

Study of CO Hydrogenation Reaction on Cobalt Titania Catalyst

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Summary: CO hydrogenation on the cobalt catalyst with Titania support (Co/TiO₂) without reduction condition and with a fixed-bed differential cylindrical reactor was kinetically studied. Internal and external mass transfer resistances of the porous catalyst are low and neglected in experimentations. Models have been developed using Langmuir-Hinshelwood-Hougen-Watson (LHHW) theory based on carbide and enolic mechanisms. Models have compared with experimental data according to Levenberg-Marquardt algorithm. The best model ($-R_{CO} = kP_{H_2}/(1 + aP_{CO})^2$) is selected because of good agreement with experimental data. Absorption step and hydrogen dissociation on surface of the catalyst is considered as a rate determination, simultaneously. Activation energy and enthalpy of the carbon monoxide consumption were obtained 82.3 kJ/mol and the 57.9 kJ/mol, respectively.

Introduction

Today, production of fuels and chemicals is mainly based on crude oil. Crude oil resources are of limited energy resources and this makes us look for a substituting way for producing fuel and chemicals. It is known that methane and coal resources are more than crude oil and converting them into synthesis gas and then producing fuel and chemicals is a convenient method to challenge with limited resources of crude oil. The process of converting the synthesis gas into liquid fuels (Fischer-tropsch synthesis) is a well-known technology. This method is useful for producing various hydro carbons such as light gases and solid waxes [1, 2]. This technology is very important from the political and economical viewpoints. Recently, many surveys have been done on CO hydrogenation to hydrocarbons over metallic catalysts. Some parameters such as temperature, pressure, gas flow rate and H₂/CO ratio in feed are very important in distribution of catalyst products. Production of hydrocarbons with low molecular weight hydrocarbons need to design and development of new catalysts in order to gain activity, selectivity, high temperature stability and long lifetime [3, 4].

Cobalt as a catalyst with high activity was generally used for production of aliphatic hydrocarbons with a carbon atom in the molecule. Low amounts of alcohols were produced on the cobalt surface catalyst in compare with other catalysts. Also, water-gas shift activity over cobalt catalyst is weak [5, 6].

In this paper, the kinetic model and Fischer-tropsch mechanism over cobalt catalyst with Titania support is studied using a fixed-bed differential cylindrical reactor.

Results and Discussion

Sum of Least Square Error method and non linear regression analysis based on the summarized value in Table-1 is used to determine the kinetic model parameters from experimental data in Table-2 with help of, Polymath software. The software uses Levenberg-Marquardt algorithm to estimate the constants of the model. Before inserting the equations in the software, Arrhenius and adsorption equation were substituted in kinetics models:

Table-1: Experimental data for consumption rate of CO in FT synthesis reaction using heterogeneous cobalt catalyst with Titania support (Co/TiO₂) [7].

Number	T(K)	P _{CO} (bar)	P _{H₂} (bar)	F ⁰ _{CO}	X _{CO}	-R _{CO} (mmol CO.g cat ⁻¹ .min ⁻¹)
1	473.15	3.8936	7.71804	0.0013032	0.0266	0.2378708
2	473.15	5.8566	7.62	0.019547665	0.0239	0.3205891
3	473.15	2.9076	7.75514	0.00097738	0.0308	0.206572
4	473.15	3.9452	3.85478	0.013032	0.0137	0.1225124
5	473.15	2.8686	7.65179	0.00097738	0.0438	0.2937615
6	473.15	1.9298	7.81397	0.0006516	0.0351	0.1569411
7	473.15	5.8602	7.62953	0.019547665	0.0233	0.3125408
8	453.15	3.9472	7.86008	0.0136069	0.0132	0.123251
9	465.15	3.9172	7.78058	0.0132559	0.0207	0.1882937
10	473.15	3.8924	7.71486	0.013032	0.0269	0.2405536
11	486.15	3.8148	7.50922	0.0126833	0.0463	0.4029666
12	498.15	3.6896	7.17744	0.0123778	0.0776	0.6591131
13	511.15	3.294	6.1291	0.012063	0.1765	1.461015

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Table-2: Elementary reactions for Fischer-tropsch synthesis.

Model	Number	Elementary reaction
FT-I	1	$\text{CO} + \text{s} \leftrightarrow \text{Cos}$
	2	$\text{Cos} + \text{s} \leftrightarrow \text{Cs} + \text{Os}$
	3	$\text{Cs} + \text{H}_2 \leftrightarrow \text{CH}_2\text{s}$
	4	$\text{Os} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{s}$
	5	$\text{H}_2 + 2\text{s} \leftrightarrow 2\text{Hs}$
FT-II	1	$\text{CO} + \text{s} \leftrightarrow \text{COS}$
	2	$\text{H}_2 + 2\text{s} \leftrightarrow 2\text{Hs}$
	3	$\text{COS} + \text{Hs} \leftrightarrow \text{HCOS} + \text{s}$
	4	$\text{HCOS} + \text{Hs} \leftrightarrow \text{CS} + \text{H}_2\text{O} + \text{s}$
	5	$\text{CS} + \text{Hs} \leftrightarrow \text{CHS} + \text{s}$
	6	$\text{CHS} + \text{Hs} \leftrightarrow \text{CH}_2\text{S} + \text{s}$
	7	$\text{OS} + \text{Hs} \leftrightarrow \text{HOS} + \text{s}$
	8	$\text{HOS} + \text{Hs} \leftrightarrow \text{H}_2\text{O} + 2\text{s}$

Equation (1) and (2) were substituted for K and α , respectively.

$$k = K_0 \exp\left(-\frac{E}{RT}\right) \quad (1)$$

$$a = \alpha_0 \exp\left(\frac{\Delta H}{RT}\right) \quad (2)$$

According to statistical obtained results by inserting the data and models in polymath, the best model can be selected now.

FT-I- model is ignored due to its negative constant. FT-I-2 and FT-II-1 models are ignored because the higher values of the confidence interval parameters in compare with its absolute values. FT-I-3 model is ignored because the calculations of partial regression related to kinetic equations exceed the maximum number of repeats or trial and errors. FT-II-2, FT-II-3, FT-II-4 models are ignored because calculations of partial regression related to kinetic equations exceed the maximum number of repeats or trial and errors and confidence interval parameter is high when compared with its absolute values.

Only FT-I-5 model remained. This model satisfies all of the mentioned rules. Diagram (1) shows the comparison between experimental results and predicted values of the FT-I-5 model equation (Fig. 1).

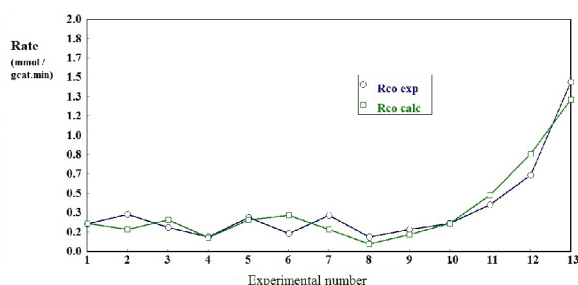


Fig. 1: Comparison of experimental data with predicted results of the FT-I-5.

So carbide mechanism is the CO hydrogenation mechanism over Co/TiO₂ catalyst and also it is the absorption rate unit and hydrogen decomposition controller unit over the catalyst. Kinetic parameters for the best model have been calculated and summarized in Table-3.

Table-3: Phrases of observed reaction rate for Fischer-Tropsch synthesis $-R_{CO}$ (mmol_{CO}.g_{cat}⁻¹.min⁻¹).

Model	Kinetic equation
FT-I-1	$-R_{CO} = \frac{KP_{CO}}{1+aP_{CO}+bP_{CO}^{0.5}}$
FT-I-2	$-R_{CO} = \frac{KP_{CO}}{(1+aP_{CO}+bP_{CO}^{0.5})^2}$
FT-I-3	$-R_{CO} = \frac{KP_{CO}^{0.5}P_{H_2}}{1+aP_{CO}+bP_{CO}^{0.5}}$
FT-I-5	$-R_{CO} = \frac{KP_{H_2}}{(1+aP_{CO})^2}$
FT-II-1	$-R_{CO} = \frac{KP_{CO}}{1+aP_{CO}+bP_{H_2}^{0.5}}$
FT-II-2	$-R_{CO} = \frac{KP_{H_2}}{(1+aP_{CO}+bP_{H_2}^{0.5})^2}$
FT-II-3	$-R_{CO} = \frac{KP_{CO}P_{H_2}^{0.5}}{(1+aP_{CO}+bP_{H_2}^{0.5})^2}$
FT-II-4	$-R_{CO} = \frac{KP_{CO}P_{H_2}}{(1+aP_{CO}+bP_{CO}P_{H_2}^{0.5}+cP_{H_2}^{0.5})^2}$

Based on statistical information of the software, it is possible to find the best predicted model which was the FT-I-5 that has the best correlation with empirical data. Calculated kinetic parameters for the best selected model are shown in Table-4.

Table-4: Obtained values of the parameters using the software for the FT-I-5 model.

Parameter	Dimension	Estimate
K_0	mmol.g Cat ⁻¹ .min ⁻¹ .bar ⁻¹	$6.518 \times 10^{+07}$
E_0	J/mol	$8.232 \times 10^{+04}$
a_0	bar ⁻¹	3.114×10^{-08}
ΔH_a	J/mol	$-5.799 \times 10^{+04}$

Experimental

In order to measure the velocity in a fixed bed reactor (FBR), 1.5 g powder Catalyst diluted with 0.00075 g SiC for distributing temperature uniformly. The experiment carried out in total pressure of 20 bar and temperature of 453-511 K. Weight hourly space velocity (WHSV) is about 3000-5000 h⁻¹ and the volume of 1.5 g catalyst is equal to 1.835 cm³. So volumetric flow rate of feed gas is:

$$V_0 = 1.538 \times 5000 = 7915 \text{ cm}^3 \text{ gas/h}$$

Molar flow rate of carbon monoxide in feed is calculated from:

$$F_{CO}^0 = \frac{v_0 P_{CO}^0}{RT}$$

where R is the gas molar constant which is equal to $83.14 \text{ cm}^3 \text{ bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. In order to obtain the consumption rate of monoxide, differential reactor formulation is used:

$$\frac{W}{F_{CO}^0} = \frac{X_{CO}}{-r_{CO}}$$

$$-r_{CO} = \frac{X_{CO} F_{CO}^0}{W}$$

Totally, 13 experimental data series were collected (Table-1) for kinetic study [7]. After some experiments, the catalyst is regenerated and then the experiments are continued. In this reaction, temperature is very significant due to negative enthalpy of reaction and consequently excessive heat production. This heat causes destruction and clogging of the catalyst and it will be selective to the lighter products like methane.

Kinetic Equations

Derivation of Kinetic Equations

In order to derive the kinetic equations of intrinsic rate where to be adjusted with Table-1 data, we should know that internal and external porous mass transfer resistances are not controller and only rate of surface reaction in reactors is the controller. Internal porous mass transfer resistance can not be the controller because the catalyst particles are too small (mesh 100–200) and activation energy is high. Hence, rate of reaction is low in compare with inside porous mass transfer. Mass transfer coefficient is a high value which is estimated as below:

$$k_{co,g} = D_{co,g}/X \quad \text{Gas diffusion coefficient of CO} \\ (D_{co,g} = 370 \text{ cm}^2/\text{Sec}) [8].$$

$$k_{co,g} = 37000 \text{ cm/Sec} \quad \text{Gas thickness film, } X = 0.01 \text{ (cm)} \\ [9].$$

The results show that external porous mass transfer resistance or gas film is not controller. We used Longmuir-Hinshelwood-Hougen-Watson theory to obtain kinetic models. According to this theory, suitable kinetic model is determined which is useful for elementary reaction and testing the different mechanism.

Two key assumption of this theory is:

- 1) Attraction heats are constant.
 - 2) Inherent reaction rates are proportional to surface covers of reactors
- To simplify the kinetic models, following assumptions are taken into consideration [10, 11]:
- 1) Presence of an irreversible controlling stage, although all of the other stages are considered to be near the thermodynamic equilibrium.
 - 2) Concentrations of all of the mediums on the catalyst surface are in steady state.
 - 3) Catalytic locations are steady and distributed homogenously.
 - 4) Thorough the whole temperature and pressure region, rate controller stage and the most abundant surface medium are remained unchanged.
 - 5) Elementary attraction of hydrogen and carbon monoxide in pseudo-equilibrium state are within concentrations of gaseous phase.
 - 6) Water is removed after the CO decomposition irreversibly.

Considering the proceeding assumptions, there are 8 possible kinetic models (Table-3). These models are shown in Table-2 based on predicted elementary stages of the fischer-tropsch reactions and carbide mechanism (FT- 1) and enolic mechanism (FT-2). codes of the model is referred to elementary reactions and the elementary reaction which is not at equilibrium (rate controller stage).

Statistical Criteria for Non-Linear Regression using Polymath Software in Order to Find the Best Model

There are some conditions to find the best model [12]:

- 1- Obtained constants must be positive.
- 2- Optimal model or equation is the one which gives the highest R_2
- 3- Coefficients of the equation must obey Ahrenius and vanthouff rules.
- 4- The equation must have the ability to predict the behavior of a differential reactor.

A good equation can satisfy all of the mentioned rules.

Different Statistical indices in Polymath software can be used to determine the quality of regression models and compare them.

Development of Kinetic Equations

To obtain the rate equations mentioned in Table-3, we use the mechanisms of Table-2 and the

assumptions of section 1-3. For example derivation of the rate equation for FT- I -1 is explained here. To do this, the first stage is considered to be the rate limiting stage and the reaction is irreversible.

If the first stage is the rate controller stage, the rate equation is:

$$-R_{CO} = k_1 P_{CO} \theta_s \text{ (mmol}_{CO}\text{.grCat}^{-1}\text{.min}^{-1}) \quad (1)$$

where $(-R_{FT-I-1})$ is the rate of CO invisibility and k_1 is the rate coefficient of forwarding reaction for the attraction of CO in gaseous phase and θ_s is the empty spaces ratio. Reactions are parallel so the rate of reaction is identical in various stages.

To determine the empty space ratio considering the assumptions, we have:

$$\theta_s + \theta_{CO} + \theta_C + \theta_O = 1 \quad (2)$$

If the next stages are assumed to be near the thermodynamic equilibrium, available surface ratios can be determined using partial pressures of reactors.

$$K_1 = \frac{k_1}{k_{-1}} = \frac{\theta_{CO}}{P_{CO} \theta_s} \Rightarrow \theta_{CO} = K_1 P_{CO} \theta_s \quad (3)$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{\theta_O \theta_C}{\theta_{CO} \theta_s} \Rightarrow \theta_O = \frac{K_2 \theta_{CO} \theta_s}{\theta_C} \quad (4)$$

In steady state, consumption rate of carbon in stage 3 is equal to elimination rate of oxygen by the stage 4 so:

$$k_3 \theta_s P_{H_2} = k_4 \theta_O P_{H_2} \Rightarrow \theta_C = \frac{k_4}{k_3} \theta_O \quad (5)$$

Substituting equation 4 and then 3 in equation 5 gives:

$$\begin{aligned} \theta_C &= \frac{k_4}{k_3} \theta_O = \frac{k_4}{k_3} \left(\frac{K_2 \theta_{CO} \theta_s}{\theta_s} \right) \\ \theta_C^2 &= \frac{K_4 K_2}{k_3} \theta_{CO} \theta_s = \frac{k_4 K_2}{k_3} (K_1 P_{CO} \theta_s) \theta_s \Rightarrow \\ \theta_C &= \left(\frac{k_4 K_1 K_2}{k_3} \right)^{0.5} P_{CO}^{0.5} \theta_s \end{aligned} \quad (6)$$

And replacing equation 6 into equation 5 gives:

$$\begin{aligned} \theta_C &= \frac{k_4}{k_3} \theta_O \Rightarrow \\ \theta_O &= \frac{k_3}{k_4} \theta_C = \frac{k_3}{k_4} \left(\left(\frac{k_4 K_1 K_2}{k_3} \right)^{0.5} P_{CO}^{0.5} \theta_s \right) \Rightarrow \\ \theta_O &= \left(\frac{k_3 K_1 K_2}{k_4} \right)^{0.5} P_{CO}^{0.5} \theta_s \end{aligned} \quad (7)$$

Putting equations 3, 4, and 7 into site balance equation:

$$\begin{aligned} \theta_s + \theta_{CO} + \theta_C + \theta_O &= 1 \Rightarrow \theta_s + K_1 P_{CO} \theta_s + \\ \frac{k_4 K_2}{k_3} (K_1 P_{CO} \theta_s) \theta_s &+ \left(\frac{k_3 K_1 K_2}{k_4} \right)^{0.5} P_{CO}^{0.5} \theta_s = 1 \end{aligned} \quad (8)$$

$$\theta_s = \frac{1}{1 + K_1 P_{CO} + \frac{k_4 K_2}{k_3} (K_1 P_{CO} \theta_s) + \left(\frac{k_3 K_1 K_2}{k_4} \right)^{0.5} P_{CO}^{0.5}} \quad (9)$$

And finally the rate equation will be:

$$\begin{aligned} -R_{CO} &= k_1 P_{CO} \theta_s = \\ \frac{k P_{CO}}{1 + K_1 P_{CO} + \frac{k_4 K_2}{k_3} P_{CO} + \left(\frac{k_3 K_1 K_2}{k_4} \right)^{0.5} P_{CO}^{0.5}} \end{aligned} \quad (10)$$

$$-R_{CO} = \frac{K P_{CO}}{1 + a P_{CO} + b P_{CO}^{0.5}} \quad (11)$$

where:

$$\begin{aligned} K &= k_1 \\ a &= \left(K_1 + \frac{k_4 K_1 K_2}{k_3} \right), b = \left(\frac{k_3 K_1 K_2}{k_4} \right)^{0.5} \end{aligned}$$

Conclusion

Intrinsic kinetic CO hydrogenation over the cobalt titania catalyst was investigated and found that, absorption step and hydrogen dissociation on surface of the catalyst is considered as a rate determination, simultaneously. Also, based on experimental data, the internal and external porous mass transfer resistances are not controllers regard to the reaction rate. The experimental data was investigated with the 8 models which were obtained

from carbide and enolic mechanisms with the help of Polymath software by non-linear regression. The results showed that the most probable kinetic equation is $-R_{CO} = kP_{H_2} / (1 + aP_{CO})^2$. Activation energy and enthalpy of the carbon monoxide consumption was obtained 82.3 kJ/mol and the 57.9 kJ/mol, respectively.

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