

NON-IDEALITY IN REACTION KINETICS OF FISCHER-TROPSCH SYNTHESIS FOR NEAR-CRITICAL AND SUPERCRITICAL SOLVENT MEDIA

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Abstract

This study reports the development of a kinetic model for Fischer-Tropsch synthesis (FTS) reaction over a cobalt-based catalyst (15%Co/Al₂O₃) in both gas-phase media and supercritical hexane (SCH) phase media. The rate equations for CO consumption and CH₄ formation were derived by using Langmuir–Hinshelwood–Hougen–Watson (LHHW) approach while assuming ideal gas model at temperature 250 °C and pressure upto 60 bar. The determined rate equations were found satisfactory to predict reaction behaviour in gas phase FTS but they fail to SCH-FTS experimental data. A modified synthesis route for SCH-FTS has been proposed to accounts for the enhanced in situ extraction of heavy hydrocarbons from catalyst pores. These available active sites are assumed to promote both adsorption of reacting molecules (CO and H₂) as well as incorporation of primary products (α -olefins) into the chain growth process. Overall, this will result in higher CO conversion rates and lower methane formation rates than the gas-phase FTS under comparable reaction conditions.

INTRODUCTION

Fischer-Tropsch synthesis (FTS) continues to receive attention as an alternative for the production of ultra-clean transportation fuels, chemicals, and other hydrocarbon products through heterogeneous catalytic conversion of syngas (a mixture of H₂ and CO) derived from readily available natural resources (coal, natural gas or biomass). Diesel fractions from FTS have unique characteristics that include very low sulfur and aromatic content, high cetane index and exceptional clean burning in compression-ignition engines. Compared to crude oil derived diesel, FTS diesel fuel has been shown to reduce emissions of carbon monoxide, nitrogen oxides, hydrocarbons and other particulates. Even of greater importance is that the FTS process can serve as a supplement to decreasing conventional oil resources. FTS performance in industrial fixed-bed-reactors (gas-phase) suffers from local overheating of the catalyst surface that results in poor heat transfer removal and thus they operate at low temperatures, thereby decreasing yield of desired products. Sasol (South African oil company which plays a major role in the development of f FTS reactors and reaction systems) subsequently developed slurry bubble column reactors (liquid-phase) to overcome limitations of the fixed-bed-reactor for FTS. Such operation provides an excellent temperature control for this highly exothermic reaction since the paraffinic solvent (e.g. octacosane C₂₈ hydrocarbon) used as a reaction medium has a thermal mass over 500 times greater than that of the gas- in the fixed-bed-reactor. However, this process is limited by lower reaction rates due to slower diffusion of syngas into the catalyst pores through the heavy hydrocarbon solvent. Catalyst

sintering and separation of products and catalysts from the heavy liquid medium are major issues in the operation of industrial slurry bubble column reactors for FTS.

The above shortcomings in industrial gas-phase FTS (fixed-bed-reactor) and liquid-phase FTS (slurry-reactor) have led to research efforts towards the application of supercritical fluid solvents in order to improve the catalyst activity and selectivity. Conducting FTS under supercritical fluid solvent conditions affords unique opportunities to manipulate the FTS reaction environment, and to enhance production of liquid fuels and value-added chemicals (such as α -olefins) from the syngas. Supercritical phase combines the desirable properties of gas-like diffusion with liquid-like heat transfer and solubility, thus overcoming several of the current industrial limitations [1]. Fine adjustments in operating conditions near the critical point can result in superior control of the FTS process, including tunable product distributions [2].

Few studies reported mechanism and kinetics modeling of SCF-FTS [3-5]. Fan et al. [3] suggested the following empirical power rate law for Sc-hexane-FTS over Ru catalysts of different pore diameter and pore size:

$$r = k P_{H_2}^x P_{CO}^y \quad (1)$$

where k is the rate constant and x and y are the exponential constants. They were able to calculate the apparent rate constant for each catalyst (of different pore diameter and size) and defined the catalyst effectiveness factor as the ratio between the rate of reaction in supercritical fluid to that in gas phase reaction.

Bochniak and Subramaniam [4] studied the effects of pressure tuning on syngas conversion and catalyst effectiveness factor. In order for them to explain the increase in syngas conversion with reactor pressure in a supercritical fluid medium, they correlated the effective rate constants (ηk_s) with the pressure. The expression for an effective rate constant (mol/(min bar g_{catalyst})) was derived by assuming a plug-flow reactor and that the syngas conversion is pseudo first order reaction in H₂.

The effective rate constant is estimated using the following simplified form of the stoichiometric equation, which implies dominant olefin formation and rapid water-gas shift activity. Upon assuming plug-flow behavior and also considering syngas conversion as pseudo first-order in hydrogen (A) partial pressure, Bochniak and Subramaniam [4] were able to derive the following expression for the effective rate constant.

$\eta k = \left(\frac{F_{S0}}{P_T F_{S0} W} \right) (-F_0 \ln(1 - x_A) + 2F_{A0} \{ \ln(1 - x_A) + x_A \})$	(2)
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EXPERIMENTAL

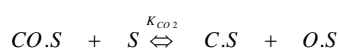
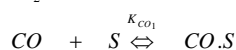
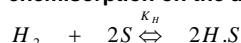
The description of the high pressure FTS unit used to measure the reaction performance of a 15% Co/Al₂O₃ catalyst purchased from United Catalysts is given elsewhere [2, 5]. In a typical experiment, hexane or pentane flow at a rate of 1ml/min (for solvent/syngas ratio 3 :1) was initiated while raising the temperature and pressure to the desired experimental condition. After the temperature and pressure stabilized, syngas flow was started at 50 sccm. The reaction experiments were continued until steady state was reached in terms of both catalyst activity (CO and syngas conversion) and product distribution. Generally, in gas phase FTS, the reaction reached steady state after ca. 40 hrs, while in SCF phase it reached steady state within ca. 24 hr. The reported results in this study represent samples that were collected after at least 50 hr of time-on-stream for both gas-phase and SCF-FTS experiments. The analysis of

reactants and products were conducted by two online gas chromatographs. The finger prints of the detected peaks were used for the selectivity and conversion calculations [2]. A Varian 3300 GC with capillary column (DB-5) and a FID detector was used for the analysis of C₂-C₄₀ hydrocarbons and oxygenates. A Varian CP-3800 GC with a packed column (Hayesep-DB100/120) and TCD were used for the analysis of the permanent gases (H₂, CO, N₂, CH₄, CO₂, C₂H₄, and C₂H₆). Quantitative analysis from Varian CP-3800 provides the necessary data for the calculation of the activity and the selectivity of the 15 % Co/Al₂O₃ catalyst.

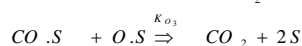
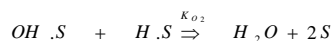
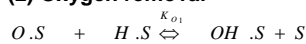
PROPOSED KIENTIC MODEL FOR SCF-FTS

Figure 1 shows our simplified reaction pathway for FTS largely based on the available kinetic models of cobalt catalysts in literature [6-9]. In the first stage, the molecular adsorption of CO with subsequent disassociation in addition to the dissociative adsorption of H₂ take place on a cobalt catalyst active site (S). The removal of surface oxygen as represented by water and CO₂ formation is seen in the second stage. The postulation of oxygen removal is based on the modified Kellener and Bell [9] surface reaction model that is used to account for the adsorbate mobility [8]. The hydrogenation of adsorbed carbon and the formation of oligomers are included in the third stage. Formation of monomer (CH₂.S) and the alkyl species (CH₃.S) are included in the fourth stage, while termination to methane is included in the fifth stage.

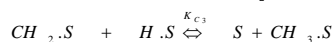
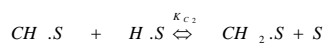
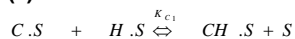
(1) Reactant dissociation and chemisorption on the active site (S)



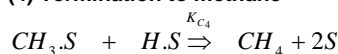
(2) Oxygen removal



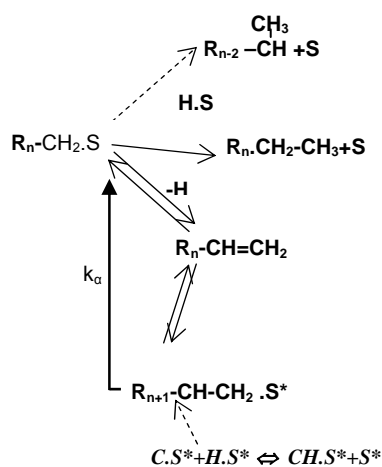
(3) Monomer formation



(4) Termination to methane



(5) Chain growth & termination sequences



(6) Enhanced activity & olefin incorporation in SCH

Figure 1: FTS reaction network including the enhanced activity and olefin incorporation sites (source [2])

The chain growth reactions (stage 5) are assumed to start by the insertion of a monomer into an alkyl species chemically bound to the surface. Termination reactions (stage 5) are assumed to take place by either hydrogen addition to an alkyl species to give paraffin (irreversible reaction), or hydrogen abstraction to produce α -olefin (reversible reaction).

The derivation of the rate equations for each of the reactions proposed in Figure 1 is carried out by using Langmuir–Hinshelwood–Hougen–Watson approach. The hydrogenation of surface carbon (the 1st reaction in stage 3), was considered as the rate limiting step, while the other steps were assumed to be at quasi-equilibrium. After the establishment of steady state operation the rate of oxygen removal by water formation (the 2nd reaction in stage 2) was assumed to be equal to the rate of carbon hydrogenation according to the stoichiometric coefficient of the 3rd reaction in the first stage. Removal of oxygen by CO₂ formation was

neglected in the overall rate due to its very low selectivity over our cobalt catalyst (<2% in gas-phase reaction and <0.5% in SCH operation).

Methods to derive the rate equation for CO consumption and for methane formation were described previously [5] and found as follows:

$$-r_{CO} = \frac{kP_{CO}^{1/2}P_{H_2}^{1/2}}{[1 + K_1P_{H_2}^{1/2} + (K_2 + K_3)P_{CO}^{1/2} + K_4P_{CO}]^2} \quad (3)$$

where

$$r_{CH_4} = \frac{\phi_1 P_{H_2} \theta_s^2}{\left[\phi_2 \left(\left(1 + \phi_3 P_{CO}^{1/2} P_{H_2}^{-1/2} \right)^{1/2} - 1 \right)^{-1} + 1 \right]} \quad (4)$$

where

$$k = k_{c_1} K_3 K_1 C_i^2, K_1 = \sqrt{K_{H_2}}, K_2 = \sqrt{\frac{K_c k_{c_1}}{k_{o_1}}}, K_3 = \sqrt{\frac{K_c k_{o_1}}{k_{c_1}}}, K_4 = K_{CO}$$

$$\phi_1 = \frac{C_i^2 K_H k_{c_3} k_{c_4}}{k_\alpha}, \phi_2 = \frac{K_4}{K_3 k_\alpha}, \phi_3 = \frac{K_6 k_{c_1} K_{cf}^{1/2}}{K_H^{1/2}}$$

K_{cf} represents the adsorption equilibrium constant for carbon and being defined with the rest of the constants as

$$\text{follows; } K_{cf} = \frac{k_{o_1}}{k_{c_1}}, K_5 = \frac{k_t}{2k_\alpha}, K_6 = \frac{4k_\alpha}{k_{c_3} k_t}$$

The performance of the 15% Co/Al₂O₃ catalyst measured by the rate of CO consumption in gas-phase FTS and SCH-FTS under different operating conditions is shown in Figure 2 at 250 °C with a total pressure of 60 bar and a syngas partial pressure, P_{syngas}, of 15 bar at three different H₂/CO ratios. In the gas-phase experiments, a partial pressure of inert helium, P_{helium}, of 45 bar was used as a pressurizing gas to achieve a total pressure of 60 bar. In the SCH experiments, the P_{syngas} was again 15 bar and the partial pressure of hexane solvent, P_{hexane}, was 45 bar thereby yielding the same total pressure of 60 bar. The experiments in both gas-phase and SCH-FTS were conducted at a constant syngas flowrate of 100 sccm. Figure 2 illustrates that increasing the H₂/CO molar feed ratio resulted in higher CO consumption rates at fixed reaction temperature in SCH operation. At low H₂/CO, an increase in reaction temperature from 240 °C to 250 °C results in only a slight increase in the CO consumption (data not shown), however, at a ratio of 2/1 a significant increase in the rate (>30%) is observed with this temperature increase (data not shown). The activity of the catalyst under SCH operation is higher than in the gas-phase at the same total pressure of 60 bar. The same result was observed in the absence of the helium pressurizing (diluent) gas whereby P_{syngas} was kept constant at 20 bar for both gas-phase and SCH operations (data not shown). However, the CO consumption rate in SCH is shown to be function of pressure that exhibits a maximum of 65 bar (data not shown).

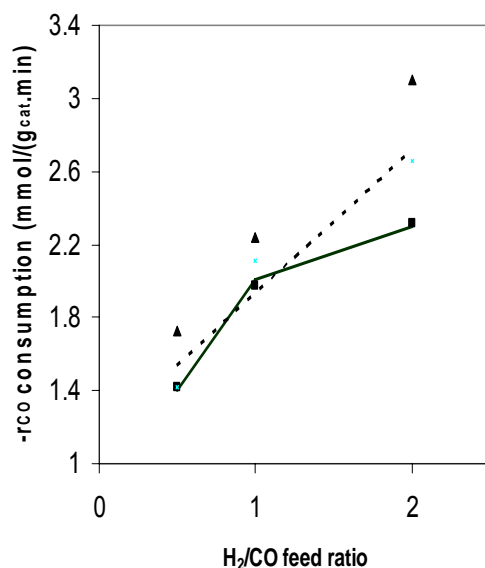


Figure 2 : CO consumption rate in gas-phase (squares) and SCH phase (triangles) as a function H₂/CO ratio at 250 °C. Total pressure is 60 bar ($P_{\text{syngas}} = 15$ bar) and syngas flow rate 100 sccm/min. The solid line represents the predicted rate in gas-phase while the dotted line represents the predicted rate in SCH FTS operation by using the estimated parameters in eq. 3 ($k = 0631$, $K_1 = 0.007$, $K_2 = 0.51$, $K_3 = 0.098$, $K_4 = 6.64 \times 10^{-5}$), source [5].

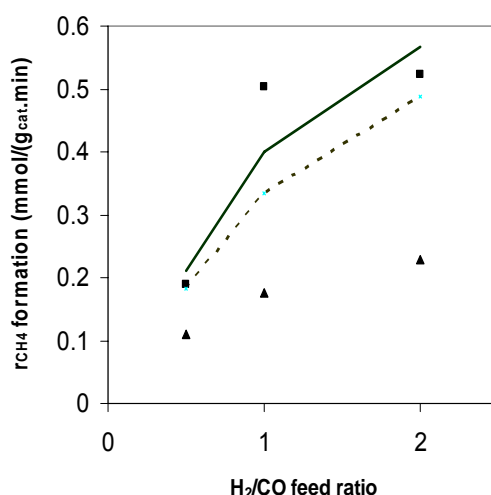


Figure 3 : CH₄ formation rate in gas-phase (squares) and SCH phase (triangles) as a function H₂/CO ratio at 250 °C. Total pressure is 60 bar ($P_{\text{syngas}} = 15$ bar) and syngas flow rate 100 sccm/min. The solid line represents the predicted rate in gas-phase while the dotted line represents the predicted rate in SCH operation by using the estimated parameters of eq. 4 ($\phi_1 \theta_s^2 = 0.0306$, $\phi_2 = 303$, $\phi_3 = 0.045$), source [5].

Figure 4 presents the rate of methane formation as a function of the H₂/CO feed ratio at the conditions described above for both gas-phase and SCH FTS at 250 °C. An increase in H₂/CO ratio results in higher methane production rate in both gas-phase and SCH FTS. However, this rate in SCH is much lower than that in gas-phase and the difference between the two increases with increasing H₂ concentration. In addition to this phenomenon of the reduced methane formation under SCH conditions, it was also observed that SCH FTS resulted in higher olefin/paraffin ratio and shifts of product distributions towards the heavy hydrocarbons (data not shown) compared to gas-phase FTS at the previously specified conditions.

The kinetic model in eq 3 and eq 4 closely predict the CO consumption rates and CH₄ production in gas-phase operation as seen in Figures 2&3. However, both of the models do a

poor job in the prediction of those rates under SCH operation. Higher methane formation rate than the actual was predicted by eq 4, while lower CO consumption rate was also predicted by eq 3 for the SCH FTS.

SUMMARY AND WORK IN PROGRESS

The inconsistency of the kinetic model in predicting the SCH performance indicates that assumptions stated in developing this model for gas-phase operation is not sufficient to measure the performance under SCH operation. Two factors could contribute to the inability of this model to predict FTS performance under SCH conditions. First of all, the model relies on partial pressure (concentrations) of the reactants rather than their activities in the rate equations due to ideal gas assumptions made in previous model developments. Thermodynamic nonideality must be incorporated into the model through use of activities rather than simply partial pressures to accurately predict the kinetic rates under SCH conditions. Secondly, this model does not include solvent effects on individual rate constants in the critical region and particularly for the initiation steps. The FTS reaction pathway (Figure 1) is modified (stage 6) to include enhanced in-situ extraction of the heavy hydrocarbons from the catalyst in the SCH medium, especially for heavier hydrocarbons [2]. This modification accounts for the increased availability of active sites in the supercritical medium. This site (S^*) is assumed to promote both adsorption of the reacting molecules (CO and H_2) and incorporation of primary products (α -olefins) into the chain growth process (see [2]). It is also assumed that S^* would have a higher coverage of active carbon than the regular site, S , and therefore it suppresses methane formation [10].

The development of a kinetic model that accounts for the non-ideality of the SCH media is currently under development. The concentration terms in the rate equations for CO consumption and CH_4 formation will be determined by using Peng-Robinson equation of state. We are expecting this model to provide better prediction for the SCH-FTS experimental data because it considers phase equilibria while simultaneously solve for the kinetic model. As illustrated in stage 6 (Figure 1) we are expecting the presence of the supercritical solvent (hexanes) to affect the solubility of the trapped heavy hydrocarbons in the catalyst pores, leading to more favorable adsorption equilibrium constants for the surface reaction and thus enhancing $CO+H_2$ conversion rates.

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