Intrinsic Kinetics of the Fischer–Tropsch Synthesis on a **Cobalt Catalyst**

Ian C. Yates and Charles N. Satterfield*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received August 8, 1990. Revised Manuscript Received November 5, 1990

The rate of synthesis gas consumption over a cobalt Fischer-Tropsch catalyst was measured in a well-mixed, continuous-flow, slurry reactor at 220-240 °C, 0.5-1.5 MPa, H₂/CO feed ratios of 1.5-3.5, and conversions of 6-68% of hydrogen and 11-73% of carbon monoxide. The inhibiting effect of carbon monoxide was determined quantitatively and a Langmuir-Hinshelwood-type equation of the following form was found to best represent the results: $-R_{H_{2}+CO} = aP_{CO}P_{H_{2}}/(1 + bP_{CO})^{2}$. The apparent activation energy was 93-95 kJ/mol. Data from previous studies on cobalt-based Fischer-Tropsch catalysts are also well correlated with this rate expression.

Introduction

A number of kinetic studies of the Fischer-Tropsch synthesis over cobalt catalysts have been performed.¹⁻⁸ All of the expressions found to fit rate data on these catalysts show that carbon monoxide inhibits the rate of synthesis. However, a wide array of proposed forms for the rate expression exist which is partly a result of the considerable variation in reaction conditions studied. Further, some studies, particularly the earlier work, were performed in fixed-bed reactors. Integral kinetic data from a complex reaction such as the Fischer-Tropsch synthesis cannot be interpreted easily and a fixed-bed reactor may be difficult to maintain isothermal. In other cases, data are reported only for very low conversions.

Our objective was to develop an intrinsic kinetic expression for the rate of synthesis gas conversion on a cobalt catalyst over a range of industrially relevant conditions. A mechanically stirred, 1-L, continuous-flow slurry reactor was used. The reactor behaves as a CSTR, providing data at uniform temperature and composition which are easy to analyze. Product compositions obtained at the same operating conditions will be reported separately.

Background

The Fischer–Tropsch synthesis over cobalt-based catalysts produces mostly n-alkanes and 1-alkenes. The reaction stoichiometry may be approximated as

$$nCO + 2nH_2 \rightarrow (-CH_2 -)_n + nH_2O \tag{1}$$

Cobalt is not very active for the water gas shift reaction,⁹ thus, in contrast to most iron-based Fischer-Tropsch catalysts, only a small fraction of the water produced is subsequently converted to carbon dioxide.

The rate of the Fischer-Tropsch reaction is defined here as the moles of hydrogen plus carbon monoxide converted per time per mass of unreduced catalyst, $-R_{\rm H_2+C0}.$ Some previous studies report the rate of conversion of carbon monoxide only, $-R_{CO}$. If the extent of water gas shift is negligible, the two rate measures, $-R_{H_2+CO}$ and $-R_{CO}$, are related by a constant, as can be seen from eq 1.

Published intrinsic expressions for the rate of Fischer-Tropsch synthesis over various cobalt catalysts are presented in Table I. The rate expressions of Yang et al.,³ Pannell et al.,⁴ and Wang⁶ were all developed by regression of a power-law equation of the general form

$$-R = a P_{\rm H_0} {}^b P_{\rm CO} {}^c \tag{2}$$

In all of these kinetic expressions, the coefficient b was positive and the coefficient c was negative, suggesting inhibition by adsorbed CO.

Anderson² found the equation developed by Brötz¹ to be inadequate for data over a wide range of inlet H_2/CO ratios. From data taken in a fixed bed at atmospheric pressure over a wide range of H_2/CO ratios and temperatures, Anderson and co-workers at the Bureau of Mines¹⁰ (p 529) developed an equation, eq 4, by postulating that the rate is proportional to the desorption of chains. The concentration of growing chains on the catalyst surface was related empirically to $P_{H_2}^2 P_{CO}$. From samples withdrawn from the beginning of the bed, Anderson² (p 270) and Storch et al.¹⁰ report that eq 4 does not satisfactorily fit the data at high values of $P_{H_2}{}^2P_{CO}$. They speculate that this lack of fit may be a result of either a hot spot in the initial part of the bed or a different rate-controlling process being in effect at high values of $P_{\rm H_2}{}^2P_{\rm CO}$. Rautavuoma and van der Baan⁵ studied the rate of re-

action at atmospheric pressure, 250 °C, and conversions below 2%. They examined five possible rate-determining steps. The expression which fit their data best, eq 7, is consistent with a mechanism in which the reaction proceeds via CO dissociation and formation of a "-CH₂-" surface intermediate. The formation of this surface intermediate is the rate-determining step. The model also

⁽¹⁾ Brötz, W. Z. Elektrochem. 1949, 5, 301-306

⁽²⁾ Anderson, R. B. In Catalysis; Emmett, P. H., Ed.; Reinhold: New York, 1956; Vol. IV, pp 257-283.
(3) Yang, C.-H.; Massoth, F. E.; Oblad, A. G. Adv. Chem. Ser. 1979,

^{178.35-46}

⁽⁴⁾ Pannell, R. B.; Kibby, C. L.; Kobylinski, T. P. Proc. 7th Int. Congr. Catal. Tokyo 1980, 447-459.

⁽⁵⁾ Rautavuoma, A. O. I.; van der Baan, H. S. Appl. Catal. 1981, 1, 247-2 (6) Wang, J. Ph.D. Thesis, Brigham Young University, Provo, UT,

^{1987.} (7) Sarup, B.; Wojciechowski, B. W. Can. J. Chem. Eng. 1989, 67,

^{62-74.}

Wojciechowski, B. W. Catal. Rev.—Sci. Eng. 1988, 30, 629–702.
 Newsome, D. S. Catal. Rev.—Sci. Eng. 1980, 21, 275–322.

⁽¹⁰⁾ Storch, H. H.; Golumbic, N.; Anderson, R. B. The Fischer-Tropsch and Related Syntheses; Wiley: New York, 1951.

Table I. Summary of Kinetic Studies of the Fischer-Tropsch Synthesis on Cobalt-Based Catalysts

				conditions		_		
reference	catalyst	reactor type	<i>T</i> , ℃	P, MPa	H ₂ /CO	intrinsic kinetic expression ^a	eq	
Brötz ¹ Anderson ²	Co/MgO/ThO ₂ /kieselguhr Co/ThO ₂ /kieselguhr	fixed bed fixed bed	185-200 186-207	0.1 0.1	2 0.9–3.5	$\begin{array}{l} -R_{\rm H_{2}+CO} = a P_{\rm H_{2}}{}^{2}/P_{\rm CO} \\ -R_{\rm H_{2}+CO} = a P_{\rm H_{2}}{}^{2}P_{\rm CO} \\ (1 + b P_{\rm H_{2}}{}^{2}P_{\rm CO}) \end{array}$	3 4	
Yang et al. ³ Pannell et al. ⁴	Co/CuO/Al ₂ O ₃ Co/La ₂ O ₃ /Al ₂ O ₃	fixed bed Berty (low conversion)	235–270 215	0.17-5.5 0.49-0.8	1.0-3.0 2	$-R_{\rm H_2+CO} = aP_{\rm H_2}P_{\rm CO}^{-0.5} -R_{\rm H_2+CO} = aP_{\rm H_2}^{-0.55}P_{\rm CO}^{-0.33}$	5 6	
Rautavuoma and van der Baan ⁵	Co/Al ₂ O ₃	fixed bed (low conversion)	250	0.1	0.2-4.0	$-R_{\rm CO} = aP_{\rm H_2}P_{\rm CO}^{1/2}/(1+bP_{\rm CO}^{1/2})^3$	7	
Wang ⁶	$\rm Co/B/Al_2O_3$	fixed bed (low conversion)	181	0.1-0.2	0.25-4.0	$-R_{\rm CO} = a P_{\rm H_2}{}^{0.68} P_{\rm CO}{}^{-0.5}$	8	
Sarup and Wojciechowski ⁷ Wojciechowski ⁸	Co/kieselguhr	Berty	190	0.2–1.5 ^b	0.5–8.3 ^b	$\begin{array}{l} -R_{\rm CO} = a P_{\rm CO}^{1/2} P_{\rm H_2}^{1/2} / \\ (1 + b P_{\rm CO}^{1/2} + c P_{\rm H_2}^{1/2} + d P_{\rm CO})^2 \\ -R_{\rm CO} = a P_{\rm CO} P_{\rm H_2}^{1/2} / \\ (1 + b P_{\rm CO} + c P_{\rm H_2}^{1/2})^2 \end{array}$	9 10	

a, b, c, and d in these equations are temperature-dependent constants. ^b These ranges of operating conditions are estimated from their experimental data.

assumes that hydrogen is adsorbed onto the catalyst surface dissociatively; however, the authors suggest that the predominant surface species is dissociated CO and therefore do not include a term for dissociated H₂ in the denominator of the rate expression.

In the most recently published work, Sarup and Wojciechowski⁷ describe six different possible mechanisms for the Fischer-Tropsch reaction on cobalt catalysts that are compared to experimental data obtained at 190 °C in a Berty internal recycle reactor. The rate of reaction was measured both by the rate of carbon disappearance and by the rate of oxygen appearance as H_2O plus CO_2 . A wide range of values of $P_{\rm H_2}$ and $P_{\rm CO}$ were studied, but conversions are not reported.

Four of their proposed expressions presume that dissociated CO participates in the reaction, while two postulate that CO is adsorbed but not dissociated. The development of kinetic expressions from each of their proposed mechanisms is detailed by Sarup and Wojciechowski⁷ and reviewed by Wojciechowski.8

The general form of rate expression they propose is

$$-R_{\rm CO} = \frac{k P_{\rm CO}{}^a P_{\rm H_2}{}^b}{(1 + \sum K_i P_{\rm CO}{}^{c_i} P_{\rm H_2}{}^{d_i})^2}$$
(11)

In eq 11, k is a kinetic parameter, a and b are the reaction orders of the rate-controlling step, K_i represents an adsorption parameter for the *i*th adsorption term, and c_i and d_i describe the dependence of surface coverage of the *i*th adsorption term on the reactant partial pressures. All of the possible reaction mechanisms considered by Sarup and Wojciechowksi involve a bimolecular surface reaction, and thus the denominator of eq 11 is squared.

To discriminate among the six models, they regress their data nonlinearly. Because no a priori assumptions are made about the relative magnitude of possible inhibition terms, the regression determines all of the model parameters, k and various values of K_i . Three of the models fit the data comparably on the basis of residual sum of squares, the sum over all the data points of the squared difference of the actual minus the predicted rate. These three models are eq 9 and 10 (Table I) and eq 12 (Sarup and Wojciechowksi's models 1, 5, and 6, respectively).

$$-R_{\rm CO} = \frac{aP_{\rm CO}P_{\rm H_2}}{(1+bP_{\rm CO}+cP_{\rm H_2}^{1/2}+dP_{\rm CO}P_{\rm H_2}^{1/2})^2} \quad (12)$$

a, b, c, and d in eqs 9, 10, and 12 are model-specific, tem-

perature-dependent constants.

Of the three models, eq 12 fits their data best but is rejected by Sarup and Wojciechowski, because one of the adsorption coefficients, either b, c, or d in eq 12, not stated by authors, is negative, representing a physically unreasonable situation.

The constant d in eq 9 is reported to be statistically insignificant and they remove it from the model and reregress the data, making the final form of the equation

$$-R_{\rm CO} = \frac{aP_{\rm CO}^{1/2}P_{\rm H_2}^{1/2}}{(1+bP_{\rm CO}^{1/2}+cP_{\rm H_2}^{1/2})^2}$$
(13)

The authors state that they are unable to distinguish between eqs 10 and 13 on the basis of goodness of fit.

Experimental Section

In this study, the experiments were performed in a continuous, mechanically stirred, 1-L autoclave. The slurry reactor and ancillary equipment are described in detail elsewhere.¹¹ The reactor and its contents are well mixed. Studies with iron-based catalysts of similar particle sizes, catalyst loadings, and reaction rates show that the reactor operated without mass-transfer limitations,¹¹⁻¹³ as indicated by the lack of effect of stirring rate and other variables.¹² Calculations as described by Satterfield¹⁴ further indicate that there are no mass-transfer limitations, either gas-liquid or within the catalyst particles.

The reactor was initially charged with 400 g of n-octacosane (>99% purity, Humphrey Chemical, Inc.). The *n*-octacosane had been previously recrystallized in tetrahydrofuran (>99.9% purity, Mallinkrodt, Inc.) to remove a bromine impurity.

The cobalt catalyst used is a Co/MgO on SiO_2 . This catalyst was prepared for us by an outside laboratory and is of the approximate composition of the cobalt catalysts used at Ruhrchemie.¹⁰ The nominal composition of the catalyst, as reported to us by its manufacturer, is 21.4 wt % Co (as Co), 3.9 wt % Mg (as Mg), and remainder diatomaceous earth.

Supplied as an extrudate, the catalyst was ground and sieved to 52-92 μ m (170-270 ASTM Mesh). Following sieving, 17 g of the catalyst was placed in a tubular reduction vessel. The catalyst was held in this reduction unit with 7- μ m stainless-steel sintered frits while hydrogen (prepurified, MedTech Gases, Inc.) was brought on-stream at a flow of 1.36 L(STP)/min (approximately 10000 V/V/h). At this flow rate, the pressure in the vessel was

⁽¹¹⁾ Huff, G. A., Jr.; Satterfield, C. N. Ind. Eng. Chem. Fundam. 1982,

 ⁽¹¹⁾ Hull, G. A., Jr., Saterlield, C. N. Ind. Eng. Chem. Pundam. 1982, 21, 479–483.
 (12) Huff, G. A., Jr., Sc.D. Thesis, M.I.T., Cambridge, MA, 1982.
 (13) Huff, G. A., Jr.; Satterfield, C. N. Ind. Eng. Chem., Process Des. Dev. 1984, 23, 696–705.

⁽¹⁴⁾ Satterfield, C. N. Mass Transfer in Heterogeneous Catalysis, reprint ed.; Krieger: Melbourne, FL, 1981.

Table II. Activity Data for Repeated Conditions of 240 °C, 0.79 MPa, $H_2/CO = 2$, and Synthesis Gas Feed Rate of 0.067 $L/[\min \circ g \text{ of catalyst}]^{\circ}$

time on-stream, h	oxygen closure, mol %	R _{H2+CO} , mmol/ (min•g of catalyst)	P _{H2} , MPa	P _{CO} , MPa
257.5	97.06	0.678	0.48	0.25
617.0	101.23	0.680	0.48	0.24
1073.0 ^b	100.21	0.594	0.45	0.25
2176.5	99.89	0.694	0.47	0.24

^a Flow is calculated at standard conditions; grams of catalyst is on an unreduced basis. ^b H_2/CO and feed rate were slightly lower for this material balance at 1.95 and 0.066 L(STP)/(min-g of catalyst), respectively.

0.79 MPa. The temperature of the reduction tube was increased steadily from 25 to 330 °C over 4 h while the inlet flow rate was held constant. During this period the pressure in the reduction vessel increased to 0.97 MPa. The reduction unit was held at 330 °C for 1.5 h and then pressured with helium and rapidly cooled. The unit with the catalyst was weighed and comparison with the initial weight indicated that the catalyst lost 18 wt % during reduction. The reduced catalyst was added to the 1-L autoclave reactor which was being held under helium.

The reactor was brought on-stream at 0.79 MPa, 187 °C, and $H_2/CO = 2.0$ at a flow rate of 2.0 L(STP)/min. The CO used in these experiments was CP grade (Northeast Airgas, Inc.) and the H_2 was prepurified grade (MedTech Gases, Inc.). These gases passed through a 13 X molecular sieve, an activated carbon trap, and a 2- μ m filter before entering the base of the reactor. The zeolite and activated carbon remove various potential impurities from the feed gases, including iron carbonyls, water, and sulfur compounds.

The reactor conditions were held constant for the first 65 h and then the reactor temperature was increased to 240 °C over a period of 7 h. The reactor was then kept at 0.79 MPa, 240 °C, and $H_2/CO = 2.0$ at a flow rate of 2.0 L(STP)/min for 72 h to allow the catalyst to achieve steady-state activity and to ensure that the overhead products were representative of those being synthesized.

Material balances over a wide range of conditions were performed for periods of 6-24 h, with at least 12 h allowed between material balances to ensure steady-state operation. When the reactor temperature or pressure was changed, at least 48 h was allowed between material balances.

The products, liquid hydrocarbons and water, were condensed in two traps, one kept at 85 °C and reactor pressure, the other at 1 °C and 0.34 MPa. Material balances, including analyses of all condensed and noncondensed products, closed between 97 and 103% on oxygen, which was chosen as the material balance closure criterion because carbon and hydrogen accumulate in the reactor in the form of high molecular weight hydrocarbons.^{12,15} Table II shows that returning to a standard set of conditions periodically verified that the catalyst did not deactivate significantly during the run.

Reactor temperature was set between 220 and 240 °C. Pressures were changed from 0.5 to 1.5 MPa and H_2/CO feed ratios from 1.5 to 3.5. Total synthesis gas conversion was varied from 11 to 70% by changing space velocity between 0.085 and 0.008 L(STP)/min/g of catalyst (unreduced basis).

Products were analyzed with three gas chromatographs, as described by Huff et al.¹⁶ A Hewlett-Packard 5880 with a dimethylsilicone capillary column and flame ionization detector (FID) was used for hydrocarbon analyses of noncondensable gases and the organic phases from the hot and cold traps. Aqueous liquid samples from the hot and cold traps and noncondensed water and oxygenated hydrocarbons were analyzed with a Hewlett-Packard 5710 using a glass column packed with 60/80 mesh Tenax and a thermal conductivity detector (TCD). A Carle/Hach refinery gas analyzer Series S AGC 111-H was used for the analysis



Figure 1. Plot showing lack of covariance between $P_{\rm H_2}$ and $P_{\rm CO}$ at 220 °C.



Figure 2. Plot showing lack of covariance between P_{H_2} and P_{CO} at 240 °C.

of noncondensable gases, particularly H₂, CO, and CO₂. Tie components, CO₂, CH₄, and C₂ and C₃ compounds, were used to match the analyses from the three gas chromatographs and provide complete product distributions for each material balance. The partial pressures of H₂ and CO in the reactor were calculated from the molar flow rates of all vapor-phase species present. For the organic products the molar flow rates of each species were calculated by a computer program. There was little change in H₂/CO usage ratio with reaction conditions. This averaged slightly above 2.

Results and Discussion

The forms of eqs 3-13 all have subtle differences in their functional dependence on $P_{\rm H_2}$ and $P_{\rm CO}$, so experiments were run over a broad range of $\rm H_2/\rm CO$ ratios in an attempt to avoid a covariance between these two independent variables of regression. Figures 1 and 2 are plots of $P_{\rm H_2}$ versus $P_{\rm CO}$ at 220 and 240 °C. These figures show no significant correlation between reactant partial pressures.

It was decided that the rate expression should contain only two adjustable parameters, a simplifying approach appropriate for reaction systems with this degree of complexity. In terms of Langmuir-Hinshelwood kinetics, one of these parameters would represent a surface rate constant and the other an adsorption coefficient.

Additional adjustable parameters make the kinetic expression unnecessarily complex. Potential inhibitors of the rate of synthesis are frequently closely related (i.e. covary), for example $bP_{\rm CO}^{1/2}$ and $dP_{\rm CO}$ in eq 9. Thus, the addition

⁽¹⁵⁾ Donnelly, T. J.; Yates, I. C.; Satterfield, C. N. Energy Fuels 1988, 2, 734-739.

⁽¹⁶⁾ Huff, G. A., Jr.; Satterfield, C. N.; Wolf, M. H. Ind. Eng. Chem. Fundam. 1983, 22, 258-263.



Figure 3. Test of eq 17 with experimental results at 240 °C. Solid line is best fit linear regression line.

of numerous inhibition terms in the denominator can rarely be justified statistically. An example of this covariance between inhibition terms for the rate of Fischer-Tropsch synthesis on a reduced fused magnetite catalyst is illustrated by Yates and Satterfield.¹⁷ There, it is shown that the inhibiting effects of H₂O on the synthesis had been incorrectly attributed to CO₂ by previous researchers, as a result of the high degree of correlation between $P_{\rm H_2O}$ and $P_{\rm CO_2}$.

Equations 4 and 7 both contain only two parameters and are thus examined as possible rate expressions without modification. Equations 9, 10, and 12 contain more than two adjustable parameters. In the case of eqs 10 and 12, it was assumed that CO was the predominant surface species, which is justified by nonreacting, single-component adsorption data on cobalt surfaces;¹⁸ these data indicate that \dot{CO} is more strongly adsorbed than H_2 . The same simplification is also made by Rautavuoma and van der Baan in the development of eq 7. In the case of eq 9, which has terms for surface coverage of undissociated CO and dissociated CO, it was assumed that dissociated CO was the predominant surface species. This assumption was implicitly made by Sarup and Wojciechowski⁷ when they removed the constant d from eq 9 and reregressed their data. The following equations represent the simplified, two-parameter forms of eq 9, 10, and 12:

$$-R_{\rm CO} = \frac{aP_{\rm CO}^{1/2}P_{\rm H_2}^{1/2}}{(1+bP_{\rm CO}^{1/2})^2}$$
(14)

$$-R_{\rm CO} = \frac{aP_{\rm CO}P_{\rm H_2}^{1/2}}{(1+bP_{\rm CO})^2}$$
(15)

$$-R_{\rm CO} = \frac{aP_{\rm CO}P_{\rm H_2}}{(1+bP_{\rm CO})^2}$$
(16)

In eqs 14–16, a and b are assumed to be temperature-dependent constants, a representing a kinetic parameter and b an adsorption coefficient.

Equations 4, 7, 14, 15, and 16 were taken to be the five proposed models. All equations were expressed in terms of the rate of hydrogen plus carbon monoxide consumption. As discussed earlier, in the absence of appreciable water gas shift activity, this rate measure is related to the

Table III. R^2 for Linearized Expressions

				-		
 eq	<i>T</i> , °C	R^2	eq	<i>T</i> , °C	R^2	
17	220	0.954	20	220	0.970	
	240	0.909		240	0.886	
18	220	0.938	21	220	0.968	
	240	0.945		240	0.984	
19	220	0.927				
	240	0.590				

Table IV. Nonlinear Regression Statistical Analyses

			•	
eq	residuals [sum of squared errors]	F ratio	R ²	
4	0.340	42.06	0.663	
7	0.072	303.27	0.929	
14	0.245	85.82	0.758	
15	0.214	101.61	0.788	
16	0.062	361.22	0.938	

Table V. Results of Nonlinear Fit of Data from This Study at 220 and 240 °C to Eq 16

reactor temp, °C	aª	std error of a ^a	t value ^b of a	b¢	std error of b ^b	t value ^b of b	
240 220	75.76 53.11	9.20 1.38	8.23 38.63	11.61 22.26	0.97 3.63	12.02 6.62	

^a In mmol/(min-g of catalyst-MPa²). ^bThere were 23 data points collected at 240 °C and 17 at 220 °C. Critical t values for 99% confidence that the parameters are statistically significant are $t_{0.995,21} = 2.831$ for 240 °C; $t_{0.995,15} = 2.947$ for 220 °C. t values above these critical values indicate that one can be 99% confident that the parameters are significant. ^c In 1/MPa.

rate of carbon monoxide consumption by a constant.

Three methods were used to determine which expression best fit the data. First, the equations were linearized and plotted to look for outlying data points and general goodness of fit. Second, the linearized forms of the expressions were regressed to quantify goodness of fit. Third, the data were regressed nonlinearly with the models and model parameters being tested for statistical significance. The proposed equations were first linearized as follower:

The proposed equations were first linearized as follows:

$$\frac{P_{\rm H_2}^2 P_{\rm CO}}{-R_{\rm H_2+CO}} = \frac{1}{a} + \frac{b P_{\rm H_2}^2 P_{\rm CO}}{a} \tag{17}$$

$$\left[\frac{P_{\rm H_2}P_{\rm CO}^{1/2}}{-R_{\rm H_2+CO}}\right]^{1/3} = \frac{1}{a^{1/3}} + \frac{bP_{\rm CO}^{1/2}}{a^{1/3}}$$
(18)

$$\left[\frac{P_{\rm H_2}^{1/2}P_{\rm CO}^{1/2}}{-R_{\rm H_2+CO}}\right]^{1/2} = \frac{1}{a^{1/2}} + \frac{bP_{\rm CO}^{1/2}}{a^{1/2}}$$
(19)

$$\left[\frac{P_{\rm H_2}^{1/2}P_{\rm CO}}{-R_{\rm H_2+CO}}\right]^{1/2} = \frac{1}{a^{1/2}} + \frac{bP_{\rm CO}}{a^{1/2}}$$
(20)

$$\left[\frac{P_{\rm H_2}P_{\rm CO}}{-R_{\rm H_2+CO}}\right]^{1/2} = \frac{1}{a^{1/2}} + \frac{bP_{\rm CO}}{a^{1/2}}$$
(21)

The majority of the data were collected at 220 and 240 °C. The data at 240 °C were regarded as more meaningful since they covered a wider range of relative rates. Figures 3-7 show plots of the data at 240 °C according to the five linearized forms given by eqs 17-21. Best-fit linear regression lines are plotted to facilitate visual estimation of goodness of fit and scatter. Similar plots were made for the data at 220 °C but are not shown here. Table III gives R^2 values for the fit of the data to the linearized forms of

 ⁽¹⁷⁾ Yates, I. C.; Satterfield, C. N. Ind. Eng. Chem. Res. 1989, 28, 9-12.
 (18) Vannice, M. A. Catal. Rev. Sci. Eng. 1976, 14, 153-191.



Figure 4. Test of eq 18 with experimental results at 240 °C. Solid line is best fit linear regression line.



Figure 5. Test of eq 19 with experimental results at 240 °C. Solid line is best fit linear regression line.



Figure 6. Test of eq 20 with experimental results at 240 °C. Solid line is best fit linear regression line.

the proposed rate expressions at both 220 and 240 °C. The equation which fits the data best is eq 21, the linearized form of eq 16.

Visual examination and regression of linearized rate expressions is a useful tool but can be misleading because variance in the original data is distorted when the rate expressions are linearized. Table IV shows the results of



Figure 7. Test of eq 21 with experimental results at 240 °C. Solid line is best fit linear regression line.



Figure 8. Parity plot comparison of data with prediction from eq 16. Solid line gives predicted values.

nonlinear regression of the data which confirms that eq 16 fits the data best. Table V presents the parameter values and some related regression information for the fit of eq 16 to the data from this study. The parameters aand b of eq 16 are highly statistically significant at both 220 and 240 °C. The substantially higher value of b at 220 °C is as would be expected from inhibition by adsorption of CO.

A further test of eq 16 could in principle be obtained by casting a and b into exponential form and calculating the effect of temperature on the exponent. With data from a temperature range of only 20 °C, it was not reasonable to do in the present case. However, an apparent activation energy was calculated from rate data for two sets of values of $P_{\rm H_2}$ and $P_{\rm CO}$ that were nearly the same at 220 and 240 °C. The apparent activation energies were 92.7 and 94.5 kJ/mol which are very close to activation energies reported previously: 102 kJ/mol calculated by Anderson² (p 266) from the data of Fischer and Pichler,¹⁹ 103 kJ/mol reported by Storch et al.¹⁰ (p 530), 96 kJ/mol calculated by Anderson² (p 266) from data of Gibson and Hall,²⁰ and 84 kJ/mol reported by Anderson² (p 265). These apparent activation energies were calculated from the slopes of plots of the logarithm of the rate of reaction versus the reciprocal

⁽¹⁹⁾ Fischer, F.; Pichler, H. Brennst. Chem. 1939, 20, 41-60. (20) Gibson, E. J.; Hall, C. C. J. Appl. Chem. 1954, 4, 49-61.



Figure 9. Test of eq 21 with data from Rautavuoma and van der Baan.⁵



Figure 10. Test of eq 21 with data from Wang⁶ (pp 100-101).

of absolute temperature for data collected at similar pressures, feed rates, and feed compositions. Yang et al.³ report an apparent activation energy of 100 kJ/mol for their constant a in eq 5 which was regressed from their data.

Five of the six studies, including the present one, yield apparent activation energies within the close limits of 93-103 kJ/mol. This is perhaps surprising considering the wide range of conditions that were studied.

Figure 8 shows the fit of eq 16 to the data from this study in the form of a parity plot. Within the scatter in the data, the two-parameter model fits the data well. Data points not included in the regression taken at 230 °C are also well predicted by the rate equation, indicating that the estimates of the parameters a and b are reasonably good at both 220 and 240 °C.

Comparison to Literature Data

Data from three of the studies listed in Table I are available in the literature.^{5,6,8} Having developed a twoparameter model that was different from any of those recommended by these researchers, we decided to fit their data to eq 16. The linearized form, eq 21, is used to ex-



Figure 11. Test of eq 21 with data from Sarup and Wojcie-chowski.⁷

amine goodness of fit and to look for outlying data points. Figure 9 shows the data of Rautavuoma and van der Baan,⁵ Figure 10 the data of Wang⁶ (pp 100 and 101), and Figure 11 the data of Sarup and Wojciechowski.⁸ All three sets of data fit the linear relationship of eq 21 well and have positive slopes and intercepts, as would be expected.

Conclusions

Data for the rate of synthesis gas consumption on a cobalt catalyst were obtained over a wide range of industrially relevant conditions. Five different two-parameter rate models were examined for fit to the data by three methods: visual examination of linearized forms of the rate models, regression of these linearized expressions, and nonlinear regression of the expressions. Equation 16 is found to provide the best fit to our data. Data from three previous kinetic studies are also well fit by this kinetic expression. Apparent activation energies for five of six studies, including the present one, all fall within the narrow range of 93-103 kJ/mol.

Acknowledgment. This study was supported by the Office of Fossil Energy, U.S. Department of Energy, under contract No. DE-AC22-87PC79816.

Nomenclature

- temperature-dependent constant, the product of a surface rate constant and adsorption constants (equation specific)
- b temperature-dependent adsorption constant (equation specific)
- c temperature-dependent adsorption constant (equation specific)
- d temperature-dependent adsorption constant (equation specific)
- P_i partial pressure of component *i*, MPa -*R* rate of disappearance of either hydrogeneric partial pressure of the partia

а

- R rate of disappearance of either hydrogen plus carbon monoxide or carbon monoxide, mmol/ min/g of catalyst (unreduced basis)
- -R_{H2+C0} rate of disappearance of hydrogen plus carbon monoxide, mmol/min/g of catalyst (unreduced basis)
- -R_{CO} rate of disappearance of carbon monoxide, mmol/min/g of catalyst (unreduced basis)
 - Registry No. Co, 7440-48-4; MgO, 1309-48-4; CO, 630-08-0.