

Research Article

Lump Kinetic Analysis of Syngas Composition Effect on Fischer-Tropsch Synthesis over Cobalt and Cobalt-Rhenium Alumina Supported Catalyst

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Abstract

This study investigated lump kinetic analysis of Fischer-Tropsch synthesis over Cobalt and Cobalt-Rhenium Alumina supported catalyst ($\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co-Re}/\gamma\text{-Al}_2\text{O}_3$) at 20 bars and 483 K using feed gas with molar H_2/CO ratios of 1.0 to 2.1. Syngas with H_2/CO molar ratio of 1.0 represents syngas characteristic derived from biomass, while the 2.1 molar ratio syngas derived from coal. Rhenium was used as the promoter for the cobalt catalyst. Isothermal Langmuir adsorption mechanism was used to build kinetic model. Existing kinetic model of Fischer-Tropsch synthesis over cobalt alumina supported catalysts only valid for operating pressure less than 10 bar. CO insertion mechanism with hydrogenation step of catalyst-adsorbed CO by catalyst-adsorbed H component as the rate-limiting step is valid for operating condition in this research. Higher H_2/CO ratio makes faster hydrogenation step and less-product dominated in the associative CO adsorption step and dissociative H_2 adsorption equilibrium step. Kinetic constant for hydrogenation step increases 73-421% in syngas with 2.1 H_2/CO molar ratio compared to condition with 1.0 H_2/CO molar ratio. Faster hydrogenation step (with higher kinetic constant) results in higher reactant conversion. Equilibrium constant for associative CO adsorption and dissociative H_2 adsorption step decreases 53-94% and 13-82%, respectively, in syngas with higher H_2/CO molar ratio. Less product dominated reactant adsorption step (lower equilibrium constant for CO and H_2 adsorption step) gives higher CH_4 product selectivity, which occurred on 2.1 molar ratio of syngas. Rhenium (Re) metal on cobalt catalyst with composition 0.05%Re-12%Co/ $\gamma\text{-Al}_2\text{O}_3$ only gives effect as structural promoter, which only increases reactant conversion with the same product selectivity. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: Fischer-Tropsch; lump kinetic-model; reaction mechanism; syngas composition; structural promoter

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1. Introduction

Fischer-Tropsch (FT) process converted synthesis gas, a mixture of predominantly CO and H_2 , into a multicomponent mixture of hydrocarbons.

In Indonesia, biomass and lignite coal is the most suitable source to produce synthesis gas due to their high availability [1,2]. After being refined, liquid synthetic fuel is produced from the FT process. Liquid synthetic fuel produced with the FT process is environmentally friendly due to a very low aromaticity and absence of sulfur [3]. This liquid synthetic fuel can be used as a best solution for fulfilling the

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need of transportation fuel in Indonesia.

FT process is catalyzed by cobalt, iron, rhenium, or ruthenium. Comparing with iron catalyst, cobalt catalyst is more durable and gives higher yield of product and selectivity of linear paraffin [4]. However, cobalt catalyst has less reactivity on water gas shift reaction, so this catalyst is usually used for FT process of synthesis gas with 2.0-2.1 H₂/CO molar ratio [5]. Gasification process of biomass and lignite coal usually produce synthesis gas with H₂/CO molar ration in between 0.45 to 1.5 [6]. Higher H₂/CO molar ratio of synthesis gas is usually obtained from natural gas and bituminous coal.

Tristantini [7] has been published the result for direct use of H₂ poor biosyngas in FT synthesis over un-promoted and rhenium-promoted alumina supported cobalt catalyst. The FT process was conducted in fixed bed reactor with operating pressure 20 bar [7]. Cobalt was dispersed in gamma-alumina support in order to increase cobalt catalyst activity by giving higher surface area of catalyst [4]. Rhenium was added as promoter in order to increase the activity, selectivity, and stability of cobalt cata-

lyst [8].

In this study, lump kinetic analysis of FT process with varied H₂/CO molar ratio of syngas from 1.0 to 2.1 was conducted for unpromoted and rhenium-promoted alumina supported cobalt catalyst from Tristantini [7] research data. Kinetic reaction model was obtained using assumption of Langmuir isothermic adsorption mechanism [9]. A mathematical model represents the production rate of each component in this FT process could be obtained from the kinetic reaction model. Both kinetic reaction and mathematical model could be used in the optimization and scale up step of FT process development before commercialization. Recently, kinetic reaction and mathematical model research of FT process using cobalt catalyst in fixed bed reactor only conducted on operating pressure less than 10 bar with H₂/CO molar ratio 1.0-3.0 [10].

2. Method

2.1. Experimental data

Table 1 shows the summary of experimen-

Table 1. Summary of experimental conditions and results at P = 20 bar and T = 210 °C [7]

| Catalyst | P _{CO} (Pa) | P _{H₂} (Pa) | X _{CO} (%) | Product Component | S (%) | r _{FT} (Pa.h ⁻¹) |
|--------------------------------------|-------------------------|------------------------------------|------------------------|-------------------|----------|--|
| Co/Al ₂ O ₃ | 1013250 | 1013250 | 23.63 | CH ₄ | 5.89 | 1222.06 |
| | | | | C ₂ - | 0.61 | 124.18 |
| | | | | C ₂ = | 0.16 | 48.90 |
| | | | | C ₃ - | 0.67 | 129.09 |
| | | | | C ₃ = | 2.44 | 447.05 |
| | 810600 | 1215900 | 28.25 | CH ₄ | 8.01 | 1804.01 |
| | | | | C ₂ - | 0.90 | 183.42 |
| | | | | C ₂ = | 0.23 | 46.33 |
| | | | | C ₃ - | 0.96 | 183.93 |
| | | | | C ₃ = | 2.54 | 519.82 |
| | 653709 | 1372790 | 28.98 | CH ₄ | 10.01 | 1750.59 |
| | | | | C ₂ - | 0.92 | 144.09 |
| | | | | C ₂ = | 0.24 | 24.85 |
| | | | | C ₃ - | 1.12 | 172.82 |
| | | | | C ₃ = | 2.69 | 395.53 |
| Co-Re/Al ₂ O ₃ | 1013250 | 1013250 | 25.21 | CH ₄ | 5.85 | 1295.57 |
| | | | | C ₂ - | 0.59 | 127.05 |
| | | | | C ₂ = | 0.15 | 45.56 |
| | | | | C ₃ - | 0.63 | 130.21 |
| | | | | C ₃ = | 2.38 | 509.86 |
| | 810600 | 1215900 | 29.43 | CH ₄ | 7.93 | 1589.82 |
| | | | | C ₂ - | 0.81 | 144.48 |
| | | | | C ₂ = | 0.18 | 31.08 |
| | | | | C ₃ - | 0.94 | 177.70 |
| | | | | C ₃ = | 2.49 | 485.14 |
| | 653709 | 1372790 | 29.99 | CH ₄ | 9.98 | 1519.68 |
| | | | | C ₂ - | 0.84 | 115.74 |
| | | | | C ₂ = | 0.21 | 25.7 |
| | | | | C ₃ - | 1.05 | 146.75 |
| | | | | C ₃ = | 2.66 | 394.02 |

tal conditions and results of study held by Tris-tantini [7]. The operating condition of FT synthesis used in this study was 20 bar and 210 °C with Alumina supported Cobalt and Cobalt-Rhenium catalyst. The H₂/CO ratio of synthesis gas feed was varied from 1.0 to 2.1. This data would be fitted with the kinetic model which is developed in this study. P_{CO} and P_{H_2} represents the initial component CO and H₂ gas pressure, X_{CO} represents the CO reactant conversion, S represents the selectivity of each product component, and r_{FT} represents the rate of formation of each product component. Reaction rate and selectivity used in this study only from CH₄ to C₃ product component. The rest of product component (C₄₊) was not analyzed in this kinetic study.

2.2. Mechanistic aspect

Two mechanisms, CO insertion and carbide mechanism, were offered on the basis of various monomer formation (elementary reactions) and carbon chain distribution pathway. The CO insertion mechanism assumes the associative adsorption of CO and H₂ which allows for oxygenate formation. However, the carbide mechanism assumes that CO and H₂ adsorbed dissociatively [11]. Table 2 summarized the elementary reaction set for each model.

2.3. Kinetic analysis and parameter estimation

In order to derive a kinetic model equation from elementary reaction mechanism set in Table 2 to be adjusted with the data in Table 1, Langmuir-Hinshelwood-Hougen-Watson (LHHW) theory was used in this study. By this

Table 2. Elementary reactions mechanism set for Fischer-Tropsch

| Model | Number | Elementary Reaction |
|--------------|--------|--|
| CO Insertion | (1) | CO + s ⇌ COs |
| | (2) | H ₂ + 2s ⇌ 2Hs |
| | (3) | COs + Hs ⇌ HCOs + s |
| | (4) | HCOs + Hs ⇌ HCHOs + s |
| | (5) | HCHOs + Hs ⇌ CHs + H ₂ O + s |
| | (6) | CHs + Hs ⇌ CH ₂ s + s |
| | (7) | CH ₂ s + Hs ⇌ CH ₃ s + s |
| Carbide | (1) | CO + s ⇌ COs |
| | (8) | COs + s ⇌ Cs + Os |
| | (2) | H ₂ + 2s ⇌ 2Hs |
| | (9) | Os + COs ⇌ CO ₂ + 2s |
| | (10) | Cs + Hs ⇌ CHs + s |
| | (6) | CHs + Hs ⇌ CH ₂ s + s |
| | (7) | CH ₂ s + Hs ⇌ CH ₃ s + s |

theory, one of the elementary reaction steps in the mechanism set was assumed as rate-determining step, while the other steps were considered at equilibrium [10].

As example, derivation of the kinetic equation for CO Insertion (3) is explained here. Firstly, the step (3) in CO insertion model was considered to be the rate limiting step and the reaction was irreversible. The remaining steps could be considered to be quick and at equilibrium. The rate of hydrocarbon production is presented in Equation (11).

$$r_{FT} = \frac{dP_{HC}}{dt} = k_3 \theta_{CO} \theta_H \quad (11)$$

where r_{FT} is the rate of production of hydrocarbon component, k_3 is the kinetic rate constant of step number (3) in CO insertion model. The θ_i is the catalyst surface fraction occupied by adsorbed species i . Fraction of vacant site, θ_v , was calculated from Equation (12).

$$\theta_v + \theta_{CO} + \theta_H + \theta_{HCO} + \theta_{HCHO} + \theta_{CH} + \theta_{CH_2} + \theta_{CH_3} = 1 \quad (12)$$

Adsorbed dissociated hydrogen and carbon monoxide was assumed to occupy most fraction of the total number of catalyst sites. Other species were assumed to be negligible in Equation (12), becomes:

$$\theta_v + \theta_{CO} + \theta_H = 1 \quad (13)$$

Fraction of catalyst surface covered by carbon monoxide and dissociated hydrogen could be calculated from the site balance. Reaction step (1) and (2) of CO Insertion model were assumed at quasi equilibrium:



$$k_1 P_{CO} \theta_v - k_{1,des} \theta_{CO} = 0 \quad (15)$$

$$\theta_{CO} = K_1 P_{CO} \theta_v \quad (16)$$

$$K_1 = \frac{k_1}{k_{1,des}} \quad (17)$$

where K_1 is the equilibrium constant of CO adsorption step (reaction step (1) of CO Insertion model). By the same step of derivation with an equilibrium assumption of reaction step (2) of CO Insertion model (dissociative adsorption of Hydrogen molecule), the fraction of catalyst surface covered by dissociated hydrogen could

be calculated by equation :



$$\theta_H = \theta_v \sqrt{K_2 P_{H_2}} \quad (19)$$

where K_2 is the equilibrium constant of H_2 dissociative adsorption step (reaction step (2) of CO Insertion model).

By substitution of Equations (16) and (19) to Equation (13), the ratio of vacant catalyst site could be expressed as in Equation (20).

$$\theta_v = \frac{1}{(1 + K_1 P_{CO} + \sqrt{K_2 P_{H_2}})} \quad (20)$$

Substituting Equations (16), (19), and (20) to Equation (11), the kinetic equation of CO insertion (3) model is obtained as stated in Equation (21).

$$r_{FT} = \frac{dP_{HC}}{dt} = \frac{K_1 \sqrt{K_2} k_3 P_{CO} \sqrt{P_{H_2}}}{(1 + K_1 P_{CO} + \sqrt{K_2 P_{H_2}})^2} = \frac{k P_{CO} \sqrt{P_{H_2}}}{(1 + a P_{CO} + b \sqrt{P_{H_2}})^2} \quad (21)$$

By the same method, kinetic equation for other model were obtained. Table 3 shows certain selected kinetic models that were fitted in this study with the experimental data obtained by Tristantini [7]. Then, the all of the models obtained were fitted separately against the experimental data.

To determine the kinetic and equilibrium constant from equation listed in Table 2, least square method and non-linear regression analysis based on data summarized in Table 1 using Polymath software. The software uses Levenberg-Marquardt algorithm to estimate the parameters value of the kinetic equation model. Some requirements required to find the best model : (a) Obtained constants must be positive; (b) Model gives reliable R^2 as a measurement of fitted model; (c) All constants have small uncertainties (Δ) less than 10% [11].

3. Results and Discussion

3.1. Reaction mechanism of FT synthesis using alumina supported cobalt catalyst

Based on non-linear regression analysis done in this study, CO Insertion (3) model

Table 3. Kinetic equation modelling for the FTS fitted in this study r_{FT} (Pa. h^{-1})

| Model of Rate-Determining Step | Kinetic Equation |
|--------------------------------|---|
| CO Insertion (1) | $r_{FT} = \frac{k P_{CO}}{(1 + a \sqrt{P_{CO}})^2}$ |
| CO Insertion (3) | $r_{FT} = \frac{k P_{CO} \sqrt{P_{H_2}}}{(1 + a P_{CO} + b \sqrt{P_{H_2}})^2}$ |
| CO Insertion (4) | $r_{FT} = \frac{k P_{CO} P_{H_2}}{(1 + a P_{CO} + b \sqrt{P_{H_2}} + c P_{CO} \sqrt{P_{H_2}})^2}$ |
| CO Insertion (5) | $r_{FT} = \frac{k P_{CO} (P_{H_2})^{3/2}}{(1 + a \sqrt{P_{H_2}} + b P_{CO} P_{H_2})^2}$ |
| Carbide (1) | $r_{FT} = \frac{k P_{CO}}{(1 + a \sqrt{P_{H_2}})}$ |
| Carbide (2) | $r_{FT} = \frac{k P_{CO}}{(1 + a P_{CO} + b \sqrt{P_{H_2}})^2}$ |
| Carbide (6) | $r_{FT} = \frac{k P_{CO} P_{H_2}}{(1 + a \sqrt{P_{H_2}} + b P_{CO})^2}$ |
| Carbide (7) | $r_{FT} = \frac{k P_{CO} (P_{H_2})^{3/2}}{(1 + a \sqrt{P_{H_2}} + b P_{CO})^2}$ |

where hydrogenation step of catalyst-adsorbed CO by catalyst-adsorbed H component as the rate-limiting step is valid for FT synthesis with alumina supported cobalt and cobalt-rhenium catalyst at operating pressure 20 bar and temperature 210 °C. The other models gave some negative constant, low R^2 value, and have high uncertainties (Δ) of constant which indicated that the models is not fitted for FT synthesis in this study. Barrier energy analysis for each elementary step of FT synthesis using alumina supported cobalt catalyst (Co/Al₂O₃) at 508 K with CO and H₂ pressure synthesis gas feed varied from 4 to 10 bar has been done by Ojeda *et al.* [12].

Figure 1 shows that, direct dissociation step of catalyst-adsorbed carbon monoxide (COs + s \rightleftharpoons Cs + Os) has higher forward barrier energy (367 kJ/mole) than hydrogenation step of catalyst-adsorbed carbon monoxide by catalyst-adsorbed H component (COs + Hs \rightleftharpoons HCOs + s) (125 kJ/mole) for FT Synthesis using alumina supported cobalt catalyst. Naturally, the reaction mechanism would prefer lower forward energy barrier (E_f) resulted by the catalyst. Compared to the result of analysis by Ojeda *et al.* [12], same phenomena was found in this study. Insertion CO mechanism pathway described in Table 2 is also more preferably for FT Synthesis using alumina supported cobalt catalyst in this study (with T = 210 °C or 483 K and P = 20 bar) [12].

When backward barrier energy is less than or equal with forward barrier energy ($E_r \leq E_f$), the elementary reaction step is at equilibrium state. While the backward barrier energy is higher than forward barrier energy ($E_r > E_f$), the elementary reaction step is considered as rate lim-

iting step since little possibility of reaction to be directed in reverse direction since high backward barrier energy [5]. Figure 1 shows that hydrogenation step of catalyst-adsorbed carbon monoxide (COs) by catalyst-adsorbed H component (Hs) (COs + Hs \rightleftharpoons HCOs + s) has much higher backward barrier energy (E_r) compared to its forward barrier energy (E_f). As indicated by kinetic analysis in this study, this step is the rate limiting step of Insertion CO mechanism for FT Synthesis using alumina supported cobalt catalyst at operating temperature 483 K and pressure 20 bar. This pathway was named as CO Insertion (3) model in this study. As result of least square method and non-linear regression analysis using Polymath, kinetic and equilibrium constant from equation CO Insertion (3) model was obtained and listed in Table 4.

3.2. Effect of H₂/CO in synthesis gas feed on FT Synthesis reaction mechanism using alumina supported cobalt catalyst

Table 4 shows that variation on H₂/CO ratio in synthesis gas feed does not change reaction mechanism pathway. FT synthesis using alumina supported cobalt and cobalt-rhenium at various H₂/CO ratio of synthesis gas feed follows CO Insertion (3) model. Table 5 shows that K_1 and K_2 parameter value decreases with higher H₂/CO ratio in synthesis gas feed. While, k_3 parameter value increases with higher H₂/CO ratio in synthesis gas feed. Higher value of k_3 indicates faster kinetic reaction that causes higher reactant (carbon monoxide) conversion at the higher H₂/CO ratio in synthesis gas feed. The increase of k_3 parameter value shows that hydrogenation step of COs (catalyst-adsorbed CO molecule) by Hs (catalyst-adsorbed H atom) at step (3) of CO Insertion model occurred faster.

Decrease of K_1 and K_2 parameter value shows that COs and Hs component produced at step (1) and (2) of CO Insertion model is less. Although kinetic reaction of HCOs formation a step (3) is faster, the HCOs resulted in 2.1 H₂/CO ratio of synthesis gas is also less since fewer COs component resulted at step (1) and (2). At higher H₂/CO ratio of synthesis gas, excess of Hs component (higher ratio of Hs and HCOs component) in system is occurred due to the decrease of COs formation in step (1) is more significant than decrease of Hs formation in step (2). By this reason, FT synthesis with higher H₂/CO ratio of synthesis gas feed tends to produce CH₄ product component which required higher ratio of Hs and

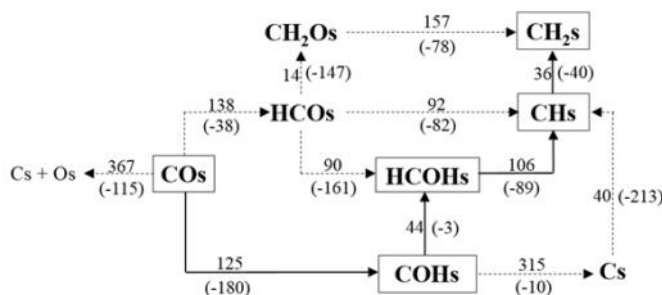


Figure 1. Barrier energy forward (E_f) and backward (E_r) in kJ/mol of FT synthesis elementary reaction with alumina supported cobalt catalyst at T = 508 K and P = 4-10 bar [12]. Note : (a) \rightarrow CO Insertion (3) reaction mechanism pathway; (b) Positive value shows forward barrier energy (E_f) while negative value in bracket shows backward barrier energy (E_r).

Table 4. Kinetic and equilibrium constant of CO Insertion (3) equation model. Note: k_3 is the kinetic rate constant of step number (3) in CO Insertion model in unit $\text{h}^{-1}.\text{Pa}^{-1/2}$; K_1 is the equilibrium constant of CO adsorption step (reaction step (1) of CO Insertion model); K_2 is the equilibrium constant of H_2 dissociative adsorption step (reaction step (2) of CO Insertion model)

| Hydro-carbon Product | Constant Parameter Estimated | Catalyst [H_2/CO Ratio in Synthesis Gas Feed] | | | | | |
|----------------------|------------------------------|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | Co[1.0] | Co[1.5] | Co[2.1] | CoRe[1.0] | CoRe[1.5] | CoRe[2.1] |
| CH ₄ | K_1 | 6.72×10^{-7} | 6.66×10^{-7} | 3.11×10^{-7} | 6.72×10^{-7} | 6.67×10^{-7} | 3.07×10^{-7} |
| | K_2 | 3.26×10^{-5} | 2.24×10^{-5} | 2.11×10^{-5} | 3.08×10^{-5} | 2.40×10^{-5} | 2.30×10^{-5} |
| | K_3 | 5.21×10^5 | 5.24×10^5 | 1.11×10^6 | 5.21×10^5 | 5.29×10^5 | 1.16×10^6 |
| C ₂₌ | K_1 | 7.74×10^{-6} | 6.64×10^{-6} | 4.65×10^{-7} | 7.34×10^{-6} | 6.65×10^{-6} | 4.55×10^{-7} |
| | K_2 | 8.32×10^{-3} | 1.88×10^{-3} | 1.52×10^{-3} | 8.78×10^{-3} | 1.81×10^{-3} | 1.65×10^{-3} |
| | K_3 | 5.25×10^4 | 6.00×10^4 | 9.37×10^4 | 5.57×10^4 | 6.19×10^4 | 9.64×10^4 |
| C ₂₋ | K_1 | 2.15×10^{-6} | 8.52×10^{-7} | 4.16×10^{-7} | 2.05×10^{-6} | 8.66×10^{-7} | 4.42×10^{-7} |
| | K_2 | 3.28×10^{-4} | 2.89×10^{-4} | 2.77×10^{-4} | 3.19×10^{-4} | 2.90×10^{-4} | 2.76×10^{-4} |
| | K_3 | 3.50×10^5 | 3.93×10^5 | 1.10×10^6 | 3.65×10^5 | 4.09×10^5 | 1.14×10^6 |
| C ₃₌ | K_1 | 7.57×10^{-6} | 7.33×10^{-6} | 5.71×10^{-7} | 7.51×10^{-6} | 7.08×10^{-6} | 5.63×10^{-7} |
| | K_2 | 8.96×10^{-3} | 1.89×10^{-3} | 1.70×10^{-3} | 8.98×10^{-3} | 1.91×10^{-3} | 1.79×10^{-3} |
| | K_3 | 5.02×10^4 | 5.44×10^4 | 9.08×10^4 | 5.05×10^4 | 5.46×10^4 | 9.54×10^4 |
| C ₃₋ | K_1 | 2.22×10^{-6} | 8.92×10^{-7} | 4.30×10^{-7} | 2.22×10^{-6} | 8.58×10^{-7} | 4.51×10^{-7} |
| | K_2 | 4.06×10^{-4} | 2.96×10^{-4} | 2.90×10^{-4} | 4.01×10^{-4} | 2.91×10^{-4} | 2.82×10^{-4} |
| | k_3 | 2.69×10^4 | 3.43×10^5 | 1.07×10^6 | 2.66×10^5 | 3.38×10^5 | 1.12×10^6 |

Table 5. Value difference percentage (%) of kinetic and equilibrium constant CO Insertion (3) model between FT Synthesis using H_2/CO ratio in synthesis 1.0 and 2.1 with cobalt (Co) and cobalt-rhenium (CoRe) catalyst

| Hydrocarbon Product Component | Constant Parameter Estimated | Catalyst | |
|-------------------------------|------------------------------|----------|--------|
| | | Co | CoRe |
| CH ₄ | K_1 | -53.7 | -54.3 |
| | K_2 | -35.3 | -33.9 |
| | k_3 | +113.1 | +122.6 |
| C ₂₌ | K_1 | -94.0 | -93.8 |
| | K_2 | -81.7 | -81.2 |
| | k_3 | +78.4 | +73.1 |
| C ₂₋ | K_1 | -80.6 | -78.4 |
| | K_2 | -15.6 | -13.5 |
| | k_3 | +214.3 | +212.3 |
| C ₃₌ | K_1 | -92.5 | -92.5 |
| | K_2 | -81.0 | -80.1 |
| | k_3 | +80.9 | +74.7 |
| C ₃₋ | K_1 | -80.6 | -79.7 |
| | K_2 | -28.6 | -29.7 |
| | k_3 | +297.8 | +421.1 |

HCOs component in system. Table 6 shows that CH₄ product required highest ratio of Hs and HCOs component in system. Agree with the study from Visconti *et al.* [13], kinetic analysis of CO Insertion (3) model at various H₂/CO ratio of synthesis gas feed showed that higher H₂/CO tends to produce more CH₄ (short chain of hydrocarbon product component).

3.3. Effect of rhenium promoter on FT synthesis reaction mechanism using alumina supported cobalt catalyst

Table 4 also shows that addition of rhenium as promoter does not change reaction mechanism pathway. FT synthesis using alumina supported cobalt and cobalt-rhenium catalyst has same reaction mechanism, CO Insertion (3) model. Table 7 shows that kinetic and equilibrium constant value of CO Insertion (3) model does not change with addition of 0.05%-wt rhenium promoter at 12%-wt cobalt catalyst since the value difference between both catalyst is less than 10%. Table 1 also shows that addition of 0.05%-wt rhenium as promoter in 12%-wt supported alumina cobalt catalyst relatively does not change selectivity of each hydrocarbon product component (selectivity change less than 0.30% for each component). However, the rhenium promoter addition gives higher 1-2% of carbon monoxide (CO) reactant conversion. So, in this concentration (0.05%Re-12%Co/Al₂O₃), rhenium acts as structural promoter in FT synthesis at operating condition 210 °C and 20 bar with H₂/CO ratio in synthesis gas feed varied from 1.0 to 2.1 since no influence of rhenium promoter to the reaction mechanism and product selectivity.

Structural promoter only affects the formation and stability of the active site in catalyst material. This promoter effect is only visible on cobalt dispersion step which regulates interaction between catalyst (cobalt metal) and the support material (alumina). High dispersion of

Table 6. Ratio of HCOs and Hs required to produce each hydrocarbon product component

| Hydrocarbon Product Component | Ratio of HCOs and Hs |
|-------------------------------|----------------------|
| CH ₄ | 5.0 |
| C ₂ - | 4.0 |
| C ₃ - | 3.6 |
| C ₂ = | 3.0 |
| C ₃ = | 3.0 |

cobalt catalyst gives larger active surface on cobalt metal. As a result, higher catalyst activity and stability is produced with the increase of active site amount [8]. Higher catalyst activity and stability gives higher reactant conversion in the addition 0.05%-wt of Rhenium as promoter in 12%-wt supported alumina cobalt catalyst. Product selectivity is not affected by the performance of the structural promoter in 0.05%Re-12%Co/Al₂O₃.

Compared to study by Jacobs *et al.* [14] in Table 8, addition of 0.48%-wt rhenium promoter in 25%-wt supported alumina cobalt catalyst (0.48%Re-25%Co/Al₂O₃) results in product selectivity changes relatively around 0.70 to 2.60% [14]. In 0.05%Re-12%Co/Al₂O₃, rhenium promoter increases 1-2% reactant conversion. Meanwhile in 0.48%Re-25%Co/Al₂O₃, it only increases 0.02% reactant conversion. In 0.48%Re-25%Co/Al₂O₃, rhenium acts as electronic promoter in FT synthesis at operating condition 220 °C and 21 bar with H₂/CO ratio in synthesis gas feed 2.1 since there is rhenium promoter influence to the reaction mechanism and product selectivity.

Table 7. Value difference percentage (%) of kinetic and equilibrium constant CO Insertion (3) model between FT synthesis using cobalt and cobalt-rhenium catalyst at various product component and H₂/CO ratio synthesis gas feed

| Hydro-carbon Product | Estimated Constant Parameter | H ₂ /CO Ratio in Synthesis Gas | | |
|----------------------|------------------------------|---|-------|-------|
| | | 1.0 | 1.5 | 2.1 |
| CH ₄ | <i>K</i> ₁ | 0 | +0.15 | -1.29 |
| | <i>K</i> ₂ | -5.52 | +7.14 | +9.00 |
| | <i>k</i> ₃ | 0 | +0.95 | +4.50 |
| C ₂ = | <i>K</i> ₁ | -5.17 | +0.15 | -2.15 |
| | <i>K</i> ₂ | +5.53 | -3.72 | +8.55 |
| | <i>k</i> ₃ | +6.10 | +3.17 | +2.88 |
| C ₂ - | <i>K</i> ₁ | -4.65 | +1.64 | +6.25 |
| | <i>K</i> ₂ | -2.74 | +0.35 | -0.36 |
| | <i>k</i> ₃ | +4.29 | +4.07 | +3.64 |
| C ₃ = | <i>K</i> ₁ | -0.79 | -3.41 | -1.40 |
| | <i>K</i> ₂ | +0.22 | +1.06 | +5.29 |
| | <i>k</i> ₃ | +0.60 | +0.37 | +5.07 |
| C ₃ - | <i>K</i> ₁ | 0 | -3.81 | +4.88 |
| | <i>K</i> ₂ | -1.23 | -1.69 | -2.76 |
| | <i>k</i> ₃ | -1.12 | -1.46 | +4.67 |

Higher rhenium amount added to the cobalt catalyst in 0.48%Re-25%Co/Al₂O₃ (rhenium added to the catalyst is 2% of cobalt weight) delivers stronger bond between cobalt metal catalyst and rhenium metal to be an alloy. Cobalt-rhenium alloy formation will change electron configuration on the catalyst and change the reaction mechanism consequently [15]. This alloy formation would not occur in little amount of rhenium added to the cobalt catalyst like in 0.05%Re-12%Co/Al₂O₃ (rhenium added to the catalyst only 0.4% of cobalt weight).

4. Conclusions

For FT Synthesis using alumina supported cobalt and cobalt-rhenium catalyst with operating pressure 20 bar and temperature 210 oC in fixed bed reactor, CO insertion mechanism with hydrogenation step of catalyst-adsorbed CO by catalyst-adsorbed H component as the rate-limiting step. Higher H₂/CO ratio at synthesis gas feed increase the CH₄ product selectivity with the same reaction mechanism. Rhenium promoter addition (0.05%Re-12%Co/Al₂O₃) only gives effect as structural promoter by increasing reactant (CO) conversion. No changes on reaction mechanism and product selectivity by addition of 0.05%Re at 12% Co/Al₂O₃ catalyst.

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Table 8. Effect of rhenium promoter addition at 0.48%Re-25%Co/Al₂O₃ to the product selectivity and reactant conversion at H₂/CO ratio 2.1 in synthesis gas feed (T = 220 oC; P = 21 bar) [14]

| Parameter | Catalyst [H ₂ /CO] | | Difference Value |
|---------------------------------|-------------------------------|------------|------------------|
| | Co[2.1] | Co-Re[2.1] | |
| CH ₄ Selectivity (%) | 7.9 | 7.2 | -0.70 |
| C ₄₊ Selectivity (%) | 83.4 | 86.0 | +2.60 |
| CO Reactant Conversion (%) | 49.4 | 49.6 | +0.20 |

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