Kinetics, selectivity and scale up of the Fischer-Tropsch synthesis
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Experimental

3.1 Experimental Setup

Continuous laboratory reactors are used to measure reaction kinetics and product distributions of the Fischer-Tropsch synthesis. Most studies were performed in atmospheric gas-solid packed bed reactors. Packed beds at higher pressures were applied by, for example, Lox et al. [1], Bub and Baerns [2], and Bukur et al. [3]. Wojciechowski [4] showed that integral reactors are unsuitable for fundamental studies of the FTS. Continuous recycle reactors are to be preferred for gas-solid kinetic measurements: for example, the Berty reactor [5, 6] or the spinning basket reactor [7]. Slurry phase Fischer-Tropsch experiments are performed in slurry reactors with either a continuous gas-phase and a liquid batch of FT-wax or a high-boiling solvent. These reactor systems commonly are perfectly mixed recycle reactors with turbine impellers [8] or gas-inducing stirrers.

Measurements used for the development of kinetic expressions and selectivity models were carried out in several experimental setups. The equipment for the experiments of the gas-solid and gas-slurry Fischer-Tropsch synthesis as well as the product analysis and the experimental procedures are described below. Fischer-Tropsch experiments were carried out in a gas-continuous Spinning Basket Reactor (SBR) [9] and in a slurry reactor (SR), both in a setup shown in Figure 3.1. H\textsubscript{2} (1) and CO (2) (purities of 99.999 % and 99.8 %, respectively) were fed with separate mass flow controllers (5,6) (range: 0-4.2 \text{ 10\textsuperscript{-3} Nm\textsuperscript{3} s\textsuperscript{-1}}). Two purification columns (7) were used to remove possible catalyst poisons like iron carbonyl, sulfides, and oxygen. The columns were packed with BASF R3-11 and BASF R5-10 catalysts at 473 K and 323 K, respectively. Synthesis gas was preheated at 523 K (12). To prevent product condensation, the product tubes from the reactor down to the high-pressure gas-liquid separator and condenser (19) \((P=\text{P}_{R}, \text{T} \approx 423 \text{ K})\) were heated at 473 K. Condensed wax products were removed periodically (20). The reactor pressure was measured (13) (range: 0.1-10.0 MPa; accuracy 0.01 MPa) and kept constant via a PID-controlled pneumatic needle valve (22). The remaining gaseous stream was reduced to atmospheric pres-
Figure 3.1 Experimental set-up.

sure. A small sample flow was split from the main flow and led to a heated injection valve of an on-line gas chromatograph (26). The volumetric flow rate of the gaseous stream was determined with a thermostated flow meter (29) (373 K). The flow was measured via the displacement of a mercury-sealed piston in a glass tube. Finally, the product stream was transported to a low-pressure condenser at 273 K (25, 32). The condensed products from this condenser were separated manually into an aqueous and an oil phase (24, 33).

3.1.1 Spinning Basket Reactor

The spinning basket reactor shown in Figure 3.2 is a stainless steel reactor (V = 285 cm³, H = 8.6 cm, D = 6.5 cm) with the catalyst particles placed in four baskets (3)
mounted on the stirrer shaft (2). A stirrer speed of 33 s\(^{-1}\) ensured complete mixing of the gas phase, and resulted in high mass and heat transfer rates. Preliminary experiments showed that the conversion of synthesis gas and the hydrocarbon selectivity did not change by varying the stirrer speed between 20 and 33 s\(^{-1}\). Vortex formation was prevented by four vertical baffles (1) with a width of 8 mm each. The reactor was electrically heated (4), and the temperature was measured with a PT-100 resistance thermometer (TT) (range: 373-773 K; accuracy: 0.2 K).

### 3.1.2 Slurry Reactor

The slurry reactor is a 1.8 dm\(^3\) autoclave (\(H= 18.2\) cm, \(D= 12.0\) cm) made by Medimex (Figure 3.3). The autoclave was connected to a magnetic stirrer (5). The shaft of
the impeller was hollow with small holes in the stirrer blades and sleeves in the top of the shaft. This enabled the vapor in the reactor to be recycled through the liquid by the suction created by the impeller. Above 15 s⁻¹ strong circulation of the gas phase in the autoclave was observed. The impeller was always driven at 25 s⁻¹ to ensure complete mixing of the liquid phase, uniform distribution of the catalyst, and high mass and heat transfer rates [10]. A turbine impeller (4) mounted on the top of the shaft was applied to obtain a homogeneous gas phase. Four vertical baffles (1) (width 10 mm) were used to prevent the formation of vortices. A distance ring of 3 mm (8) was applied to prevent undesired catalyst accumulation between the reactor wall and the baffles. The temperature of the reactor was controlled by the combination of a 3000 W electric heating mantle with air cooling and a cooling coil (air) in the slurry phase (6). The temperature was measured with a PT-100 resistance thermometer (range 273-773 K; accuracy: 0.2 K) inserted in the liquid phase (2).

During the Fischer-Tropsch reaction, liquid products can be formed. The level of the slurry was maintained constant using a home-made filtering unit (7). The liquid products were removed via a filter (sintered metal 5 μm), whereas the catalyst particles remained inside the reactor. The liquid and gas phase volumes applied were 730 and 985 cm³, respectively.

Initially, the reactor was filled with FT wax (Sasol-Schumann type 4110) mainly consisting of paraffins with carbon number between 21 and 36. The product distribution of the wax was bell-shaped with a maximum at carbon number 28. The liquid density of the applied wax was determined volumetrically as:

\[
\rho_L = 820.0 - 0.569(T - 273.15) \ [\text{kg m}^{-3}] \tag{3.1}
\]

### 3.2 Catalyst

The catalyst applied was a commercial precipitated iron catalyst (type LP 33/81) synthesized by Ruhrchemie AG (Oberhausen, Germany). The synthesis procedure was described by Frohning et al. [11]. The Fe, Cu, and K content was measured by atomic absorption spectroscopy and the SiO₂ gravimetrically. The elemental composition was found to be 74.3 % Fe, 3.7 % Cu, 3.1 % K, and 18.6 % SiO₂. The composition of this catalyst was also determined by Bukur et al. [12], Lox et al. [1], and by Donnelly and Satterfield [13]. Their results are in reasonable agreement with ours. The catalyst pellets were calcined in air at 573 K for 5 h and crushed and sieved to the appropriate particle diameter range.
3.2.1 BET Measurements

The specific surface areas and the texture of the catalysts were determined by nitrogen physisorption according to the Braun-Emmett-Teller (BET) method. The measurements were performed with a Micromeritics ASAP 2400. Sieve fractions between 140 and 150 μm were out-gassed at 525 K for 2 hours before the actual measurements.

Table 3.1 Texture of the catalyst (BET).

<table>
<thead>
<tr>
<th></th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average mesopore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>323</td>
<td>0.64</td>
<td>8.0</td>
</tr>
<tr>
<td>Calcined</td>
<td>309</td>
<td>0.61</td>
<td>7.9</td>
</tr>
<tr>
<td>After FT reaction¹</td>
<td>88</td>
<td>0.31</td>
<td>13.9</td>
</tr>
</tbody>
</table>

¹ After SBR experiments (1800 hrs time-on-stream)

3.2.2 Scanning Electron Microscopy (SEM)

SEM studies of both the fresh catalyst and the catalyst subjected to FT synthesis for 1800 hours on stream are shown in Figure 3.4a and Figure 3.4b, respectively. The catalyst particles are composed of agglomerated crystals. We observed a substantial increase of crystal size after 1800 hrs of duty, relative to virgin catalyst (Figure 3.4b). The SEM micrograph in Figure 3.4b shows a different (more smooth) surface structure with white-colored edges on the crystals in comparison to the fresh catalyst sample (Figure 3.4a).

Figure 3.4 SEM micrographs of the Ruhrchemie catalyst samples. a. As-received catalyst; b. Catalyst after 1800 FT synthesis.
3.3 Product Analysis

Kinetic research of the FTS requires an accurate product analysis. The analytical section has to measure the complete product distribution of at least $C_{1-30}$ paraffins and olefins as well as the reactants (CO and $H_2$) and CO$_2$ and H$_2$O. Analysis of isomers (branched products) and oxygenates is necessary if the concentration of these components is significant. Most gas chromatographic systems have a complex arrangement of multiple columns and detectors [14–16]. However, on-line single column gas chromatographic analysis are reported as well [17, 18]. In most studies the reactants and non-condensable products (CO$_2$ and $C_{1-5}$ hydrocarbons) are analyzed on-line, while the condensed products (C$_{6+}$ hydrocarbons, and H$_2$O) are collected, weighed, separated in two phases and analyzed off-line, see for example [3, 4, 13]. Some disadvantages of this approach are [14, 19, 20]: 1) Difficult quantification; components appear in more phases and samples. 2) Reactors must run at high conversions or high catalyst load in order to accumulate condensates. 3) Long analysis times. In contrast, on-line analysis of all products is rapid and accurate, so this is the preferred method.

The analysis system used in this study is illustrated in Figure 3.5. The total product stream was split in three flows: on-line gaseous, oil phase (low-pressure condenser), and wax phase (high-pressure condenser).

![Figure 3.5 Scheme of the liquid and gaseous streams in the condensers and analysis system.](image)

The gaseous phase was analyzed with a Hewlett-Packard 5980A Gas Chromatograph (GC). The gaseous components were linear paraffins $C_{1-10}$, $\alpha$-olefins $C_2-C_{10}$, 1-alcohols $C_1-C_4$, CO$_2$, H$_2$O, CO, and H$_2$. The gas chromatograph was equipped with a heated (473 K) 10-port gas injection valve, with a sample loop and a loop for the Deferred Standard (DS), methane. The DS method for on-line gas chromatographic
Figure 3.6 Typical on-line gas chromatograms for an SBR experiment (523 K, 1.50 MPa, \((\text{H}_2/\text{CO})_{\text{feed}}=2, \Phi_{e,0}/W=1.51 \times 10^{-3} \, \text{Nm}^3 \, \text{kg}^{-1} \, \text{s}^{-1}\)). a. TCD signal; b. FID signal.

analysis was reported by Marsman et al. [21]. The relative DS technique improves the reliability of the analysis and reduces the calibration efforts. Sample injection on the column was performed after the injection of the DS. The DS and sample were subsequently injected at an initial temperature of the GC of 303 K. The initial temperature was maintained for 8 min, after which the oven temperature was increased to 393 K at the rate of 20 K/min. After 5 min at 393 K the temperature was increased with 10 K/min to 453 K. After another 5 min the temperature was increased at the rate of 10 K/min to the final temperature of 523 K. This temperature was maintained until all the components of interest had eluted. The complete on-line analysis time was 60 min. The components were separated on a capillary column (25 m x 0.53 mm i.d. coated with 0.020 mm Poraplot Q, carrier flow, 0.017 ml s\(^{-1}\)). \text{H}_2, \text{CO}, \text{CO}_2, \text{and H}_2\text{O} were detected with a Thermal Conductivity Detector (TCD, see Figure 3.6a) (548 K) and the hydrocarbon products with a Flame Ionization Detector (FID, see Figure 3.6a) (548 K; hydrogen flow, 0.53 ml s\(^{-1}\); air flow, 7.5 ml s\(^{-1}\)) placed in series. Both detectors were connected to an integrator and a personal computer for peak integration and data storage. Since the thermal conductivity of hydrogen almost equals that of
helium, detection is very difficult due to negative peaks, non-linearity, and poor sensitivity. Therefore, the mole fraction of hydrogen was determined in a separate analysis with nitrogen as a carrier gas. Peaks were identified using a gas chromatograph-mass spectrometer (GC-MS) Hewlett Packard 5890A combination and taking into account the logical sequence of retention times of homologous series of hydrocarbons.

The mole fractions of all detected components \( i \) were calculated from the integrated peak areas \( A_i \), according to:

\[
y_i = C_i \frac{A_i}{A_{DS}}
\]

where \( C_i \) is the calibration factor for component \( i \) and \( A_{DS} \) is the integrated area of the deferred standard. Calibration of \( \text{H}_2\), \( \text{CO} \), \( \text{CO}_2\), paraffins \( \text{C}_1-\text{C}_5\), olefins \( \text{C}_2-\text{C}_4\), and \( \text{CH}_3\text{OH} \) was performed with calibration mixtures supplied by Scott Specialty Gases (Breda, The Netherlands). For the remaining hydrocarbon components \( \text{C}_{5+} \), a correlation for the calibration factors proposed by Dierickx et al. [22] was used. It is based on the standard Gibbs energy change \( (-\Delta G^0_{o x}) \) at 298 K for complete oxidation to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \). The calibration constants were calculated relative to pentane using relative molar response factors \( \text{RMR}(i) \):

\[
C_i = C_{\text{pentane}} \frac{\text{RMR}(\text{pentane})}{\text{RMR}(i)}
\]

The thermal conductivity detector was calibrated for water by injection of a gas flow with a known concentration of water. The concentration of water in the carrier gas nitrogen was adjusted with two mass flow controllers and a continuous evaporator mixer from Bronkhorst (Ruurlo, The Netherlands).

The hydrocarbons in the oil phase of the low-pressure condenser (\( \text{C}_{10}-\text{C}_{20} \)) were separated on an HP-SIL 5-CB capillary column with a Hewlett Packard 5890A gas chromatograph (see Figure 3.7a). For these components the mass response factors of the flame ionization detector were taken as constant.

The wax samples of the high-pressure condenser contain \( \text{C}_{15+} \) hydrocarbons and were analyzed with a 10 m HT-SimDist column on a Hewlett Packard 5890A gas chromatograph. The wax samples were dissolved in CS\(_2\) (0.5-1 mass\%) and were injected on-column to the capillary column to prevent splitter discrimination [4] at an initial temperature of 313 K. The temperature was raised with an optimized program to 673 K to elute components until \( \text{C}_{40} \) (see Figure 3.7b). Peak identification was performed using injection of pure components.
Figure 3.7 Typical off-line analysis of an SBR experiment at 523 K, 1.50 MPa, \((\text{H}_2/\text{CO})_{\text{feed}}=2\) and a space velocity of \(1.51 \times 10^{-3} \text{Nm}^3 \text{kg}^{-1} \text{s}^{-1}\). a. Hydrocarbon analysis of the low-pressure condensate, 1: 1-octene, 2: octane, 3: cis-2-octene, 4: trans-2-octene, 5: 1-hexanol. b. Wax analysis of high-pressure condenser, 1: 1-dodecene, 2: dodecane.
3.3.1 Flash Calculations

The product composition of the reactor outlet flow \( (F) \) at reactor pressure and temperature was obtained by combining the analysis of several samples, see Figure 3.5. The composition and flow rate \( (L) \) of the liquid phase \( (x_i) \) were determined by GC analysis of the wax samples and gravimetrically, respectively. The composition of the gas phase from the high-pressure condenser was determined by combining the on-line analysis \( (C_{1-10}) \) and the oil phase of the low-pressure condenser \( (C_{10-20}) \). The flow rate \( (V) \) was calculated using a thermostated volumetric flow meter, whereas the liquid flow rate \( (L) \) was calculated from the weighed mass and the analyzed composition of the high-pressure condensate. The liquid phase was assumed to obey Raoult’s law and the gas phase the ideal gas law. Furthermore, it was assumed that the hydrocarbon products behave like paraffins. The vapor pressures of the pure paraffins at a given temperature were calculated using the method of Caldwell and van Vuuren [23]:

\[
P_n = P_0 \beta^n
\]

where

\[
\beta = \exp(-427.218(1/T - 1.029807 \times 10^{-3}))
\]

The equilibrium constant was calculated using Raoult’s law:

\[
K_i = y_i / x_i = P_i / P
\]

A molar balance for component \( i \) gives:

\[
F z_i = L x_i + V y_i
\]

and the total molar balance:

\[
F = L + V
\]

Solving eqs 3.4-3.8 gives the molar composition of the outlet stream of the reactor \( (F, z_i) \). Figure 3.8 shows an example of the GC analysis from the on-line and off-line (wax and fuel) samples resulting in a complete product distribution using vapor-liquid equilibria and flash calculations.
Figure 3.8 Product distributions of on-line and off-line GC analysis and vapor-liquid equilibria and flash calculations for a typical SBR experiment (A1).
3.4 Experimental Procedure

Blank experiments showed that the packed purification columns and the reactor, without catalyst, caused no significant conversion of the synthesis gas. The catalyst was pretreated with hydrogen at a flow rate of \(0.83 \times 10^{-3} \text{Nm}^3 \text{kg}^{-1} \text{s}^{-1}\) according to Bukur et al. [24] in all experiments. The gas space velocity was based on the total mass of the unreduced catalyst. The reactor temperature, \(T\), was increased linearly from 293 K to 553 K by 0.017 K s\(^{-1}\). \(T\) remained at 553 K for 24 hours at atmospheric pressure. The reactor pressure in the slurry reactor was maintained at 1.0 MPa to prevent excessive solvent evaporation. After reduction, synthesis gas was fed to the reactor at reference conditions. For the kinetic experiments in the spinning basket reactor these conditions were: 523 K, 1.50 MPa, \((\text{H}_2/\text{CO})_{\text{feed}}=2\) and a space velocity of \(1.51 \times 10^{-3} \text{Nm}^3 \text{kg}^{-1} \text{s}^{-1}\). For the slurry reactor they were: 523 K, 1.50 MPa, \((\text{H}_2/\text{CO})_{\text{feed}}=0.67\) and a space velocity of \(0.50 \times 10^{-3} \text{Nm}^3 \text{kg}^{-1} \text{s}^{-1}\).

The experimental conditions for the experiments in both the spinning basket reactor and the slurry reactor are summarized in Table 3.2. A summary of relevant experimental data is given in Appendixes A and B.

<table>
<thead>
<tr>
<th>Series</th>
<th>Reactor</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SBR</td>
<td>SR</td>
<td>SR</td>
</tr>
<tr>
<td>(T) (°C)</td>
<td>225-275</td>
<td>250</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>(P) (MPa)</td>
<td>0.8-4.0</td>
<td>1.2-4.0</td>
<td>1.2-4.0</td>
<td></td>
</tr>
<tr>
<td>(\Phi^i_n/W) ((10^{-3}) Nm(^3) kg(^{-1}) s(^{-1}))</td>
<td>0.5-2.0</td>
<td>0.25-0.50</td>
<td>0.17-0.77</td>
<td></td>
</tr>
<tr>
<td>(F) (-)</td>
<td>0.25-4.0</td>
<td>0.25-4.0</td>
<td>0.5-4.0</td>
<td></td>
</tr>
<tr>
<td>(W) ((10^{-3}) kg)</td>
<td>2.34</td>
<td>7.32</td>
<td>7.26</td>
<td></td>
</tr>
<tr>
<td>(d_p) ((\mu)m)</td>
<td>125-160</td>
<td>40-50</td>
<td>40-50</td>
<td></td>
</tr>
</tbody>
</table>

Liquid products were accumulated in high and low-pressure condensers for a typical period of 6-8 hours during steady state of the reactor system. The products were collected and weighed before analysis. Several on-line GC analysis were performed during this period. After changing the process conditions the reactor operated undisturbed before a new mass balance period was started. The stabilization time for the SBR between two subsequent experiments was taken as 4 gas residence times:

\[
t_{\text{steady}} = 4 \frac{1.013 \times 10^2 P V}{RT \Phi_{v,0} C_{G,0}}
\] (3.9)
Figure 3.9  Stabilization time in gas-slurry reactor \( t_i^{\text{steady}} \), eq 3.10 for paraffins (solid lines) and olefins (dashed lines) as a function of carbon number \( n \) at: 1. \( P_R = 40 \text{ bar} \) and \( \Phi_{v,0} = 2 \times 10^{-4} \text{ Nm}^3 \text{ s}^{-1} \), 2. \( P_R = 20 \text{ bar} \) and \( \Phi_{v,0} = 2 \times 10^{-4} \text{ Nm}^3 \text{ s}^{-1} \), 3. \( P_R = 20 \text{ bar} \) and \( \Phi_{v,0} = 3 \times 10^{-4} \text{ Nm}^3 \text{ s}^{-1} \).

where \( \Phi_{v,0} \) and \( C_{G,0} \) are the flow rate and gas concentration at normal conditions \( (T_0 = 273 \text{ K}, P_0 = 0.1013 \text{ MPa}) \). The maximum time for achieving steady state was 7.9 hours. Therefore, minimal 12 h waiting time between two experiments was applied in the spinning basket reactor experiments.

The stabilization time of component \( i \) leaving the reactor in the gas phase after changing the reactor conditions takes into account the gas-liquid solubility of products in the slurry liquid:

\[
t_i^{\text{steady}} = \frac{4 \times 10^3 (P V_G + m_i^{GL} P V_L)}{R T \Phi_{v,0} C_{G,0}}
\]

(3.10)

where \( V_G \) and \( V_L \) are the gas and liquid volume, respectively and \( m_i^{GL} \) is the solubility \( (C_L/C_G) \) of component \( i \). The stabilization time is a function of carbon number and increases rapidly with chain length due to increasing solubility. Figure 3.9 shows the
required stabilization time for several experimental conditions as a function of carbon number, as calculated with eq 3.10. The relevant gas-liquid solubilities of paraffins and olefins were obtained from Marano and Holder [25]. A minimum stabilization time of 48 hours was applied in the slurry reactor experiments. Several on-line GC analysis were performed to ensure steady state in the gas flow from the reactor.

The consistency and accuracy of both the analysis and the reactor system was checked regularly using atomic balances for the components H, C, and O. For example, the carbon balance gives:

\[
\Delta C = \frac{(yCO)_{in} \Phi_{i,0}^{in}}{(yCO + yCO_2 + \sum_{n=1}^{n} nyc_H_{2n+2} + \sum_{n=2}^{n} nyc_H_{2n})_{out}} \Phi_{i,0}^{out} \quad (3.11)
\]

Mass and atomic balances were typically within 80-100 %.

Internal diffusion is insignificant for \(d_p < 0.16 \text{ mm}\) [26, 27]. Calculation of the criteria of Weisz and Prater [28] for the reactants CO and H\(_2\) also proved that no intra-particle diffusion limitations occurred at the highest rates observed in both the slurry and the spinning basket reactor, assuming the catalyst pores to be filled with long-chain (C\(_{28}\)) hydrocarbon waxes.

### 3.5 Reaction Rates and Selectivities

The formation rate of a product, \(R_i\), follows from a material balance over the reactor, assuming ideal gas behavior:

\[
R_i = y_i \frac{\Phi_{i,0}^{in} P_0}{W} \frac{P_0}{RT_0} \quad (3.12)
\]

where \(y_i\) is the mole fraction of component \(i\) in the reactor effluent, \(P_0\) and \(T_0\) correspond to normal conditions at 0.1013 MPa and 273 K, \(W\) is the weight of the catalyst, and \(\Phi_{i,0}\) is the reactor outlet flow at normal conditions. Reaction rates of the reactants H\(_2\) and CO follow from:

\[
-R_i = \left( y_i^{in} \Phi_{i,0}^{in} - y_i^{out} \Phi_{i,0}^{in} \right) \frac{P_0}{RT_0 W} \quad (3.13)
\]

The corresponding conversions of H\(_2\) and CO are:

\[
X_i = 1 - \frac{y_i \Phi_{i,0}^{out}}{y_i^{in} \Phi_{i,0}^{in}} \quad (3.14)
\]
and the total synthesis gas conversion:

$$X_{CO+H_2} = 1 - \frac{(y_{H_2} + y_{CO})\Phi_{e,0}}{(y_{H_2} + y_{CO})\Phi_{e,0}}$$  \hspace{1cm} (3.15)

The synthesis reactions can be considered as a combination of the Fischer-Tropsch (FT) and the water gas shift (WGS) reactions (see eqs. 1.1-1.2). Water is a primary product of the FT reaction, and CO$_2$ can be produced by the water gas shift reaction ($R_{WGS} = R_{CO_2}$). The reaction scheme neglects formation of oxygenated products. The selectivity to alcohols was lower than 5 wt% for the on-line products in our experiments. No alcohols were detected in the waxy fractions, leading to a much lower selectivity in the total product yield. The CO consumption to hydrocarbons follows from:

$$R_{FT} = -R_{CO} - R_{WGS} \quad [\text{mol kg}_{cat}^{-1} \text{ s}^{-1}]$$  \hspace{1cm} (3.16)

The molar selectivity to product $i$ was calculated from the experimental mole fractions relative to all products ($n$) considered:

$$m_i = \frac{y_i}{\sum_{j=1}^{n} y_j}$$  \hspace{1cm} (3.17)

The mass selectivity of a single product or of a product range was calculated from the corresponding selectivity or mole fraction $y_i$ and molar mass $M_i$:

$$w_i = \frac{y_i M_i}{\sum_{j=1}^{n} y_j M_j}$$  \hspace{1cm} (3.18)

$$w_{2-4} = \frac{\sum_{i=2}^{4} w_i}{\sum_{i=1}^{n} w_i}$$  \hspace{1cm} (3.19)

### 3.5.1 Model Parameters

The adjustable model parameters for the several kinetic and selectivity models in Chapters 4-6 were calculated by minimizing the $\chi^2$ function with the Levenberg-Marquardt method [29]:

$$\chi^2 = \sum_{i} \frac{(x_i^{exp} - x_i^{mod})^2}{\sigma^2}$$  \hspace{1cm} (3.20)
where $x_{i}^{\text{exp}}$ and $x_{i}^{\text{mod}}$ are the experimental and model value of the selectivity or the reaction rate, respectively, $\sigma^{2}$ is the relative variance of the experimental data point. The Levenberg-Marquardt method makes use of a combination between the steepest descent and the inverse hessian method.

The accuracy of the fitted model relative to the experimental data was obtained from the MARR (Mean Absolute Relative Residual) function

$$MARR = \frac{1}{n} \sum_{i} \left| \frac{x_{i}^{\text{exp}} - x_{i}^{\text{mod}}}{x_{i}^{\text{exp}}} \right| \times 100$$

(3.21)

where $n$ is the total number of optimized data points, $x_{i}^{\text{exp}}$ is the experimental selectivity or reaction rate of the $i$th data point, and $x_{i}^{\text{mod}}$ is the model prediction of the selectivity or reaction rate.

The relative variance ($s_{\text{rel}}$) was used to compare several models with different numbers of model parameters:

$$s_{\text{rel}} = \left( \frac{1}{n} \sum_{i} \left( \frac{x_{i}^{\text{exp}} - x_{i}^{\text{mod}}}{x_{i}^{\text{exp}}} \right)^{2} \frac{1}{n} \right)^{\frac{1}{2}} \times 100$$

(3.22)

with $n$, the number of data points included and $m$, the number of optimized parameters.

The relative residual ($RR$) between experimental and predicted data will be used to show the deviations between model and experiment:

$$RR = \frac{x_{i}^{\text{exp}} - x_{i}^{\text{mod}}}{x_{i}^{\text{exp}}} \times 100$$

(3.23)

Bartlett’s test was used to investigate whether the differences in accuracy of the various kinetic models were statistically significant [30]. For a number of $H$ competitive models, the Bartlett’s test calculates a critical $\chi_{C}^{2}$ value:

$$\chi_{C}^{2} = \ln S_{av}^{2} \sum_{h=1}^{H} df_{h} - \sum_{h=1}^{H} df_{h} S_{h}^{2}$$

$$1 + \frac{1}{3(H-1)} \left( \sum_{h=1}^{H} df_{h}^{-1} - \left( \sum_{h=1}^{H} df_{h} \right)^{-1} \right)$$

(3.24)

where $S_{h}^{2}$ is the total variance between the experiments and model $h$ and $S_{av}^{2}$ is the average total variance of $H$ models:

$$S_{h}^{2} = df_{h}^{-1} \sum_{i=1}^{n} \left( R_{i}^{\text{exp}} - R_{i}^{\text{mod}} \right)^{2}$$

(3.25)
$S^2_{aw} = \frac{\sum_{h=1}^{H} \text{df}_h S^2_h}{\sum_{h=1}^{H} \text{df}_h}$

(3.26)

df$_h$ is the degrees of freedom for the $h$th model predictions and is equal to df$_h = n - m_h$, $n$ is the number of data points and $m_h$ is the number of optimized parameters of the $h$th model. Bartlett’s test compares $\chi^2_c$ with a tabulated $\chi^2(H - 1)$ value [31]. Models were subsequently rejected, until $\chi^2_c$ was below the tabulated value.

### 3.6 Catalyst Activity and Selectivity

A detailed description of the activity and selectivity of the commercial Ruhrchemie iron catalyst is given in Chapters 4-6. A brief comparison between our catalyst tests and available literature data with the same catalyst is presented here.

In Table 3.3 the catalyst activity and selectivity is compared to that reported by Bukur et al. [3] in a fixed bed reactor and of Donnelly and Satterfield [13] in a slurry reactor at approximately similar conditions and the same commercial Ruhrchemie catalyst. Since the results of Bukur et al. [3] were obtained in an integral fixed bed reactor, reaction rates and conversions vary with position and cannot be compared directly. The selectivity to gaseous hydrocarbon products is similar. The olefin content in our experiments is slightly lower than in their study. The observed differences can probably be attributed to the differences in activation procedures, different catalyst aging patterns and to the different reactor types applied. The data of Donnelly and Satterfield [13] are obtained at a higher reactor temperature and in a slurry reactor. The reactor type influences the activity as well as the selectivity of the process. Both the conversion and the reaction rate of synthesis gas are higher in our experiments, whereas the hydrocarbon selectivity is higher to low-molecular hydrocarbons.

### 3.7 Catalyst Deactivation

Dry [32] mentioned four factors responsible for FT catalyst aging: (1) conversion of active phase, (2) sintering, (3) deposition of carbonaceous material, and (4) chemical poisoning by, for example, sulfur. The BET surface areas of the catalyst before and after FT reaction in an SBR test were determined by N$_2$-physisorption (see Table 3.1). The BET area of the fresh and calcined catalyst was 323 and 309 m$^2$ g$^{-1}$, respectively.
Table 3.3 Ruhrchemie catalyst comparison: activity and selectivity.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>A3</th>
<th>A16</th>
<th>C3</th>
<th>C15</th>
<th>[3]</th>
<th>[13]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time-on-stream (h)</td>
<td>290</td>
<td>985</td>
<td>443</td>
<td>1550</td>
<td>528</td>
<td>-</td>
</tr>
<tr>
<td>T (K)</td>
<td>523</td>
<td>523</td>
<td>523</td>
<td>523</td>
<td>523</td>
<td>523</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>0.70-0.78</td>
</tr>
<tr>
<td>P (MPa)</td>
<td>1.6</td>
<td>2.4</td>
<td>1.5</td>
<td>2.4</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>$\Phi_{v,0}^i W \left(10^{-3} \text{Nm}^3 \text{kg}_{\text{cat}}^{-1} \text{s}^{-1}\right)$</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>H$_2$ + CO conversion (%)</td>
<td>47.5</td>
<td>55.5</td>
<td>53.7</td>
<td>53.5</td>
<td>56.0</td>
<td>33.6</td>
</tr>
<tr>
<td>Reaction medium</td>
<td>Gas</td>
<td>Gas</td>
<td>Slurry</td>
<td>Slurry</td>
<td>Gas</td>
<td>Slurry</td>
</tr>
</tbody>
</table>

Hydrocarbon selectivities$^1$ (wt%)

<table>
<thead>
<tr>
<th></th>
<th>$w_1$</th>
<th>$w_{2-4}$</th>
<th>$w_{5-10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>14.4</td>
<td>39.5</td>
<td>46.1</td>
</tr>
<tr>
<td>A16</td>
<td>10.3</td>
<td>40.6</td>
<td>49.0</td>
</tr>
<tr>
<td>C3</td>
<td>14.8</td>
<td>37.4</td>
<td>47.7</td>
</tr>
<tr>
<td>C15</td>
<td>8.5</td>
<td>40.7</td>
<td>50.8</td>
</tr>
<tr>
<td>[3]</td>
<td>13.4</td>
<td>46.7</td>
<td>39.9</td>
</tr>
<tr>
<td>[13]</td>
<td>7.8</td>
<td>37.1</td>
<td>55.0</td>
</tr>
</tbody>
</table>

Olefin selectivity (wt%)

<table>
<thead>
<tr>
<th></th>
<th>$w_{O,2-4}$</th>
<th>$w_{O,5-10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>66.1</td>
<td>60.7</td>
</tr>
<tr>
<td>A16</td>
<td>75.3</td>
<td>72.9</td>
</tr>
<tr>
<td>C3</td>
<td>55.9</td>
<td>45.4</td>
</tr>
<tr>
<td>C15</td>
<td>79.1</td>
<td>76.8</td>
</tr>
<tr>
<td>[3]</td>
<td>75.0</td>
<td>70.0</td>
</tr>
<tr>
<td>[13]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$ Selectivities based on carbon number $n \leq 10$

After FT reaction for more than 1800 hours the BET surface area decreased to 88 m$^2$ g$^{-1}$. Previous studies with the same catalyst showed similar results [1, 12, 33]. Prior to N$_2$-physisorption, the spent catalyst sample was heated with hexane under reflux conditions and degassed to remove waxy deposits from the pores. Gas chromatographic analysis of the extracted hydrocarbons revealed that the mixture consisted of linear paraffins with a carbon number in the range of 20 to 60. The decrease in the BET surface area results from sintering [1], formation of carbonaceous deposits resulting in blocking of pores [12] or increase of the skeletal density of the catalyst [1]. In agreement with previous literature studies, the average pore diameter as determined by BET, increased from 8 to 14 nm (see Table 3.1) and the pore size distribution shifted to larger sized pores.

3.7.1 Gas-solid Experiments

For accurate kinetic measurements, the catalyst activity has to be stable. Periodically standard experiments are necessary to check for possible deactivation effects on
activity and selectivity of the catalyst [3, 13]. During the catalyst tests in the SBR (Appendix A), 6 reference experiments were performed (see Table 3.4). After an initial period of 100 h (4 days) steady state was achieved. The catalyst activity, reaction rate to hydrocarbon products ($R_{FT}$) and of the water gas shift ($R_{WGS}$), changed slowly over 1200 h time-on-stream (see Figure 3.10a). The selectivity of the Ruhrchemie catalyst is plotted in Figure 3.10b. The selectivity to lighter products increases slightly with time-on-stream, whereas the olefin content decreases.

Table 3.4 Effect of time-on-stream on the catalyst activity and selectivity in the spinning basket reactor (Appendix A).

<table>
<thead>
<tr>
<th>Run</th>
<th>A1</th>
<th>A5</th>
<th>A11</th>
<th>A12</th>
<th>A17</th>
<th>A20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time-on-stream (h)</td>
<td>240</td>
<td>388</td>
<td>699</td>
<td>862</td>
<td>1011</td>
<td>1224</td>
</tr>
<tr>
<td>$H_2 + CO$ conversion (%)</td>
<td>35.9</td>
<td>31.7</td>
<td>30.7</td>
<td>26.7</td>
<td>33.7</td>
<td>35.8</td>
</tr>
<tr>
<td>$R_{FT}$ ($10^{-3}$ mol kg$^{-1}$ s$^{-1}$)</td>
<td>7.5</td>
<td>8.0</td>
<td>7.9</td>
<td>7.1</td>
<td>8.5</td>
<td>8.7</td>
</tr>
<tr>
<td>$R_{WGS}$ ($10^{-3}$ mol kg$^{-1}$ cat$^{-1}$ s$^{-1}$)</td>
<td>2.9</td>
<td>2.7</td>
<td>2.6</td>
<td>2.0</td>
<td>3.4</td>
<td>3.6</td>
</tr>
<tr>
<td>$STY$ ($10^{-3}$ mol kg$^{-1}$ cat$^{-1}$ s$^{-1}$)</td>
<td>21.1</td>
<td>21.3</td>
<td>20.6</td>
<td>17.9</td>
<td>22.6</td>
<td>24.0</td>
</tr>
</tbody>
</table>

Hydrocarbon selectivities (wt%)

| $w_1$ | 17.5 | 18.2 | 20.2 | 20.5 | 21.5 | 21.2 |
| $w_2-4$ | 35.3 | 39.8 | 46.8 | 43.3 | 42.9 | 41.5 |
| $w_{5-10}$ | 47.2 | 42.0 | 33.1 | 36.2 | 35.6 | 37.2 |

Olefin selectivity (wt%)

| $w_{O,2-4}$ | 65.9 | 66.2 | 62.2 | 66.8 | 61.2 | 61.7 |
| $w_{O,5-10}$ | 63.8 | 63.5 | 58.7 | 62.9 | 58.1 | 58.8 |

$^1$ $P= 1.50$ MPa, $T= 523$ K, $F= 2$, $\Phi_{in}^{L}/W = 1.5 \times 10^{-3}$ Nm$^3$ kg$^{-1}$ cat$^{-1}$ s$^{-1}$

3.7.2 Slurry Experiments

The possible effects of catalyst aging on activity and selectivity was determined in both slurry reactor runs (Appendix B). At regular time intervals, reference experiments were repeated. The major results of the reference experiments in both runs are given in Table 3.5. Remarkably, the reaction rate of CO to hydrocarbons is higher in Run C resulting in higher synthesis gas conversions and space time yields. The selectivities of the hydrocarbon groups in reference experiment C4 are different due to analysis problems with the $C_{10}$ hydrocarbons, which could not be determined accurately. A sharp decrease of the $C_{5-10}$ selectivity was observed in Run C between reference experiment C10 and C13.
Figure 3.10 Effect of time-on-stream (TOS) on catalyst activity (a) and selectivity (b). Experimental conditions: $T = 523$ K, $F = 2$, $P = 1.50$ MPa, $\Phi_{v,0}/W = 1.51 \times 10^{-3}$ Nm$^{-3}$ kg$^{-1}$ cat s$^{-1}$ Run: A1, A5, A11, A12, A17, A20.

Table 3.5 Effect of time-on-stream on the catalyst activity and selectivity in slurry reactor runs (Appendix B).

<table>
<thead>
<tr>
<th>Run$^1$</th>
<th>B1</th>
<th>B4</th>
<th>B8</th>
<th>C1</th>
<th>C4$^2$</th>
<th>C6</th>
<th>C10</th>
<th>C13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time-on-stream (h)</td>
<td>156</td>
<td>577</td>
<td>643</td>
<td>345</td>
<td>552</td>
<td>802</td>
<td>1056</td>
<td>1395</td>
</tr>
<tr>
<td>$\text{H}_2 + \text{CO}$ conversion (%)</td>
<td>32.0</td>
<td>32.8</td>
<td>40.1</td>
<td>46.8</td>
<td>53.2</td>
<td>50.8</td>
<td>49.1</td>
<td>41.9</td>
</tr>
<tr>
<td>$R_{FT}$ ($10^{-3}$ mol kg$^{-1}$ cat$^{-1}$ s$^{-1}$)</td>
<td>2.1</td>
<td>2.3</td>
<td>2.9</td>
<td>4.0</td>
<td>4.3</td>
<td>4.1</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>$R_{WGS}$ ($10^{-3}$ mol kg$^{-1}$ cat$^{-1}$ s$^{-1}$)</td>
<td>1.9</td>
<td>1.8</td>
<td>1.8</td>
<td>2.3</td>
<td>1.9</td>
<td>2.2</td>
<td>2.4</td>
<td>1.6</td>
</tr>
<tr>
<td>$STY$ ($10^{-3}$ mol kg$^{-1}$ cat$^{-1}$ s$^{-1}$)</td>
<td>7.3</td>
<td>7.5</td>
<td>9.1</td>
<td>10.7</td>
<td>12.2</td>
<td>11.6</td>
<td>11.3</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Hydrocarbon selectivities (wt%)

- $w_1$: 9.5 9.6 9.7 16.0 12.1 10.0 9.4 10.9
- $w_{2-4}$: 38.3 36.0 39.7 38.0 38.8 35.9 36.1 48.0
- $w_{5-10}$: 52.2 54.5 50.6 46.0 49.1 54.2 54.5 41.1

Olefin selectivity (wt%)

- $w_{O,2-4}$: 78.8 77.2 79.5 69.0 65.7 77.7 79.5 79.2
- $w_{O,5-10}$: 79.2 74.9 78.2 63.1 62.9 75.0 78.0 71.6

$^1$ $P = 1.50$ MPa, $T = 523$ K, $F = 0.67$, $\Phi_{v,0}/W = 0.5 \times 10^{-3}$ Nm$^{-3}$ kg$^{-1}$ cat s$^{-1}$

$^2$ On-line analysis $n \leq 9$
References


