASF behavior of the product distribution but at present the behavior of chain growth probability (α) with reaction parameter is the main matter of concern. Lox *et al.*,¹⁰ and Song *et al.*,¹¹ employed reaction mechanisms to explain the dependence of product selectivity upon temperature. They confirmed the dependence of chain growth probability on temperature and partial pressure of hydrogen and carbon monoxide. Their results showed that the value is considerably reduced in the high-temperature

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range. According to Todici *et al.*,³ mechanistic reasons behind the behavior of α is not crystal clear but they explained the dependence of α on the reaction parameter by the secondary pathway of reaction. For 0.48% Re–25% Co/Al₂O₃ catalyst in a slurry bed reactor, it was observed that the variation in H₂/CO ratio affects the value of α considerably while with increasing pressure and decreasing temperature, a small increase in the value of α is evident. Y.-Y. Ji *et al.*,¹² emphasized the unclear point regarding product distribution in the FT process. They observed that the carbon number distribution for Fe–Mn catalyst depends on the physical properties of hydrocarbon. Whereas in the case of alkenes, the change in product distribution with the operating condition depends on the thermodynamic properties. Some studies are available in the field of FT process related to the effect of operating condition. These effects were studied either on the %CO conversion or the quality of liquid product distribution which is characterized by the variation of chain growth probability α . A combined study is needed to select an optimum reaction conditions under which all the responses show optimum values.

In the present work, a detailed investigation was done to observe the performance of promoted iron catalyst along with varying operating parameters. While selecting the optimum reaction conditions, variation in the %CO conversion, C₅₊ selectivity, liquid product distribution and chain growth probability were analyzed in detail. Some experiments were done by varying range of process conditions (temperature, pressure, H₂/CO molar ratio and space velocity). Performance of Fe–Cu–K catalyst prepared using co-precipitation method was investigated in a fixed bed reactor system.

2. Experimental

Silica-supported Fe–Cu–K (wt% 35.5/5/1) catalyst was prepared using co-precipitation followed by wet impregnation technique. A detailed description of catalyst preparation and characterization were discussed elsewhere.¹ Fresh calcined catalyst were characterized with different techniques such as BET, TPR-TPD, XRD, EDX, etc. The spent catalyst was also characterized using XRD, TGA to understand the catalyst deactivation. The results describe the effect of loading of active components on catalysts and their influence on the textural and morphological properties. Catalytic activity, selectivity towards product distribution were related to the morphological changes and the nature of coke formation.^{1,2} The increasing K content increases the coke formation which increases the rate of catalyst deactivation. The optimum composition of the catalyst was observed to be Fe–Cu–K (35.5/5/1, wt%).

The CO-hydrogenation reaction was investigated in a fixed bed reactor (12.6 mm × 290 mm) of total volume 36.14 cm³. Detailed description of the experimental set up has been described elsewhere.⁷ In a typical experiment, 3 g (2.49 cm³) of the calcined catalyst was diluted with inert silicon carbide with a volume ratio of 1:5. Initially, the catalyst was reduced in situ at 220 ± 3 °C in a pure hydrogen atmosphere for 6 h under atmospheric pressure. GHSV (gas hourly space velocity) is defined as the volumetric gas flow rate (cc/h) per unit weight of the catalyst (gcat). The flow rate of H₂ was maintained at GHSV of 12000 cc/gcat-h for the reduction of the calcined catalyst. After complete reduction, the temperature of the reactor was increased gradually at a rate of 3 °C/min to the reaction temperature and the desired pressure was maintained. Gas-liquid separator was installed at the outlet where a higher fraction of liquid hydrocarbon get condensed and uncondensed gases go to a gas chromatograph for further analysis.^{7,13} The gaseous products were analyzed by a gas chromatograph equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). Liquid products were analyzed by Simulated Distillation Analyzer using ASTM D2887 method. The carbon balance as determined for each run was near to 95 ± 2%. The identification of different key components present in liquid products formed over catalyst was analyzed by GC-MS (Model: Perkin-Elmer Clarus-600).

The effect of various process variables (*viz.*, T, P, H₂/CO molar ratio and GHSV) on the catalytic performance of the Cu-K promoted silica supported Fe based catalyst (Fe/Cu/K, wt%: 35.5/3/1) was investigated. Effect of temperature was examined in the range of 215 to 245 °C and pressure was varied from 5 to 25 bar. Similarly, the range for H₂/CO molar ratio was 0.7 to 3.0 and GHSV was varied from 1000 to 4000 cc/gcat-h. In all the runs, reduced catalyst was tested for ~100 h at the different operating condition. CO conversion and percent product selectivity are shown in Figures 1 to 6. CO conversion and product selectivity (%) on carbon basis were calculated using following Eq.refeq1 and Eq.refeq2, respectively².

$$\begin{aligned} \text{CO conversion(\%)} \\ = \frac{(\text{moles of CO})_{\text{in}} - (\text{moles of CO})_{\text{out}}}{(\text{moles of CO})_{\text{in}}} \times 100 \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Product selectivity(\%)} \\ = \frac{(\text{moles of product})}{(\text{moles of CO reacted})} \times 100 \end{aligned} \quad (2)$$

3. Results and Discussion

To achieve the optimum conditions for maximum CO conversion and C₅₊ selectivity, results have been compared at varying conditions. Results in terms of olefin to paraffin ratio (O/P), product distributions in gas phase and liquid phase were examined at various operating conditions. The temperature is an important reaction

parameter which affects the CO conversion and product selectivity. The reactor temperature should be properly controlled to maintain a constant temperature throughout the catalyst bed. To achieve maximum CO conversion and desirable product selectivity, the selection of an appropriate reactor temperature is necessary. The reactor pressure in FT synthesis can be used for the maximization of liquid hydrocarbon yields. Space velocity is the ratio of the feed flow rate to the reactor volume or size and is used for rating the size of the reactor. The implication of varying the syngas space velocity in a commercial FT application is of interest, as the relationship of space velocity to the size of the FT reactor vessel is inversely proportional.

3.1 Effect of process condition on %CO conversion and C_{5+} selectivity

As the temperature is increased from 215 to 245 °C, CO conversion increased from 32% to 50% (Figure 1a). At the same time, selectivity to C_{5+} fraction diminished from 85% to 45%. It is reported that the CO dissociation increases with increasing temperature and provides more surface C species for hydrocarbons formation and thereby increases CO conversion.^{14,15} It can be noticed that the change in conversion is not significant from temperature 225 °C to 245 °C, however, decrease in C_{5+} selectivity is significant. A good trade-off between high conversion and high C_{5+} selectivity was observed at temperatures between 225 and 235 °C. Figure 1b shows the influence of the pressure on CO conversion and C_{5+} selectivity during the FT synthesis. The results show that an increase in pressure from 5 to 25 bar, %CO conversion increases from 28.8 to 42.9%. Also, the selectivity of liquid hydrocarbons (C_{5+}) increased by increasing the pressure. Collision probability of the reactant to the catalysts surfaces increases with increasing pressure which in turn enhances the concentration of active surface carbon species.¹⁶ It is also reported that with increasing pressure, contact time of the reactant species with solid surface increases and is responsible for increased CO conversion with pressure. The increased selectivity to long chain hydrocarbon can be attributed to the fact that at higher pressure individual CH_2 units are available on the catalyst surface which favor chain growth reactions.¹⁷ Hydrogenation and oligomerization reaction is also favored at high pressure on the surface of the catalyst. Therefore, C_{5+} selectivity increases with the pressure. On comparing the combine response of conversion and C_{5+} selectivity, it was observed that at a higher pressure above 15 bar there is no significant change in conversion level. However, selectivity

to C_{5+} increases significantly. In Figure 1c, the effect of varying feed gas velocity is examined for CO conversion and C_{5+} selectivity. The CO conversion decreased progressively from 50% to 28% as the space velocity increased from 1000 to 4000 cc/gcat-h. At the same time selectivity to C_{5+} also decreases with increasing space velocity. Increasing space velocity decreases the residence time and suppresses the chain growth leading to the more formation of light hydrocarbons and less formation of C_{5+} hydrocarbons. The results obtained are in contradiction with the findings of few researchers.^{16,18} However, Iglesia *et al.*,¹⁹ observed the same trend and suggested that as residence time increases, C_{5+} selectivity increases. Reason relied on was the secondary reactions which contribute to chain growth probability and increases product with higher molecular weight. Chain growth probability for C_{5+} chains is strongly affected by residence time of the reactant. It can also be explained with the help of chain termination probability which decreases for C_2 - C_{15} chains, as the reactant gets more time for exposure at catalyst site. The net rate of chain termination of olefins decreases, depending upon the extent of readsorption of larger olefin. On the contrary, rate of chain termination to form paraffin is not affected significantly. At higher space velocity chain growth probability is suppressed leading to less formation of higher hydrocarbons.²⁰ While investigating the effect of H_2 /CO ratio of feed gas (Figure 1d), it was observed that CO conversion increases along with increasing H_2 /CO molar ratio (0.7 to 2). It reaches a maximum value at H_2 /CO = 2 and then decreases for further increase in the H_2 /CO ratio. C_{5+} hydrocarbon decreases with increase in H_2 /CO ratio. Our finding of CO conversion trend corroborates with the results obtained by Mirzaei *et al.*,¹⁸ and Sarkari *et al.*²¹ They indicated that after H_2 /CO = 2.5, there is a large difference in the partial pressure of H_2 and CO and relatively small amount of adsorbed CO is surrounded by adsorbed H species. The consequences of the process end up producing lower chain hydrocarbon. Also, at very low H_2 /CO ratio, activity for FT synthesis is low because of the relative adsorption rate of CO and H_2 . At low H_2 /CO ratio, the rate of adsorption of CO is higher than that of H_2 which creates a scarcity of H_2 at the surface and leads to a lower FT activity.¹⁵ In contrast to our findings, Luo *et al.*,²² related the results of CO conversion with the H_2 utilization rate and carbide phase formation rate. At high H_2 /CO ratio, H_2 utilization decreases and at the same time lower partial pressure of CO affects the carbide phase formation of an iron catalyst which in turn decreases FT activity. C_{5+} hydrocarbon decreases with increase in H_2 /CO ratio. Formation of long-chain hydrocarbon (C_{5+}) depends on the probability of chain

Figure 1. Effect of process condition on %CO conversion and C₅₊ Selectivity. (a) Effect of T; (b) Effect of P; (c) Effect of GHSV; (d) Effect of H₂/CO ratio. (H₂/CO = 2, GHSV = 2000 cc/gcat-h and P = 15 bar, T = 225 °C).

propagation and termination step. Partial pressures of H₂ and CO directly affect these steps and shift the product selectivity to either long chain hydrocarbon or light hydrocarbon. Increasing H₂/CO ratio to high H₂ concentration increases the termination of growing chain, and as a result, C₅₊ selectivity decreases.^{23–25} Similarly, increased C₅₊ fraction at lower H₂/CO molar ratio can also be explained by different reaction steps involved. At lower H₂/CO ratio, condensation steps dominate over the hydrogenation steps. On comparing the combined response of CO conversion and C₅₊ production, it was observed that at H₂/CO ratio of 1 and 2, the results are in favor of high CO conversion with high selectivity to C₅₊ product.

In the view of above discussion, a range of operating parameters were selected for further investigation. Combining the change in responses with the change in all four parameters, it can be observed that temperature

range of 215–225 °C, the pressure of 15–20 bar, GHSV of 1000–2000 cc/gcat-h and the H₂/CO ratio of 1 to 2 are suitable for maximum %CO conversion along with maximum C₅₊ selectivity. To narrow down the selected range of process parameter, the variation in the product distributions in gas as well as liquid range were investigated in the next section.

3.2 Effect of process condition on product distribution

Figure 2 reveals the effect of varying reaction conditions on product distribution. Results reveal that hydrocarbon distribution is significantly changed by the change in temperature. As the reaction temperature is increased, the selectivity to methane (C₁) increased from 4.9% to 9.3%, and selectivity to lighter fraction (C₂–C₄) increased from 5.7% to 20%. As discussed above,

Figure 2. Effect of process conditions on product distribution. (a) Effect of T; (b) Effect of P; (c) Effect of GHSV; (d) Effect of H₂/CO ratio. (H₂/CO = 2, GHSV = 2000 cc/gcat-h and P = 15 bar, T = 225 °C).

the temperature affects the CO dissociation rate in a positive manner which creates an abundant amount of surface H species and enhances methane formation. Because of high rates of CH₄ production, the concentration of H₂ and CO within the catalyst bed changes. Increased H₂/CO ratio inside the reactor affects the readsorption of olefins and secondary hydrogenation reaction. These reactions become less dominant, and as a result, the ratio of olefin to paraffin increases with reaction temperature. Another important parameter is chain growth probability which is defined as the ratio of the rate of chain propagation to the sum of rate of termination and propagation. Increase in temperature decreases the chain growth probability which causes

higher amount of lighter fraction (C₂-C₄) in the product stream.^{26,27} Results of Tian *et al.*,¹⁵ also corroborated with our finding and indicated that increasing temperature reduced CO coverage and increased the H coverage, and therefore, the selectivity to desired liquid hydrocarbon fraction (C₅+) decreased, whereas, methane and lighter hydrocarbon fraction (C₁ and C₂-C₄) increased. Increasing temperature shifts the product towards lower range hydrocarbons. Thermodynamically, methane and lower hydrocarbons show higher stability at higher temperature conditions. In case of higher hydrocarbons, cracking and de-alkylation reactions can quickly take place at high temperature as they are sensitive at a higher temperature. Also, at high temperature, polymer-

ization reactions are less favored; therefore the yield of higher hydrocarbon decreased. Dalai *et al.*,²⁸ indicated that increasing temperature favors desorption of hydrocarbon rather than propagation step. Cracking of higher hydrocarbons at a higher temperature could also be the reason for improved selectivity to lower hydrocarbon fraction. It is reported that high partial pressure of H_2 on K promoted catalyst surface increases the rate of chain termination step to lower paraffin (i.e., CH_4). α -Olefins readsorption is a way towards the formation of C_{5+} hydrocarbon. However, increase in temperature affects the concentration of re-adsorbed α -olefin as it favors desorption rather than readsorption of the compound.²⁹

It is well known that the relative activities of Fischer-Tropsch Synthesis (FTS) and WGS reaction affect the CO conversion level and change the product selectivity. In the product stream, CO is distributed among hydrocarbon and CO_2 . Formation of these products takes place *via* FTS reaction and WGS reaction. It can also be observed from our finding that FTS rate is relatively higher than WGS at lower CO conversion level ($\sim$ at a temperature of 215 °C) due to which higher fraction of CO was converted to hydrocarbons. It is also reported in the literature that the addition of K in catalyst favors FTS rate and inhibits WGS reaction.³⁰ However, the rapid rate of FTS decreases H_2/CO ratio inside the reactor and rate-determining step shifts from FTS to WGS reaction. Thus, at 245 °C, WGS rate and the selectivity towards CO_2 were increased for K promoted catalyst. From our finding (Figure 2a), it is observed that selectivity to lower hydrocarbons (C_2 - C_4) shows an opposite trend concerning C_{5+} selectivity. In contrast to our results, Li *et al.*,³¹ reported that the C_{5+} fraction increases with increase in temperature because condensation steps are having a smaller value of activation energy than those for hydrogenation of light hydrocarbons. Results obtained by Madon *et al.*,³² also contradicts with our finding. They indicated that with increasing temperature, there is a sharp reduction in CO_2 selectivity and whereas the C_{5+} selectivity remained constant.

In case of increasing pressure (Figure 2b), selectivity towards methane and C_2 - C_4 gaseous product decreases. The decrease in CH_4 formation with an increase in pressure is attributed to an increase in the rate of formation of long chain hydrocarbon due to olefin readsorption. From Figure 3b, it is clear that CO_2 selectivity decreases with increase in pressure. Madon *et al.*,³² explained the reason in terms of water gas shift activity. At lower pressure, the rate of water gas shift reaction is higher, however at higher pressure reverse water gas shift reaction becomes dominant. At higher pressure

hydrogen produced by water gas shift reaction is consumed as a reactant which results in lower formation of CO_2 .

With the increase in space velocity, selectivity to CH_4 , C_2 - C_4 , and CO_2 is enhanced at the specified range of GHSV (Figure 2c). Our finding corroborates the results obtained by Dalil *et al.*,²³ which explained the reason for the term of contact time of reactant on active site. Increasing the GHSV could not provide sufficient times for different step involved in the process of long chain formation such as chain propagation step, secondary reactions, olefins readsorption and production of paraffin. Also, due to pore filling phenomenon, diffusion of reactant plays an influential role in the removal of hydrocarbons from the catalyst surface however at high gas space velocity mass transfer limitations get eliminated which entirely change the product distribution.³³ At lower GHSV, methane interacts with the reactants while attached to the surface and the chain propagates to produce long chain hydrocarbons. However, at high reactant flow rate CH_4 may desorb without interacting other following reactant and it will end up forming more and more methane. Thus, an optimum flow rate is required to the catalyst surface to facilitate chain growth and production of long chain hydrocarbon.

Decreased selectivity to CO_2 with increasing H_2/CO ratio (Figure 2d) can be explained with the help of water gas shift activity. The WGS is inhibited due to higher H_2 content in the gas of higher H_2/CO ratio. It is also observed from that increasing H_2/CO ratios in the feed stream result in the higher amount of lower range hydrocarbons (C_1 and C_2 - C_4), the lower olefin to paraffin ratios (O/P). These results corroborate with the result obtained by Donnelly and Satterfield.³⁴ Results also reveal that the selectivity to methane increases with increasing H_2/CO ratio in the feed.

In the light of above discussion, selection of optimum reaction parameters at which maximum CO should convert into the desired hydrocarbon with minimization of loss of carbon through the production of methane and CO_2 , is possible. On comparing the product distribution at temperatures 215 °C and 225 °C, the former one was suitable for desired product distribution. However, the CO conversion was maximum at 225 °C. In case of pressure, product distribution was almost comparable at both pressure of 20 bar and 25 bar. H_2/CO ratio of 0.7 and 1 is comparable. However, the %CO was maximum at the ratio of 1. Similarly, in case of GHSV of 1000 and 2000 cc/gcat-h, the product distribution was almost similar. To present a clearer picture, further analysis was done for the olefin to paraffin ratio over varying range of reaction conditions.

Figure 3. Effect of process condition on olefin-to-paraffin (O/P) ratio. (a) Effect of T; (b) Effect of P; (c) Effect of GHSV; (d) Effect of H₂/CO ratio. (H₂/CO = 2, GHSV = 2000 cc/gcat-h and P = 15 bar, T = 225 °C).

3.3 Effect of process condition on O/P ratio

Figure 3a indicates that the ratio of the selectivity to a light olefin-to-paraffin ratio (O/P) over the iron-based catalyst increases with increasing temperature (215 °C to 245 °C). The fraction of unsaturated hydrocarbons was significantly increased by increasing the reaction temperature. The explanation was based on the fact that the rate of dehydrogenation reaction increases with an increase in temperature.³⁵ The rate of formation of 1-olefin compared to rate olefin hydrogenation is the decisive factor on which increase or decrease of selectivity depends. Addition of K promoter enhances CO chemisorption and restrains H₂ adsorption which results in an increased olefin formation and low hydrogenation activity. Therefore, olefin selectivity will increase with

reaction temperature for K loaded catalysts. Our results corroborate with the finding of several researchers, and they found that for K promoted iron catalysts, olefin-to-paraffin ratio increases with increasing temperature.^{25,36} Secondary reactions (isomerization and hydrogenation) may also be responsible for such behavior of the product distribution with temperature. The ratio of 2-butene to 1-butene ratio is an important measure of secondary reactions. It can be seen from Figure 3a that isomerization activity of the catalyst decreases whereas olefin/paraffin selectivity increases with temperature. Reduced hydrogen adsorption at high temperature can be a cause of low isomerization activity.

Effect of pressure is evident on gaseous olefin to paraffin ratio (O/P). Formation of α -olefin is the primary reaction during FT synthesis which hydrogenates

to form the corresponding paraffin. It is observed from Figure 3b that the selectivity for low carbon number olefins (C_2 - C_4 olefins) decreased with increase in pressure from 5 to 25 bar. This may be due to increase in secondary hydrogenation. It is also confirmed through various literature reports that an increase in total reactor pressure result in condensation of hydrocarbons which saturates the catalyst pores.^{25,37} At high pressures, the presence of liquid phase in catalyst pores could affect the rate of elementary steps and the concentrations of carbon monoxide and hydrogen in the vicinity of catalyst site. To reach the active site, reactants have to diffuse through the liquid filled pore and depending upon the diffusivity of the reactant, H_2 /CO molar ratio changes. At the same time reaction products have to diffuse in the opposite direction. It was observed that olefins re-adsorbed on the active sites and reinserted in the growing chain (forming heavier hydrocarbons) or can be hydrogenated to the corresponding paraffin.³⁸ So the increased pressure strongly affects the liquid product selectivity. It is also reported in the literature that increasing pressure in the system, increases the partial pressure of H_2 . This enhances hydrogenation reaction. Olefins produced from the process get saturated. Madon *et al.*,²⁹ indicated that the hydrogenation of the primary α -olefin product becomes more effective at higher pressure. The ratio of 2-butene to 1-butene increases with pressure indicating that the isomerization of the product is also increased. Therefore, the linearity of the paraffinic hydrocarbon will diminish with the increasing pressure.

It is observed from Figure 3c that selectivity ratio of $C_2 = \text{C}_2/\text{C}_2$, $C_3 = \text{C}_3/\text{C}_3$ and $C_4 = \text{C}_4/\text{C}_4$ increased with the increase of space velocity from 1000 to 4000 cc/gcat-h. Selectivity to paraffin decreased and that of olefins increased with space velocity. Teng *et al.*,²⁶ also reported the similar trend that with increasing space velocity, olefin-to-paraffin ratio increased significantly. Similar trend was observed by Kuipers *et al.*,³⁸ Bukur *et al.*,⁴ and Iglesia *et al.*,²⁸ on various FT catalysts. These results indicate that the GHSV is an important parameter which plays a decisive factor on the catalytic performance of K-promoted iron-based catalysts for hydrogenation of CO. Another very important observation is that selectivity ratio of 2-butene to 1-butene decreased with increasing space velocity. Our finding corroborates with the results obtained by Donnelly *et al.*,³⁴ and Iglesia *et al.*²⁰ They suggested that increasing reactant flow rate diminish the selectivity to 1-butene. This depletion of α -olefins in the product are not caused by secondary hydrogenation or double bond migration reaction. This is due readsorption of 1-butene to the surface which subsequently helps in chain growth. So the

selective readsorption steps may be responsible for the decreased olefin-to-paraffin ratios with increasing residence time. Dictor *et al.*,³⁹ had reported a slight decrease in selectivity ratio of 2-butene to 1-butene olefin content with increased space velocity on potassium-free Fe_2O_3 powders at high H_2 /CO ratios.

While observing the effect of H_2 /CO ratio, it was observed that the selectivity to both heavier hydrocarbons (C_{5+}) and olefin-to-paraffin ratio (O/P) (Figures 1d and 4d) decreased by increasing the H_2 content in the feed gas. The relatively higher concentration of hydrogen inhibits the formation of long-chain hydrocarbon and favors the termination of hydrocarbon chains into lower paraffin. Therefore, H_2 rich feed gas increases the termination rate of product in the form of paraffin, reducing the number of olefins. At the other end, olefin fraction increases with lowering H_2 /CO molar ratio. As already discussed, the formation of α -olefin is a primary step of FT synthesis. At lower H_2 concentration, these species either readsorb to form a long chain or desorb to form olefin but do not get hydrogenated and O/P ratio remain high in product stream.^{32,40} It is clear that α -olefins mainly consume by either incorporation in growing chain or by hydrogenation. At higher H_2 /CO ratio hydrogenation reaction dominates. Another reason for high O/P ratio at low H_2 /CO is restricted mobility of H_2 . The consequence of reduced H_2 motility, as well as reduced hydrogen adsorption rate, is the decrease in the rate of hydrogenation of alkenes to alkanes. The selectivity ratio of 2-butene to 1-butene increased with increase in inlet H_2 /CO molar ratio (Figure 4d). This indicates that selectivity ratio of 2-butene to 1-butene increases with increasing H_2 partial pressure. These results are corroborating with the results of Donnelly *et al.*,³⁴ and Dictor *et al.*,³⁹ where it was reported that 2-butene to 1-butene ratio increases with increasing H_2 partial pressure and relatively independent of CO pressure.

In the above discussion, the focus was to show the effect of process condition on the distribution of gaseous hydrocarbons which is the important part of the product. Lower range olefins (C_2 - C_4) are important derivatives of petrochemical industries. In order to maximize the carbon utilization in the process, it is important that along with the liquid product, the gaseous product should also consist of valuable chemicals. Also, the measure of the ratio of 2-butene to 1-butene helps to anticipate the nature (linear or branched) of long-chained liquid hydrocarbons. While selecting the optimum conditions, higher temperature (245 °C) and higher GHSV (4000 cc/gcat-h) are excluded due to their low conversion level. Similarly, lower pressure (5 and 15 bar) and lower H_2 /CO ratio (0.7) cannot be considered for the same

Figure 4. Effect of process condition on C_{5+} liquid hydrocarbons products distribution. (a) Effect of T; (b) Effect of P; (c) Effect of GHSV; (d) Effect of H_2/CO molar ratio. ($H_2/CO = 2$, GHSV = 2000 cc/gcat-h and $P = 15$ bar, $T = 225$ °C).

reason. Temperature range of 215–225 °C, pressure 25 bar, GHSV of 2000 cc/gcat-h and the H_2/CO ratio of 1 are suitable for the reaction.

3.4 Liquid product distribution and chain growth probability (α)

The purpose of the work is to select appropriate reaction conditions for the maximization of the production of liquid hydrocarbon with the optimum CO conversion. In view of the aim of the work, quantitative analysis of the liquid product is equally important. As discussed earlier in section 3.1, reaction condition significantly affects the selectivity to C_{5+} product. To present a clearer picture, quantitative analysis of the liquid products was done and compared at varying reaction conditions. Effects of all four process parameters on liquid hydrocarbons

(C_{5+}) distribution are shown in Figure 4. The detailed liquid product distribution data at two selected reaction conditions based on carbon number are fitted in the Anderson–Schulz–Flory (ASF) model (Figure 5). Anderson *et al.* introduced the first product distribution model in terms of ASF equation.^{8,9} The model includes chain growth probability factor α which is a ratio of the rate of chain propagation to rates of chain termination plus propagation.

Increasing the temperature from 225 °C to 245 °C, the fraction of lower range hydrocarbons ($< C_{11}$) increases. At lower temperature (225 °C), as a result of secondary reactions which involve readsorption and incorporation of olefins into growing chains, the fraction of heavy paraffins is high. The influence of reaction pressure on distribution of liquid hydrocarbon product is shown in Figure 4b. Chain propagation is favored at

Figure 5. Effect of process condition on chain growth probability α (a) Effect of T (b) Effect of P (c) Effect of GHSV (d) Effect of H_2/CO molar ratio. ($H_2/CO = 2$, GHSV = 2000 cc/gcat-h and P = 15 bar, T = 225 °C).

a higher pressure. As a result, higher molecular weight hydrocarbon increases with increase in pressure. The ASF distributions were also obtained at two different pressure levels. In agreement with selectivity data, the increase of pressure leads to a significant variation in the slope of the corresponding ASF plot. Increasing pressure from 15 to 25 bar, the chain growth probability increased from 0.70 to 0.73 (Figure 5b). Our finding corroborates the results obtained by Sarkari *et al.*¹⁸ Effect of GHSV on C_{5+} liquid hydrocarbons products distribution at $H_2/CO = 2$, temperature = 225 °C and the pressure = 15 bar as shown in Figure 4c. The details of liquid product analyzed data at two different GHSV based on carbon number basis and the ASF chain growth fitted mechanism is presented (Figure 5c). With increasing GHSV from 2000 to 4000 cc/gcat-h, catalyst showed a higher amount of lighter hydrocarbons. The result shows that percentage of higher

molecular weight hydrocarbons is higher at 2000 cc/gcat/h ($< C_{11}$) compared to 4000 cc/gcat-h. With the increase of reaction GHSV from 2000 to 4000 cc/gcat-h, the ASF chain growth probability decreases from 0.7 to 0.68. Kuipers *et al.*,⁴¹ gave a most reasonable explanation for the decrease in chain growth probability with an increase in GHSV which explains that the occurrence of secondary reactions which include hydrogenation, reinsertion, hydrogenolysis, and isomerization severely minimizes with the increasing GHSV. Iglesia *et al.*,¹⁹ indicated that the increasing C_{5+} selectivity and CO conversion with increasing reactor residence time are poor of the contribution of secondary reaction in chain growth. Also, the olefin content for each carbon number group decreases, but chain growth probability for C_{5+} chains is increased with increased bed residence time. The influence of H_2/CO ratio on liquid hydrocarbons products distribution and the ASF chain

growth probability at temperature = 225 °C, GHSV = 2000 cc/gcat-h and the pressure = 15 bar is shown in Figures 4d and 5d, respectively. With increasing H₂/CO molar ratio from 1 to 2, catalyst showed a lower amount of heavier hydrocarbons. However, the catalyst has shown higher percentage of heavier hydrocarbons ($\geq C_{10}$) at H₂/CO = 1 compared to H₂/CO = 2. It is also clear that higher H₂/CO ratio is preferential for the chain termination to produce light hydrocarbons, while the lower H₂/CO ratio is preferential for chain growth and the production of heavy hydrocarbons.⁴² Figure 5d shows the relationship between the ASF chain growth probability and the H₂/CO ratio. It is found that the chain growth probability of the Fe-based catalyst decreases from 0.75 to 0.71 when the H₂/CO ratio increases from 1 to 2. This observation is consistent with the FTS mechanism, namely the competitive elementary steps of chain growth and chain termination. When the H₂/CO feed ratio changes from 1 to 2, the concentration of H₂ at the surface of the catalyst increases. This leads to high hydrogenation (chain termination) rates and lowers the ASF chain growth probability. Our finding corroborates the literature results.^{18,39}

The above discussion shows that the quality of the C₅₊ liquid product is shifted toward a desired range of hydrocarbon (C₁₁-C₂₀) at selected optimum reaction conditions (Temp - 225 °C, pressure - 25 bar, GHSV - 2000 cc/gcat-h and H₂/CO ratio - 1).

3.5 Effect of operating condition on the rate

The rate of FT reaction and WGS reaction is equally important in case of iron-based catalyst. Therefore while selecting the optimum reaction parameters, it mandatory to examine their effect on the rates. The rate of the WGS and FT reactions are defined below.

$$r_{WGS} = r_{CO_2}$$

$$r_{FT} = r_{CO} - r_{CO_2}$$

Where, r_{CO_2} is the rate of formation of CO₂ and r_{CO} is the rate of consumption of CO (conversion). r_{FT} is the FTS reaction rate (hydrocarbon formation rate). The rate of the water gas shift reaction is defined as the rate of CO₂ formation. Rate is expressed as g gcat⁻¹ s⁻¹. Water produced by the FT is limiting reactant for WGS reaction so the rate cannot be greater than the rate of the FT reaction. The effects of reaction parameters on the reaction rates are shown in Figure 6.

Increasing reaction temperature from 225 °C to 245 °C shows a positive effect on the conversion rate of CO. An increasing trend in FTS reaction rate with increasing temperature is observed (Figure 6a). Results

are in agreement with the literature reports.^{43,44} The observation shows a linear relation between FT rate and temperature. It is observed that CO₂ formation rate is low at 225 °C, whereas CO consumption and FTS rate are relatively higher. Also, at 225 °C temperature, liquid product (C₅₊) selectivity (Figure 1a) is also significant. It is also reported in the literature that at this temperature, WGS reaction is far away from equilibrium.^{45,46} Considering the above, 225 °C is considered as optimum temperature for FTS reaction for the selected catalyst.

In Figure 6b, it is evident that the rate of FTS reaction and rate of CO conversion increases with increasing pressure, whereas rate of CO₂ formation decreases. The reason may be the enhanced collision probability of the reactant to the catalyst active site which increases with the increased surface concentration of carbon species. As a result, the rate of CO conversion reaction is enhanced. It is observed that rate of CO₂ formation is lowest at 25 bar pressure, whereas CO consumption and FTS rate are highest. Also, at 25 bar pressure, C₅₊ selectivity (Figure 1b) is also higher. Considering the above, 25 bar pressure is considered as optimum pressure for hydrocarbon formation for the selected catalyst.

As space velocity increases from 1000 to 2000 cc/g cat/h, there is a sharp increase in the rate of FTS reaction however further increase up to 4000 cc/g cat/h shows a gradual increase in the same (Figure 6c). Almost similar trends are observed in case of CO conversion rate and CO₂ formation rate. At higher space velocities, FT rate dominates the water gas shift rate. However at lower space velocity both FT and water gas shift rates decrease and conversion increases. It can be concluded that CO₂ formation rate at GHSV of 2000 cc/gcat-h is lower, whereas CO conversion (Figure 1a) is reasonably good. Optimum GHSV of 2000 cc/gcat-h is considered for hydrocarbon formation rate for selected Cat-1K catalyst.

As mentioned above, FTS reaction and product selectivity also depend on the H₂/CO ratio. Figure 6d shows the effect of H₂/CO ratio on the reaction rates. It is observed that rate of CO₂ formation decreases with increasing H₂/CO ratio. This is due to increase in the hydrogen concentration which eventually increases partial pressure and shifts the water gas shift reaction in the opposite direction.⁴⁷ The CO conversion rate and FTS reaction rate increased up to H₂/CO molar ratio of 1, and after that, it decreases with increase in H₂/CO ratio. Also, liquid hydrocarbon selectivity is higher at a lower H₂/CO ratio (Figure 1d). It is evident from the results that proper H₂/CO ratio in feed gas ends up attaining optimum selectivity to light olefins and

Figure 6. Effect of process condition on FTS rate and WGS reaction rates. (a) Effect of T; (b) Effect of P; (c) Effect of GHSV; (d) Effect of H₂/CO molar ratio. (H₂/CO = 2, GHSV = 2000 cc/gcat-h and P = 15 bar, T = 225 °C).

liquid hydrocarbons. It can be concluded from Figure 6c that CO₂ formation rate at H₂/CO ratio of close to 1 is reasonably lower, whereas CO consumption and FTS rate are also comparatively higher. An H₂/CO molar ratio near to 1 is considered as the optimum ratio for hydrocarbon formation for the selected catalyst.

From the above study, the optimum operating conditions for FT synthesis of silica-supported Fe–Cu–K catalyst are the temperature of 225 °C, the pressure of 25 bar, H₂/CO ratio of ~1 and GHSV of 2000 cc/gcat-h. The selected Cat-1K catalyst is tested at the above optimum operating conditions and performance of the catalyst is given in Table 1. At optimized operating conditions, CO conversion is 45.9 wt% once-through-mode operation (without recycle). C₅₊ selectivity for Cat-1K catalyst is 77.4 wt%.

4. Conclusions

Detailed study of FT reaction parameters was conducted in a fixed bed reactor over selected Cu, and K-promoted silica-supported Fe-based catalyst. CO conversion, selectivity to a lighter fraction (C₁ and C₂–C₄) increased, and C₅₊ fraction decreased by increasing the reaction temperature from 215 °C to 245 °C. It is also observed that selectivity to an olefin-to-paraffin ration increased with increasing temperature. With the increase in pressure from 5 to 25 bar, CO conversion increased. The selectivity of the liquid hydrocarbons (C₅₊) increased substantially by increasing the pressure, however, selectivity to methane, C₂–C₄ gaseous products and CO₂ decreased. It is observed that the selectivity for low carbon number olefins (ethylene, propylene and

Table 1. Conversion and product selectivity at optimized conditions.

Catalyst	Cat-1K
Temperature, °C	225
Pressure, bar	25
H ₂ /CO ratio	1
GHSV, cc/gcat-h	2000
Catalytic Performance	
Run duration, h	100
CO conversion, wt% (without recycle)	45.9
Selectivity, wt%, C basis	
C ₁	5.31
C ₂ -C ₄	10.13
C ₅ +	77.4
CO ₂	7.12

Activation conditions: T = 220 °C, P = 1 bar, Duration = 6 h, Activating agent = H₂, H₂ flow rate = 200 mL/g.Fe.

C₄ olefins) decreased with increase in pressure from 5–25 bar. CO conversion decreased with increasing space velocity from 1000 to 4000 cc/g cat/h. It is also observed that increase in space velocity, selectivity to CH₄, C₂-C₄, and CO₂ is enhanced at the specified range of GHSV. Selectivity ratio of C₂ = /C₂, C₃ = /C₃, and C₄ = /C₄ increased with the increase of space velocity. As H₂/CO molar feed ratio is increased from 0.7 to 2, CO conversion increases with the increase of ratio up to 2 then decreases for further increase of the H₂/CO ratio. Increasing H₂/CO feed ratio in the reactor also increases the amount of lighter hydrocarbons (C₁ and C₂-C₄) and decreases the selectivity to C₅+ and olefin to paraffin ratios.

The reaction temperature, pressure and space velocity positively affect the FTS reaction rate. However, FTS reaction rate passes through optimum value in case of increasing H₂/CO ratio. At optimized operating conditions (temperature – 225 °C, pressure - 25 bar, H₂/CO ratio - 1 and GHSV - 2000 cc/gcat-h), %CO conversion and C₅+ selectivity over the selected catalyst (35.5Fe/5Cu/1K) were 45.9 and 77.4%, respectively.

References

- Das S K, Mohanty P, Majhi S and Pant K K 2013 CO-hydrogenation over silica-supported iron-based catalysts: Influence of potassium loading *Appl. Energy* **111** 267
- Das S K, Majhi S, Mohanty P and Pant K K 2014 CO-hydrogenation of syngas to fuel using silica supported Fe–Cu–K catalysts: Effects of active components *Fuel Process. Technol.* **118** 82
- Todic B, Ma W, Jacobs G, Davis B H and Bukur D B 2014 Effect of process conditions on the product distribution of Fischer–Tropsch synthesis over a re-promoted cobalt-alumina catalyst using a stirred tank slurry reactor *J. Catal.* **311** 325
- Bukur D B, Patel S A and Lang X 1990 Fixed bed and slurry reactor studies of Fischer–Tropsch synthesis on precipitated iron catalyst *Appl. Catal.* **61** 329
- Arsalanfar M, Mirzaei A A, Bozorgzadeh H R and Atashi H 2012 Effect of process conditions on the surface reaction rates and catalytic performance of MgO supported Fe–Co–Mn catalyst for CO hydrogenation *J. Ind. Eng. Chem.* **18** 2092
- Özkara-Aydinoğlu Ş, Ataç Ö, Gül Ö F, Kınayyigit Ş, Şal S, Baranak M and Boz I 2012 α -Olefin selectivity of Fe–Cu–K catalysts in Fischer–Tropsch synthesis: Effects of catalyst composition and process conditions *Chem. Eng. J.* **181** 581
- Khobragade M, Majhi S and Pant K K 2012 Effect of K and CeO₂ Promoters on the activity of Co/SiO₂ catalyst for liquid fuel production from syngas *Appl. Energy* **94** 385
- Henrici-Olivé G and Olivé S 1976 The Fischer–Tropsch synthesis: Molecular weight distribution of primary products and reaction mechanism *Angew. Chem. Int. Ed. English* **15** 136
- Friedel R A and Anderson R B 1950 Composition of synthetic liquid fuels. I. Product distribution and analysis of C₅–C₈ paraffin isomers from cobalt catalyst *J. Am. Chem. Soc.* **72** 1212
- Lox E S and Froment G F 1993 Kinetics of the Fischer–Tropsch reaction on a precipitated promoted iron catalyst. 2. Kinetic modeling *Ind. Eng. Chem. Res.* **32** 71
- Song H S, Ramkrishna D, Trinh S and Wright H 2004 Operating strategies for Fischer–Tropsch reactors: a model-directed study *Korean J. Chem. Eng.* **21** 308
- Ji Y Y, Xiang H W, Yang J L, Xu Y Y, Li Y W and Zhong B 2001 Effect of reaction conditions on the product distribution during Fischer–Tropsch synthesis over an industrial Fe–Mn catalyst *Appl. Catal. A Gen.* **214** 77
- Mohanty P, Pant K K, Parikh J and Sharma D K 2011 Liquid fuel production from syngas using bifunctional CuO–CoO–Cr₂O₃ catalyst mixed with MFI zeolite *Fuel Process. Technol.* **92** 600
- Farias F E M, Silva R C, Cartaxo S J M, Fernandes F A N and Sales F G 2007 Effect of operating conditions on Fischer–Tropsch liquid products *Lat. Am. Appl. Res.* **37** 283
- Tian L, Huo C F, Cao D B, Yang Y, Xu J, Wu B S, Xiang H W, Xu Y Y and Li Y W 2010 Effects of reaction conditions on iron-catalyzed Fischer–Tropsch synthesis: A kinetic Monte Carlo study *J. Mol. Struct. Theochem.* **941** 30
- Feyzi M, Irandoust M and Mirzaei A A 2011 Effects of promoters and calcination conditions on the catalytic performance of iron–manganese catalysts for Fischer–Tropsch synthesis *Fuel Process. Technol.* **92** 1136
- Dry M 2004 In *Fischer–Tropsch Technology* André Steynberg and Mark Dry (Eds.) (Amsterdam: Elsevier Science) Ch. 3 p. 196

18. Sarkari M, Fazlollahi F, Atashi H, Mirzaei A A and Hosseinpour V 2012 Fischer–Tropsch synthesis: Development of kinetic expression for a sol gel Fe–Ni/Al₂O₃ catalyst *Fuel Process. Technol.* **97** 130
19. Iglesia E 1997 Fischer–Tropsch synthesis on cobalt catalysts: Structural requirements and reaction pathways In *Natural Gas Conversion IV* M de Pontes, R L Espinoza, C P Nicolaides, J H Scholtz and M S Scurrell (Eds.) (Netherlands: Elsevier Science) p. 153
20. Iglesia E, Soled S L, Fiato R A and Via G H 1993 Bimetallic synergy in cobalt ruthenium Fischer–Tropsch synthesis catalysts *J. Catal.* **143** 345
21. Mirzaei A A, Shirzadi B, Atashi H and Mansouri M 2012 Modeling and operating conditions optimization of Fischer–Tropsch synthesis in a fixed-bed reactor *J. Ind. Eng. Chem.* **18** 1515
22. Luo M, O'Brien R J, Bao S and Davis B H 2003 Fischer–Tropsch synthesis: Induction and steady-state activity of high-alpha potassium promoted iron catalysts *Appl. Catal. A Gen.* **239** 111
23. Dalil M, Sohrabi M and Royae S J 2012 Application of nano-sized cobalt on ZSM-5 zeolite as an active catalyst in Fischer–Tropsch synthesis *J. Ind. Eng. Chem.* **18** 690
24. Calleja G, de Lucas A and van Grieken R 1995 Co/HZSM-5 catalyst for syngas conversion: Influence of process variables *Fuel* **74** 445
25. vander Laan G P and Beenackers A A C M 1999 Kinetics and selectivity of the Fischer–Tropsch synthesis: A literature review *Catal. Rev. Sci. Eng.* **41** 255
26. Teng, B T, Chang J, Zhang C H, Cao D B, Yang J, Liu Y, Guo X H, Xiang H W and Li Y W 2006 A comprehensive kinetics model of Fischer–Tropsch synthesis over an industrial Fe–Mn catalyst *Appl. Catal. A Gen.* **301** 39
27. Li S, Krishnamoorthy S, Li A, Meitzner G D and Iglesia E 2002 Promoted iron-based catalysts for the Fischer–Tropsch synthesis: Design, synthesis, site densities, and catalytic properties *J. Catal.* **206** 202
28. Dalai A K, Bakhshi N N and Esmail M N 1997 Conversion of syngas to hydrocarbons in a tube-wall reactor using Co–Fe plasma-sprayed catalyst: Experimental and modeling studies *Fuel Process. Technol.* **51** 219
29. Madon R J and Iglesia E 1993 The importance of olefin readsorption and H₂/CO reactant ratio for hydrocarbon chain growth on ruthenium catalysts *J. Catal.* **139** 576
30. Yang Y, Xiang H W, Xu Y Y, Bai L and Li Y W 2004 Effect of potassium promoter on precipitated iron-manganese catalyst for Fischer–Tropsch synthesis *Appl. Catal. A Gen.* **266** 181
31. Li X, Asami K, Luo M, Michiki, K Tsubaki N and Fujimoto K 2003 Direct synthesis of middle iso-paraffins from synthesis gas *Catal. Today* **84** 59
32. Madon R J and Taylor W F 1981 Fischer–Tropsch synthesis on a precipitated iron catalyst *J. Catal.* **69** 32
33. Sari A, Zamani Y and Taheri S A 2009 Intrinsic kinetics of Fischer–Tropsch reactions over an industrial Co–Ru/γ-Al₂O₃ catalyst in slurry phase reactor *Fuel Process. Technol.* **90** 1305
34. Donnelly T J and Satterfield C N 1989 Product distributions of the Fischer–Tropsch synthesis on precipitated iron catalysts *Appl. Catal.* **52** 93
35. Sethuraman R, Bakhshi N N, Katikaneni S P and Idem R O 2001 Production of C₄ hydrocarbons from Fischer–Tropsch synthesis in a follow bed reactor consisting of Co–Ni–ZrO₂ and sulfated-ZrO₂ catalyst beds *Fuel Process. Technol.* **73** 197
36. Anderson R B 1956 *Catalysts for the Fischer-Tropsch Synthesis* (New York: Van Nostrand-Reinhold)
37. Griboval-Constant A, Khodakov A Y, Bechara R and Zholobenko V L 2002 Support mesoporosity: A tool for better control of catalytic behavior of cobalt supported Fischer–Tropsch catalysts *Stud. Surf. Sci. Catal.* **144** 609
38. Kuipers E W, Scheper C, Wilson J H, Vinkenburg I H and Oosterbeek H 1996 Non-ASF product distributions due to secondary reactions during Fischer–Tropsch synthesis *J. Catal.* **158** 288
39. Dictor R A and Bell A T 1986 Fischer–Tropsch synthesis over reduced and unreduced iron oxide catalysts *J. Catal.* **97** 121
40. Zaman M, Khodadi A and Mortazavi Y 2009 Fischer–Tropsch synthesis over cobalt dispersed on carbon nanotubes-based supports and activated carbon *Fuel Process. Technol.* **90** 1214
41. Kuipers E W, Vinkenburg I H and Oosterbeek H 1995 Chain length dependence of α-Olefin readsorption in Fischer–Tropsch synthesis *J. Catal.* **152** 137
42. Krishna K R and Bell A T 1993 Estimates of the rate coefficients for chain initiation, propagation, and termination during Fischer–Tropsch synthesis over Ru/TiO₂ *J. Catal.* **139** 104
43. Schulz H 1999 Short history and present trends of Fischer–Tropsch synthesis *Appl. Catal. A Gen.* **186** 3
44. Schulz H and Claeys M 1994 Selectivity and mechanism of Fischer–Tropsch synthesis with iron and cobalt catalysts *Stud. Surf. Sci. Catal.* **81** 455
45. Wu B, Bai L, Xiang H, Li Y W, Zhang Z and Zhong B 2004 An active iron catalyst containing sulfur for Fischer–Tropsch synthesis *Fuel* **83** 205
46. Bai L, Xiang H W, Li Y W, Han Y Z and Zhong B 2002 Slurry phase Fischer–Tropsch synthesis over manganese-promoted iron ultrafine particle catalyst *Fuel* **81** 1577
47. Raje A P, O'Brien R J and Davis B H 1998 Effect of potassium promotion on iron-based catalysts for Fischer–Tropsch synthesis *J. Catal.* **180** 36