

Verification of Kinetic Parameters for Fischer-Tropsch Reaction Using Ru/Al₂O₃ Catalyst

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Abstract. Fischer-Tropsch Synthesis (FTS) over ruthenium supported alumina oxide catalyst (Ru/Al₂O₃) was performed in a fixed-bed reactor. Experimental conditions were varied as follows: H₂/CO feed molar ratios in a range of 1-3, reaction temperature in a range of 160-220 °C, reaction pressure of 2 bar, and gas hourly space velocity (GHSV) in a range of 1000-1025 ml/g_{cat}·hr. Kinetic model expression based on Langmuir-Hinshelwood-Hougen-Watson (LHHW), the rate equation over ruthenium catalyst showed in the form of $-r_{CO} = k_p b_{CO} P_{H_2}^2 P_{CO} / (1 + 2(b_{CO} P_{CO})^{1/2})^2$ was found to give the best fit to the experimental data for the performed FTS reaction. Kinetic parameters was estimated with linearization method and the rate constant of reaction (k_p) were 0.00163, 0.00058, 0.00058, 0.00225 mol/ min·g_{cat}, the equilibrium constant of CO (b_{CO}) were 0.12638, 1.86769, 2.09580, 0.13319 bar⁻¹ for reaction temperature 160, 180, 200, 220 °C respectively and the mean absolute relative residual (MARR) of this model was 0.47%.

Keywords: Fischer-Tropsch synthesis, Kinetic parameters, Fixed-bed reactor

1. Introduction

Fischer-Tropsch synthesis (FTS) plays an important role in the production of ultra-clean transportation fuels, chemicals, and other hydrocarbon products through the conversion of available syngas (CO and H₂) resources. The FTS permits one to produce high quality petroleum products that can be further processed to specific boiling-point fractions [1]. Dixit and Taviarides [2], Sarup and Woiciechowski [3] and many investigators have derived rate equations for the Fischer-Tropsch reaction based upon mechanistic equations of the Langmuir-Hinshelwood-Hougen-Watson form involving one characteristic rate determining reaction. Rate equations based upon complex mechanistic models normally require a large number of constants which are not easy to obtain [3]. Also, there are no quantitative results available in the literatures because of the complexity involved. Dixit and Taviarides [2], however, also deduced that at high conversions of carbon monoxide over ruthenium catalyst, the partial pressures of both carbon monoxide and hydrogen were important for the determination of the rate equation (power law).

The FTS is a polymerization reaction, in which the monomers are being produced in-situ from the gaseous reactants hydrogen and carbon monoxide. Thus, the reaction pathways proposed in literatures have three reaction sections: (1) generation of the chain initiator, (2) chain growth or propagation, and (3) chain growth termination or desorption [4]. The kinetic description of the FT reaction is very important for

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industrial practice, being a prerequisite for the industrial process design, optimization and simulation. Since the reaction mechanism of FTS is complex with a large number of species involved, this made it difficult to describe Fischer–Tropsch reaction kinetics. However, in the recent years, the kinetics of the Fischer–Tropsch synthesis has been the subject of several studies. For this work, the modified ruthenium-based catalyst developed in the Research and Development Center for Chemical Engineering Unit Operation and Catalyst Design (RCC) was studied. This catalyst was proved to give, high activity, high selectivity and can be very active at low conditions, which makes this catalyst durable and high stability [5].

In this paper, some of the kinetic models of Fischer–Tropsch reaction based on Journal of Industrial and Engineering Chemistry (2010), “*Kinetic study of Fischer–Tropsch process on titania-supported cobalt–manganese catalyst*” [6] were adopted in order to fit with the experimental data obtained for a case of the modified ruthenium-based catalyst. The best fitted model was pointed out and the kinetic parameters were determined.

2. Experimental

2.1. Catalyst Preparation

In this research, 10% Ru/Al₂O₃ catalyst was prepared by sol-gel method using ruthenium trichloride hydrate (RuCl₃.xH₂O) and aluminium isopropoxide (Al(OC₃H₇)₃) as precursors. Nitric acid solution was added and mixed in the precursor solution. The mixed solution was then refluxed, stirred at the temperature of 90-95 °C for 12 h. The catalyst was dried and calcined in air at 400 °C. Thereafter, the dried gel was crushed and sieved into 355-600 μm in size. The total surface area, the pore volume and the average pore diameter of catalyst prepared by BELSORP-mini instrument were 206 m²·g⁻¹, 0.179 cm³·g⁻¹ and 3.47 nm, respectively.

2.2. Fixed-bed Reactor

In this study, a fixed-bed reactor (FBR) with the length of 300 mm, internal diameter (ID) of 10.6 mm, and made from stainless steel (SS316) tube is shown in Fig. 1. The FTS’s experiments were conducted in a FBR, which had been packed Ru/Al₂O₃ catalyst particles (Mesh 355-600 μm), respectively. The Ru/Al₂O₃ catalyst was reduced with H₂ (30 mL·min⁻¹) in-situ at 400 °C overnight under atmospheric pressure. The FBR was heated by an electric tube furnace, and equipped with constant thermo-couple (K-Type) indicators located inside and outside of the catalytic bed. The reactive gases were supplied from two cylinders consisting of hydrogen (H₂) and carbon monoxide (CO), and the mass flow rates of each component were controlled by two separate mass flow controllers (Kofloc® Model 8500). The pressure of the system was regulated and kept at 1-1.5 atm by a spring-load type back pressure regulator located at the bottom of FBR. Two pressure transducers were also installed at the top and the bottom of FBR to monitor the pressure difference across the bed. After the product gas had left the FBR, it was passed through a condensing section in order to separate rather heavy components before passing through the gas detector. The liquid hydrocarbon products were collected in which the temperature was maintained at around -5 °C, and the non-condensable hydrocarbons were measured by gas chromatography (GC). The volume was measured by a bubble gas meter.

2.3. Kinetic study

The kinetic studies were performed in a fixed-bed reactor as explained in previous section. The experiments were conducted with mixed gas consisting of H₂ and CO and in a temperature range of 160–220 °C, H₂/CO molar feed ratio of 1/1–3/1, and a pressure of 2 bar as summarized in Table 1. The reaction rate was determined experimentally as follows:

$$-r_{CO} = \frac{X_{CO} \cdot F_{CO,inlet}}{\Delta W} \quad \text{Eq.1}$$

where $-r_{CO}$ is the rate of conversion of CO (mol/min·g_{cat}), X_{CO} is the conversion of CO, $F_{CO,inlet}$ is the molar flow rate of CO (mol/min), ΔW is the weight of catalyst (g).

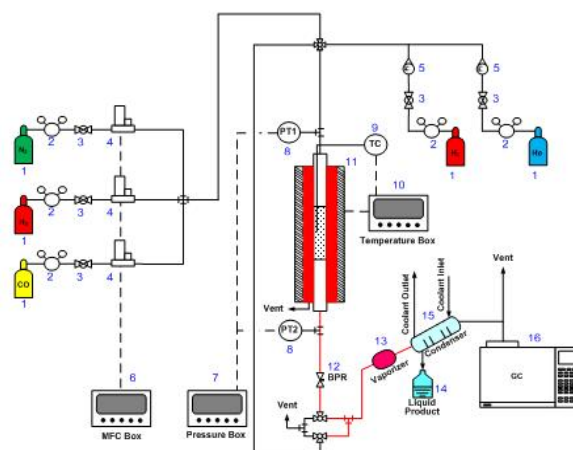


Fig. 1: Schematic diagrams of the FTS's experimental apparatus. 1-Gas cylinders, 2-Pressure regulators (BOC[®]), 3-Ball valves (Swagelok[®]), 4-Mass flow controllers (Kofloc[®]), 5-Gas Rota-meter (Kofloc[®]), 6-MFC box, 7-Pressure box, 8-Pressure Transducer (New-flow[®]), 9-Thermo-couple (Type-K), 10-Temperature box, 11- Electric tube furnace (Carbolite[®]), 12-Back pressure regulator (Tescom[®]), 13-Vaporizer, 14-Liquid Product, 15-Condenser (HAAKE[®]), 16-Gas chromatography (Bruner[®] Model) [7].

Table 1: Summary of experimental conditions for kinetic test at $P_{tot} = 2$ bar and $T = 160$ - 220 °C

Reaction No.	Temp. (°C)	P_{total} (bar)	Molar feed ratio (H_2/CO)	P_{H_2} (bar)	P_{CO} (bar)	W_{cat} (g)	CO conversion (%)	$-R_{CO}$ (mol/min·g _{cat})
1	160	2	1/1	1	1	4.68	10.1	6.915E-05
2	180	2	1/1	1	1	4.68	10.8	7.394E-05
3	200	2	1/1	1	1	4.68	11.2	7.668E-05
4	220	2	1/1	1	1	4.68	14.4	9.858E-05
5	160	2	2/1	1.33	0.67	7.2	23	1.024E-04
6	180	2	2/1	1.33	0.67	7.2	31.4	1.397E-04
7	200	2	2/1	1.33	0.67	7.2	31.9	1.420E-04
8	220	2	2/1	1.33	0.67	7.2	32.4	1.442E-04
9	160	2	3/1	1.5	0.5	7.2	29.8	9.942E-05
10	180	2	3/1	1.5	0.5	7.2	38.6	1.288E-04
11	200	2	3/1	1.5	0.5	7.2	40.6	1.354E-04
12	220	2	3/1	1.5	0.5	7.2	42.8	1.428E-04

3. Kinetic Model for Fischer–Tropsch reaction

To obtain the proper rate equation, a reaction mechanism should be investigated. Although great efforts have been allotted to explain the FTS mechanism by Yang et al. [8] but there are still many describes about this matter. For the determination of kinetic models, 4 mechanisms were offered on the basis of various monomer formation (elementary reactions) and carbon chain distribution pathways. An elementary reactions set on sites for each model is summarized in Table 2.

According to derivation of each kinetic model, initially one of the elementary reaction (in some case two or three) steps was assumed as rate determination step and all other steps were considered at equilibrium. Then, all of the models obtained were fitted separately, against experimental data. In the interest of conciseness from journal, “*Kinetic study of Fischer–Tropsch process on titania-supported cobalt–manganese catalyst*” [6]. The set of elementary reaction and reaction rate on titania-supported cobalt–manganese catalyst were showed for the 29 kinetic models. Table 2. summarizes the final form of the different rate expressions for the 4 possible kinetic models considered using 10% Ru/Al₂O₃ Catalyst.

4. Results and Discussion

The estimation of the values of the kinetic parameters through best-fit technique was determined with linearization method by fitting the experimental data of the component partial pressure to the kinetic

equations (Eqs. (2)-(5)). The objective function was to minimize the sum of the square of residuals corresponding to differences between the experimental data and those calculated for the kinetic model. FT-3 showed the best fit to the experimental data. Table 3 shows the kinetic parameters calculated for all kinetic models and the mean absolute relative residual (MARR) between experimental and calculated consumption rate of CO as in Eq. (6):

$$MARR = \sum_{i=1}^{N_{exp}} \left| \frac{r_{exp} - r_{cal}}{r_{exp}} \right| \times \frac{1}{N_{exp}} \times 100 \quad \text{Eq.6}$$

where, N_{exp} is the number of data points included. Model (FT-3) shows the best fit to the experimental data. Fig. 2. Show the comparison between experimental data and calculated intrinsic reaction rates at different temperatures using Eq. (4).

Table 2: Elementary reactions set and Reaction rate expressions for the FTS [6].

Model	No.	Elementary reaction	Rate equation	Linearized form
FT-1	1	$H_2 + s \leftrightarrow H_2s$	RDS $-r_{CO} = \frac{k_p P_{CO} (P_{H_2} b_{H_2})^2}{(1 + b_{H_2} P_{H_2})^2}$	$\frac{P_{CO}^{1/2} P_{H_2}}{-r_{CO}^{1/2}} = \frac{1}{k_p^{1/2} b_{H_2}} + \frac{P_{H_2}}{k_p^{1/2}}$
	2	$CO + 2H_2s \leftrightarrow CH_3OHs$		
	3	$CH_3OHs \leftrightarrow CH_2S + H_2O$		
Eq.2				
FT-2	1	$H_2 + 2s \leftrightarrow 2Hs$	RDS $-r_{CO} = \frac{k_p P_{CO} (P_{H_2} b_{H_2})^2}{(1 + (b_{H_2} P_{H_2})^{1/2})^4}$	$\frac{P_{CO}^{1/4} P_{H_2}^{1/2}}{-r_{CO}^{1/4}} = \frac{1}{k_p^{1/4} b_{H_2}^{1/2}} + \frac{P_{H_2}^{1/2}}{k_p^{1/4}}$
	2	$CO + 4Hs \leftrightarrow CH_3OHs$		
	3	$CH_3OHs \leftrightarrow CH_2S + H_2O$		
Eq.3				
FT-3	1	$CO + s \leftrightarrow COs$	RDS $-r_{CO} = \frac{k_p b_{CO} P_{CO} (P_{H_2} P_{CO})^2}{(1 + 2(b_{CO} P_{CO})^{1/2})^2}$	$\frac{P_{H_2} P_{CO}^{1/2}}{-r_{CO}^{1/2}} = \frac{1}{k_p^{1/2} b_{CO}^{1/2}} + \frac{2P_{CO}^{1/2}}{k_p^{1/2}}$
	2	$COs + s \leftrightarrow Cs + Os$		
	3	$Cs + Os + 2H_2 \leftrightarrow CH_2S + H_2O$		
Eq.4				

Table 2: (con't) : Elementary reactions set and Reaction rate expressions for the FTS [6].

Model	No.	Elementary reaction	Rate equation	Linearized form
FT-4	1	$CO + s \leftrightarrow COs$	RDS $-r_{CO} = \frac{k_p b_{CO} P_{CO}}{(1 + 2(b_{CO} P_{CO})^{1/2})^2}$	$\frac{P_{CO}^{1/2}}{-r_{CO}^{1/2}} = \frac{1}{k_p^{1/2} b_{CO}^{1/2}} + \frac{2P_{CO}^{1/2}}{k_p^{1/2}}$
	2	$COs + s \leftrightarrow Cs + Os$		
	3	$Cs + Os + 2H_2 \leftrightarrow CH_2S + H_2O$		
Eq.5				

Table 3: Kinetic parameters at different temperatures.

Kinetic Parameters	Temp. (°C) 160	Temp. (°C) 180	Temp. (°C) 200	Temp. (°C) 220	MARR (%)
k_p	0.00117	0.00041	0.00041	0.00163	5.98
b_{H_2}	0.19637	0.30189	0.30445	0.19832	
k_p	0.01148	0.00117	0.00115	0.01557	9.09
b_{H_2}	0.44505	3.29742	3.38899	0.38961	
k_p	0.00163	0.00058	0.00058	0.00225	0.47
b_{CO}	0.12638	1.86769	2.09580	0.13319	
k_p	0.00013	0.00011	0.00011	0.00019	7.00
b_{CO}	2.47004	1.48173	1.46933	2.45067	

where k_p is the rate constant of reaction (mol/min·g_{cat}), b_{H_2} is the equilibrium constant of H₂ adsorption step (bar⁻¹), b_{CO} is the equilibrium constant of CO adsorption step (bar⁻¹)

From the analysis results, model FT-3 showed the best fit to the experimental data presented in this paper. This can be initially concluded that CO is adsorbed more strongly than H₂, and the rate-determining step of reactions is of step 3 [9]. At this stage, CO and H₂ can adsorb dissociatively on ruthenium catalyst depending on the catalyst characteristics and reaction conditions therefore the extent of dissociation of CO is founded varied. In this paper, CO effects to the set of elementary reaction was discovered for the reaction rate of FTS.

From the experimental data of this paper, the value of maximum CO conversion is of 42.8 % over ruthenium catalyst. However, 25.1% CO conversions over cobalt catalyst was reported in the Journal of

Industrial and Engineering Chemistry [6]. For this work, the modified ruthenium-based catalyst was studied. This catalyst was proved to give, high activity, high selectivity and can be very active at low conditions, which makes this catalyst durable and high stability [5]. However, at high conversions of CO over ruthenium catalyst, the partial pressures of both CO and H₂ were important for the determination of the rate equation [2]. Therefore, the best fit model to the experimental data is found as the FT-3 model instead of FT-4 model.

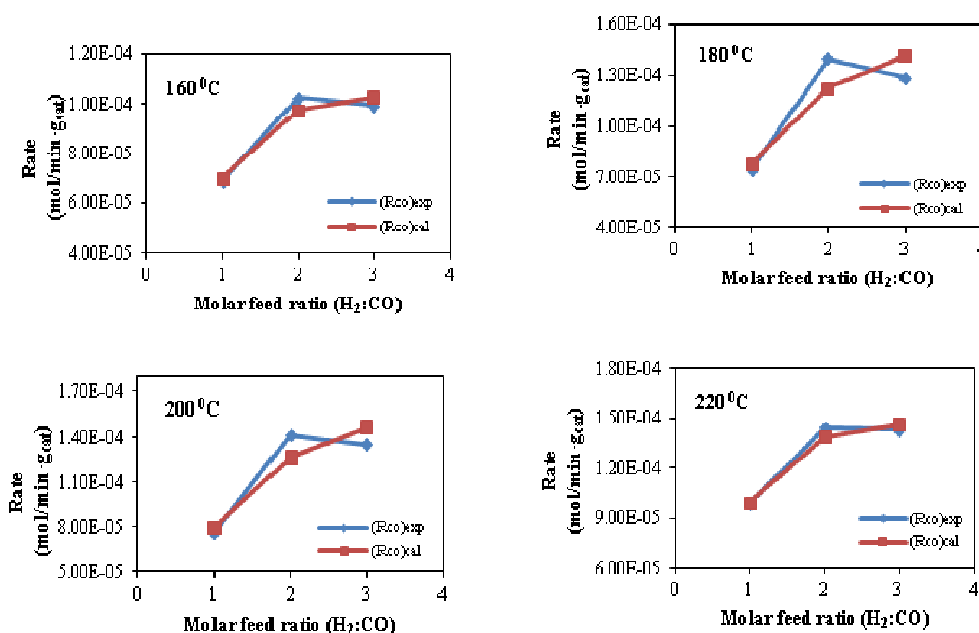


Fig. 2: Comparison between experimental and calculated reaction rates using Eq. (4). Reaction conditions: T = 160-220 °C, P = 2 bar, H₂/CO = 1/1-3/1.

5. Conclusions

Ruthenium supported alumina oxide catalyst was found as an effective catalyst for the hydrogenation of Carbon monoxide to light olefin. Sample of 10% Ru/Al₂O₃ catalyst was prepared by sol-gel method in order to be used for the kinetic model studies of FTS reaction. A number of kinetic equations based on LHHW for a case of the modified ruthenium-based catalyst, some of the kinetic models based on Journal of Industrial and Engineering Chemistry (2010), “Kinetic study of Fischer–Tropsch process on titania-supported cobalt–manganese catalyst” [6] from the elementary reactions set with the rate-determining step on the basis of a detailed set of possible reaction mechanism showed comparable and good agreement with the experimental data. The kinetic parameters estimated for this kinetic model (FT-3) presented reasonable confidence intervals. The rate constant of reaction (k_p) were 0.00163, 0.00058, 0.00058, 0.00225 mol/min·g_{cat}, the equilibrium constant of CO (b_{CO}) were 0.12638, 1.86769, 2.09580, 0.13319 bar⁻¹ for reaction temperature 160, 180, 200, 220 °C respectively and the MARR of this model was 0.47%.

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