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Hydrogenation of CO on cobalt catalyst in Fischer–Tropsch Synthesis

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Abstract

The kinetic experiments of Fischer–Tropsch synthesis (FTS) over an industrial Co/K catalyst are carried out in a micro-fixed-bed reactor under the conditions as follows: temperature of 483–513 K, pressure of 8 bar, H_2/CO feed ratio of 1–3, and space velocity of 2700–5200 h^{-1}. The optimal amount of catalyst containing 15wt.%Co/10wt.%K/Al_2O_3 was prepared using impregnation procedure. The combined enol/carbide mechanism as the rate-controlling step gives the most plausible kinetic model among the nine different models tested. The activation energies for optimal kinetic model and power law equation were obtained 111.5 kJ/mol and 100 kJ/mol, respectively.

Key words: Fischer–Tropsch Synthesis, Fixed-bed Reactor, Co/K/Al_2O_3 Catalyst, Kinetic Modeling

Introduction

The process of converting the synthesis gas into liquid fuels (FTS) is a well-known technology. This method is a promising, developing option for environmentally sound

production of chemicals and fuels from coal and natural gas. In view of large coal and natural gas reserves and dwindling petroleum reserves worldwide, it is projected to play an ever increasing role in the coming decades [1, 2].

Cobalt-based catalysts are the preferred catalysts for hydrocarbon synthesis because of their high FTS activity, selectivity for long-chain paraffins, and low activity for the water–gas shift reaction [3]. The kinetics of FTS on cobalt catalysts has received significant attention; in fact, several previous studies [4-8] report kinetic data and rate expressions. Reaction orders for H_2 and CO are in the range 0.5 to 2 and -1.0 to $+0.65$, respectively; activation energies from these studies cover a range 98–103 kJ/mol [8].

The mechanistic kinetic rate expressions for cobalt catalysts are based on the formation of the monomer species as the rate-determining step in the consumption of synthesis gas. Many kinetic equations have been proposed in the literature for various cobalt catalysts, and these have been obtained either empirically (using a power-law rate equation) or to fit a proposed mechanism [6-9].

Our objective is to develop intrinsic rate expressions for the CO conversion to Fischer–Tropsch products over an impregnation cobalt catalyst on the basis of realistic mechanisms. The kinetics of FT reaction was studied and the rate expressions were tested against experimental data that was obtained on the selected catalysts. A model was successfully devised and the kinetics parameters were determined. Also, a power law kinetic equation for the carbon monoxide rate was obtained.

EXPRIMENTAL

Catalyst preparation

The optimal amount of 15wt.%Co/10wt.%K/Al$_2$O$_3$ was prepared by impregnation with an aqueous solutions of Co(NO$_3$)$_2$.6H$_2$O and KNO$_3$ to incipient wetness of γ-Al$_2$O$_3$, which had been previously calcined at 400ºC for 8 h to remove the surface adsorbed impurities (BET surface area of 217 m^2/g, pore volume of 0.7 cm^3/g). The impregnated sample was dried at 110 C for 2 h and calcined in air at 400ºC for 8 h (heating rate of 10 C between 110 and 400ºC); the calcined catalyst was reduced in situ (in the fixed bed reactor described below) in pure H$_2$ at 400ºC for 16 h (heating rate of 10ºC between 25 and 400ºC).

Fixed bed reactor system

FTS was carried out in a fixed-bed micro-reactor made of stainless steel with an inner diameter of 12 mm. Three mass flow controllers (Brooks, Model, 5850E) were used to adjust automatically flow rate of the inlet gases comprising CO, H$_2$ and N$_2$ (purity of 99.999%). Mixture of CO, H$_2$ and N$_2$ was subsequently introduced into the reactor, which was placed inside a tubular furnace (Atbin, Model ATU 150-15). Temperature of the reaction was controlled by a thermocouple inserted into the catalytic bed and visually monitored by a computer. The catalyst was in situ pre-reduced at atmospheric pressure under H$_2$–N$_2$ flow (N$_2$/H$_2$ = 1, flow rate of each gas = 30 ml/min), at 400$^°$C for 16 h. In each test, 1.0 g catalyst was loaded and the reactor operated about 12 h to ensure steady state operations were attained.

Catalytic evaluation

Experiments were conducted with mixtures of H$_2$, CO and nitrogen in a temperature range from 210 to 240$^°$C, H$_2$/CO feed ratios of 1/1-3/1 (mol/mol) at the pressure of 8 bar. The

76 arrangements of the parameters and the related levels are shown in Table 1. In all of the

77 experiments, the space velocities were between 2700 and 5200 h^{-1}.

78   To avoid the effect of deactivation, fresh catalysts were loaded in each experiment. To

79 achieve the isothermal conditions in a catalytic bed, the catalyst was diluted with an inert

80 material (quartz). Axial temperature distribution was ensured using Mear's [10, 11]criterion ,

81 that is with $L/d_p > 50$. Also, plug-flow was assumed for the gaseous feed. The experimental

82 reaction rate was determined as follows:

$$Rate\ of\ conversion\ of\ \mathrm{CO} = \frac{(fractional\ conversion) \times (input\ flow\ rate\ of\ \mathrm{CO})}{weight\ of\ the\ catalyst} \tag{1}$$

83

Theory

Kinetic expressions

86   In order to derive rate equations to be adjusted with the data in Table 1, we used LHHW

87 theory to obtain kinetic models. According to this theory, a reaction mechanism should be

88 adopted. Two key assumption of this theory is: (1) Attraction heats are constant, (2) Inherent

89 reaction rates are proportional to surface covers of reactors. To simplify the kinetic models,

90 following assumptions are taken into consideration [12, 13]: (1) Presence of an irreversible

91 controlling stage, although all of the other stages are considered to be near the

92 thermodynamic equilibrium. (2) Concentrations of all of the mediums on the catalyst surface

93 are in steady state. (3) Catalytic locations are steady and distributed homogenously. (4)

94 Thorough the whole temperature and pressure region, rate controller stage and the most

95 abundant surface medium are remained unchanged. (5) Elementary attraction of hydrogen

96 and carbon monoxide in pseudo-equilibrium state are within concentrations of gaseous phase.

97 (6) Water is removed after the CO decomposition irreversibly.

98

99   **Statistical Criteria using Polymath Software**

100   Least square method and non-linear regression analysis based on the summarized values in

101   Table 1 is used to determine the power-law equation parameters and kinetic model

102   parameters from experimental data provided in Table 2 using polymath® software. The

103   software uses Levenberg–Marquardt algorithm to estimate the constants of the model. There

104   are some conditions to find the best model[14]: (1) Obtained constants must be positive. (2)

105   Optimal model or equation is the one which gives the reliable R^2. (3) Coefficients of the

106   equation must obey Arrhenius and Vanthouff rules. (4) The equation must have the ability to

107   predict the behavior of a differential reactor. A good equation can satisfy all of the mentioned

108   rules. Different Statistical indices in Polymath software can be used to determine the quality

109   of regression models and compare them.

110

111   # RESULTS AND DISCUSSION

112   **Development of Kinetic Equations**

113   Considering the proceeding assumptions, three mechanisms were offered on the basis of

114   various monomer formation (elementary reactions) and carbon chain distribution pathways.

115   An elementary reactions set on sites for each model is summarized in Table 2.

116   To derive each kinetic model, initially one of the elementary reaction (in some case two or

117   three) steps was assumed as rate-determining step and all other steps were considered at

118   equilibrium. Then, all of the models obtained were fitted separately against the experimental

119   data. In the interest of conciseness, only certain selected kinetic models are reported in the

120   Table 3.

121   For example derivation of the rate equation for FT-I4 is explained here. To do this, the

122   first step is considered to be the rate limiting stage and the reaction is irreversible. The

123   remaining steps can be considered to be quick and at equilibrium.

124   The rate expression of the rate-determining step for FT-I4 model where surface carbon

125   reacts with adsorbed dissociated hydrogen as the rate limiting step, can be expressed

126   irreversible adsorption as follows:

$$-r_{CO} = k_4 \theta_C \theta_H = k_6 \theta_O \theta_H \tag{2}$$

127   where $-r_{CO}$ is the rate of disappearance of CO, k_4 and k_6 are the forward rate constant for

128   elementary reaction of numbers of 4 and 6 respectively, and θ_i is the surface fraction

129   occupied with adsorbed species i. The fraction of vacant sites, θ_S, can be calculated from the

130   following balance equation:

$$\theta_S + \theta_{CO} + \theta_H + \theta_{H_2CO} + \theta_{CH_2} + \theta_O + \theta_{OH} + \theta_{H_2O} = 1 \tag{3}$$

131   In this case, it is assumed that adsorbed dissociated hydrogen and surface carbon occupies

132   a significant fraction of the total numbers of sites. Other species were assumed to be

133   negligible in the stoichiometric balance:

$$\theta_S + \theta_C + \theta_H = 1 \tag{4}$$

134   The surface coverage of carbon monoxide and adsorbed dissociated hydrogen are

135   calculated from the site balance, and the preceding reaction steps which are at quasi-

136   equilibrium:

$$CO + S \xleftrightarrow{k_1} COs \tag{5}$$

$$k_1 P_{CO} \theta_S - k_{1,des} \theta_{CO} = 0 \tag{6}$$

$$\theta_{CO} = K_1 P_{CO} \theta_S \tag{7}$$

137     $K_1 = \dfrac{k_1}{k_{1,des}}$

138   where K_1 is the equilibrium constant of CO adsorption step. Thus, if the next stages are

139   assumed to be near the thermodynamic equilibrium, available surface ratios can be

140   determined using partial pressures of reactors.

$$\theta_{\text{H}} = K_3^{1/2} P_{\text{H}_2}^{1/2} \theta_{\text{S}} \tag{8}$$

$$\theta_{\text{O}} = \frac{k_4}{k_6} \theta_{\text{C}} \tag{9}$$

$$\theta_{\text{C}} = \frac{K_2 \theta_{\text{CO}} \theta_{\text{S}}}{\theta_{\text{O}}} \tag{10}$$

141 Substituting equation (7) and then (9) in equation (10) gives:

$$\theta_{\text{C}} = \frac{K_2 \theta_{\text{CO}} \theta_{\text{S}}}{\theta_{\text{O}}} = \left(\frac{K_1 K_2 k_6}{k_4}\right)^{1/2} P_{\text{CO}}^{1/2} \theta_{\text{S}} \tag{11}$$

142 Substituting Equation (8) and (11) into Equation (4), the ratio of free active site can be

143 expressed as:

$$\theta_{\text{S}} = \frac{1}{1 + \left(\dfrac{K_1 K_2 k_6}{k_4}\right)^{1/2} P_{\text{CO}}^{1/2} + K_3^{1/2} P_{\text{H}_2}^{1/2}} \tag{12}$$

144 Substitution of the fraction of vacant sites in Equation (2), the final rate expression is

145 obtained as:

$$-r_{\text{CO}} = \frac{(k_4 k_6 K_1 K_2 K_3)^{1/2} P_{\text{CO}}^{1/2} P_{\text{H}_2}}{\left(1 + \left(\dfrac{K_1 K_2 k_6}{k_4}\right)^{1/2} P_{\text{CO}}^{1/2} + K_3^{1/2} P_{\text{H}_2}^{1/2}\right)^2} = \frac{k P_{\text{CO}}^{1/2} P_{\text{H}_2}}{\left(1 + a P_{\text{CO}}^{1/2} + b P_{\text{H}_2}^{1/2}\right)^2} \tag{13}$$

146 Table 3 summarizes the final form of the different rate expressions for the 9 possible kinetic

147 models considered, whereas Table 4 shows the kinetic and adsorption parameters for the

148 several kinetic models. It can be seen that the pressure dependency of CO and H2 in the

149 numerator ranges from 1/2 to 1, and 1/2 to 2, respectively. The denominator is quadratic in

150 case of a dual site elementary reaction, in contrast to a single site rate-determining step. The

151 denominator consists of the individual contributions of significantly plentiful species on the

152 catalyst surface.

153 Also, power law kinetic equation for the carbon monoxide rate was considered for

154 comparison with experimental data. Yang et al. [5] obtained empirical rate expressions for

155   supported cobalt catalysts using a fixed-bed reactor via regression of a power-law equation of

156   the general form:

$$-r_{CO} = k_0\, exp(\frac{-E}{RT})P_{CO}^{m}\, P_{H_2}^{n} \tag{14}$$

157   where P_{CO} the partial pressure of carbon monoxide, k_0 the reaction rate constant, E the

158   activation energy of CO consumption, m the reaction order for CO, and n the reaction order

159   for H_2.

160

161   **Model parameters and model discrimination**

162   CO consumption rate was obtained from the data in Table 1 by using the differential

163   method of data analysis. The kinetic data presented in Table 1 for CO conversion were used

164   for testing the power law equation and nine models listed in Table 3. Before inserting the

165   equations in the polymath® software, Arrhenius and adsorption equations were substituted in

166   kinetics models: Equation (15) and (16) were substituted for k and a, respectively.

$$k = k_0\, exp(\frac{-E}{RT}) \tag{15}$$

$$a = a_0\, exp(\frac{\Delta H}{RT}) \tag{16}$$

167   According to the statistical results obtained by inserting the data and models, the best

168   model can be selected. Based on the kinetic data, the only plausible mechanism was found to

169   be the FT-III model with combined enol/carbide mechanism as the rate-controlling step.

170   Based on statistical information, the best model is found to be FT-III2 that has the less

171   deviation from experimental data. Therefore there are best fitted by a LHHW approach rate

172   form $-r_{CO} = \dfrac{k_2 K_1 P_{CO} P_{H_2}}{1 + K_1 P_{CO}}$, where activation energy is obtained to be 111.5 kJ/mol.

173   The other models are ignored because: (1) calculations of partial regression related to

174   kinetic equation exceed the maximum number of iterations or trial and errors, (2) confidence

175   interval parameter is high when compared with its absolute values, (3) their constans are

176   negative, (4) do not give the responsible R^2.

177   The data of this study are fitted fairly well by a power law equation in the form

178   of $-r_{CO} = 2.1 \times 10^8 \, exp\,(\frac{-1 \times 10^5}{RT}) P_{CO}^{-0.45} \, P_{H_2}^{0.85}$. The R^2 value has been obtained 0.99, which shows

179   power law equation is well matched with the experimental data. Table 5 shows the kinetic

180   parameters calculated for the kinetic FT-IV2 model and power law equation.

181

182   **Conclusion**

183   The optimal amount of catalyst containing 15wt.%Co/10wt.%K/Al$_2$O$_3$ was prepared using

184   impregnation procedure. Experiments for the kinetics of the hydrocarbon formation over an

185   cobalt catalyst were obtained over a wide range of industrially relevant reaction conditions.

186   The data of this study are best fitted by the simple LHHW approach rate of the form

187     $-r_{CO} = \frac{k\,P_{CO}P_{H2}}{1 + aP_{CO}}$. The values of kinetic constants were obtained and the activation energy was

188   found to be 111.5 kJ/mol for the best model. The data are fitted fairly well by a power law

189   equation in the form of $-r_{CO} = 2.1 \times 10^8 \, exp\,(\frac{-1 \times 10^5}{RT}) P_{CO}^{-0.45} \, P_{H_2}^{0.85}$

190

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208

209   Tables

210   *Table 1*. Summary of experimental conditions and results at P = 8 bar and T = 210–240ºC.

Number of data	Temperature (K)	X_{CO} (%)	P_{H_2} (bar)	P_{CO} (bar)	F/W (mol/gr cat. h)	$-r_{CO}$ (mmol/gr cat. h)
1	483.15	2.6	2.81	1.95	0.172	4.471
2	483.15	3.2	2.35	2.90	0.173	5.55
3	483.15	3.6	3.55	1.93	0.154	5.528
4	483.15	4.8	2.25	3.81	0.139	6.659
5	493.15	3.2	3.05	1.94	0.289	9.254
6	493.15	2.4	1.41	1.95	0.195	4.687
7	493.15	5.3	3.33	2.84	0.287	15.20
8	493.15	2.8	2.59	0.97	0.143	4.002
9	503.15	5.1	1.81	1.90	0.186	9.505
10	503.15	7.9	4.73	1.84	0.355	28.01
11	503.15	5.5	3.61	1.42	0.272	14.94
12	503.15	6.7	2.23	2.80	0.286	19.16
13	513.15	8.8	2.88	3.65	0.698	61.42
14	513.15	7.6	3.63	2.31	0.650	49.42
15	513.15	7.1	3.41	1.86	0.520	36.92
16	513.15	8.6	4.58	2.29	0.712	61.22

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212

213   *Table 2*. Elementary reactions mechanism set for FTS.

Model	Number	Elementary Reaction
	1	CO + s ↔ COs
	2	COs + s ↔ Cs + Os
FT-I	3	H_2 + 2s ↔ 2Hs
	4	Cs + Hs ↔ CHs + s
	5	CHs + Hs ↔ CH_2s + s

	6	$Os + Hs \rightarrow HOs + s$
	7	$HOs + Hs \rightarrow H_2Os + s$
	8	$H_2O + s \rightarrow H_2Os$
	1	$CO + s \leftrightarrow Cos$
	2	$H_2 + 2s \leftrightarrow 2Hs$
	3	$COs + Hs \leftrightarrow HCOs + s$
FT-II	4	$HCOs + Hs \leftrightarrow Cs + H_2Os$
	5	$Cs + Hs \leftrightarrow CHs + s$
	6	$CHs + Hs \leftrightarrow CH_2s + s$
	7	$H_2O + s \rightarrow H_2Os$
	1	$CO + s \leftrightarrow COs$
	2	$COs + H_2 \leftrightarrow H_2COs$
	3	$H_2COs + H_2 \leftrightarrow CH_2s + H_2O$
FT-III	4	$COs + s \leftrightarrow Cs + Os$
	5	$Cs + Hs \leftrightarrow CHs + s$
	6	$CHs + Hs \leftrightarrow CH_2s + s$
	7	$Os + H_2 \rightarrow H_2Os$
	8	$H_2O + s \rightarrow H_2Os$

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216

217 *Table 3*. Reaction rate expressions for the FTS, r_{FT} (mmol g_{cat}^{-1} h^{-1})

Model of rate controlling	Kinetic equation
FT-I1	$k\,P_{CO}/(1+aP_{CO}^{1/2}+bP_{H_2}^{1/2})$
FT-I3	$k\,P_{H_2}/(1+aP_{CO}^{1/2}+bP_{H_2}^{1/2})^2$
FT-I4	$k\,P_{CO}^{1/2}P_{H_2}^{1/2}/(1+aP_{CO}^{1/2}+bP_{H_2}^{1/2})^2$
FT-I5	$k\,P_{CO}^{1/2}P_{H_2}^{3/4}/(1+aP_{CO}^{1/2}P_{H_2}^{-1/4}+bP_{H_2}^{1/2})^2$
FT-II1	$k\,P_{CO}/(1+aP_{CO}^{1/2})$
FT-II3	$k\,P_{CO}^{1/2}P_{H_2}/(1+aP_{CO}^{1/2})$
FT-III1	$k\,P_{CO}/(1+aP_{CO})$
FT-III2	$k\,P_{CO}P_{H_2}/(1+aP_{CO})$
FT-III3	$k\,P_{CO}P_{H_2}^2/(1+aP_{CO})$

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238
239 *Table 4*. Parameters for the FT kinetic models

Model of rate controlling	k (x) (mmol g^{-1} h^{-1} bar^x)	a(x) (bar^x)	b (x) (bar^x)
FT-I1	k_1 (-1)	$(k_6K_1K_2/k_4)^{1/2}$ (-1/2)	$K_3^{1/4}$ **(-1/2)**
FT-I3	k_3 (-1)	$(k_6K_1K_2/k_4)^{1/2}$ (-1/2)	$K_3^{1/4}$ **(-1/2)**

FT-I4	$(k_4 k_6 K_1 K_2 K_3)^{1/2}$ (-1)	$(k_4 K_1 K_2 / k_6)^{1/2}$ (-1)	$K_3^{1/4}$ **(-1/2)**
FT-I5	$(k_3 k_6 K_1 K_2 K_4)^{1/2}\ K_3^{1/4}$ (-5/4)	$(k_6 K_1 K_2 / k_5 K_4)^{1/2}\ K_3^{-1/4}$ (-1/4)	$K_3^{1/4}$ **(-1/2)**
FT-II1	k_1 (-1)	$(K_1 K_2 K_4 / k_3)^{1/2}$ (-1/2)	
FT-II3	$(k_3 k_4 K_1 K_2)^{1/2}$ (-3/2)	$(K_1 K_2 K_4 / k_3)^{1/2}$ (-1/2)	
FT-III1	k_1 (-1)	K_1 (-1)	
FT-III2	$k_2 K_1$ (-2)	K_1 (-1)	
FT-III3	$k_2 K_1 K_2$ (-3)	K_1 (-1)	

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244 *Table 5*. Values of the kinetic parameters, activation energy and heat of adsorption of CO with various
245 equations.

Equation	k_0 (mol.gCat^{-1}.h^{-1}.bar^x)	E(kJ/mol)	a_0 (bar$^{-0.5}$)	ΔH(kJ/mol)	m(-)	n(-)
[a] FT-III2	1.01×10^{11}	111.5	163.2	- 5.26		
[b] Power law	2.1×10^{8}	100			-0.45	0.85

246 x: a= - 2, b= - 0.4

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