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Kinetics of Fischer–Tropsch synthesis on titania-supported cobalt

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Abstract

Rate data have been obtained for CO hydrogenation on a well-characterized 11.7% Co/TiO_2 catalyst in a differential fixed bed reactor at 20 atm, 180–240°C, and 5% conversion over a range of reactant partial pressures. The resulting kinetic parameters can be used to model precisely and accurately the kinetics of this reaction within this range of conditions. Turnover frequencies and rate constants determined from this study are in very good to excellent agreement with those obtained in previous studies of other cobalt catalysts, when the data are normalized to the same conditions of temperature and partial pressures of the reactants. Based on this comparison CO conversion and the partial pressure of product water apparently have little effect on specific rate per catalytic site. The data of this study are fitted fairly well by a simple power law expression of the form $-r_{CO} = kP_{H_2}{}^{0.74}P_{CO}{}^{-0.24}$, where k=5.1×10^{-3} s^{-1} at 200°C, P=10 atm, and H_2/CO=2/1; however, they are best fitted by a simple Langmuir–Hinshelwood (LH) rate form $-r_{CO} = aP_{H_2}^{0.74}P_{CO}/(1+bP_{CO})^2$ similar to that proposed by Yates and Satterfield. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Fischer–Tropsch Synthesis; Titania-supported cobalt; Turnover frequency

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1. Introduction

Fischer–Tropsch synthesis (FTS), the production of liquid hydrocarbons from synthesis gas (CO and H_2), 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. Renewed interest in the development of cobalt FTS catalysts has been recently stimulated by developments at Shell and Exxon of new and substantially more economical wax/crack FTS processes for converting natural gas to high quality middle-distillate and diesel fuels based on new cobalt catalyst technology [1–5].

The kinetics of FTS on cobalt catalysts have received significant attention [4]; in fact, 10 previous studies [6–15] 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 [14]. Reaction conditions varied considerably among different studies, including low and high pressures (e.g., 1 vs. 10–20 bar), different ranges of temperature (e.g., 170–195°C vs. 235–270°C) and CO conversions ranging over 2–70%. Kinetic studies of commercially relevant cobalt catalysts supported on alumina, silica, and kieselguhr under industrially representative conditions were conducted by Pannell et al. [9], Sarup and Wojciechowski [12], Yates and Satterfield [14], and Iglesia et al. [15] (although the supports were not specified for this last study). No kinetic data were reported explicitly for titania-supported cobalt catalysts. There is little consensus among the different

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studies regarding the dependencies of rate on reactant concentration and temperature.

Questions regarding effects of support, promoters, heat–mass transport disguises, and catalyst deactivation on measured kinetic data were not addressed in most of the previous kinetic studies. Moreover, in large part, catalysts were not adequately characterized and statistical measures of significance were not established. For example, none of the previous studies addressed the effects of support contamination of the metal surface on reaction kinetics. In none of these studies did investigators report criteria to show whether their kinetic data were affected by pore diffusional and mass transfer disguises, although several studies were carried out using catalyst powders or small particles to minimize pore diffusional resistance; moreover, only the studies of Rautavuoma and van der Baan [10] and Wang [11] were carried out at low CO conversions (i.e., less than 2–5%), thereby assuring the absence of pore diffusional, mass transfer, and heat transfer disguises. With the exception of the studies of Wang [11] and Iglesia et al. [15], rates were not based on active metal surface area, and in none of the previous studies, except for that of Wang's, were metal surface areas and extents of reduction reported. Only two previous studies [10,14] reported statistical measures of significance for their data and fitted parameters.

In other words most of the previous studies did not meet minimum guidelines for conducting and reporting activity/kinetic data as proposed in the recent review of Ribeiro et al. [16]. These guidelines include: (1) measuring rates in the absence of pore diffusional restrictions, film mass transfer limitations, heat transfer limitations, and deactivation effects; (2) collecting data over wide ranges of temperature and reactant concentration to facilitate valid comparison with data from other laboratories and to provide meaningful data for determining temperature and concentration dependencies; and (3) reporting rates based on catalytic surface area. Ribeiro et al. [16] proposed that reporting surface areas or dispersions of catalyst samples should be a requirement for publication.

The objectives of this work were to (1) obtain statistically representative kinetic data on a well-characterized, titania-supported catalyst under commercially representative reaction conditions in the absence of heat/mass transport disguises and in the absence of deactivation; (2) report statistical measures of data significance and (3) compare, where possible at a standard set of conditions, the results of this study with those of previous studies. Every effort was made to adhere to the new guidelines [16] for collection and reporting of activity/kinetic data.

2. Experimental

2.1. Catalyst preparation

An 11.7 wt.% Co/TiO_2 was prepared by impregnation with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ to incipient wetness of TiO_2 (Degussa P25, 16% rutile), which had been previously calcined at 650°C for 2 h to produce 76% rutile (BET surface area of 30 m^2/g). The impregnated sample was dried at 110°C for 2 h and calcined in air at 400°C for 4 h (heating rate of 10°C between 110 and 400°C); the calcined catalyst was reduced in situ (in the fixed bed reactor described below) in pure H_2 at 400°C for 16 h (heating rate of 10°C between 25 and 400°C). Following reaction, the catalyst was passivated in 1% O_2/He.

2.2. Chemisorption and extent of reduction measurements

Static hydrogen chemisorption uptakes were measured using a standard volumetric glass adsorption apparatus by the following procedure: (1) catalyst samples reduced in pure H_2 at 400°C were evacuated 1 h at 400°C and cooled to 25°C in vacuum and (2) total H_2 uptake was determined at 25°C by measuring uptake as a function of pressure over the range of 100–400 Torr and extrapolating the straight-line portion of the isotherm to zero pressure. The extent of reduction was determined by O_2 titration of the reduced catalyst at 400°C; the extent of formation of Co_3O_4 and of CoO oxides during titration was determined from XRD and found to be approximately 50 mol% each.

2.3. Rate measurements

Rate measurements were conducted on 1.5 g of catalyst powder (100–200 mesh) diluted with 0.75 g of

Table 1
CO conversion and TOF data for CO hydrogenation on 11.7% Co/TiO_2[a] measured in consecutive runs at P_{Tot}=20 bar and GHSV (STP)=5000 h^{-1} after 10–20 h of reaction at each given condition in a fixed bed reactor (FBR)

Runs[b]	T (°C)	P°_{CO} (bar)	$P^\circ_{H_2}$ (bar)	P°_{He} (bar)	$(H_2/CO)_o$[c]	X_{CO} (%)[d]	TOF[e] ×10^3 (s^{-1})
1A	200	3.0	8.0	9.0	2.67	5.03	20
2A	200	3.0	8.0	9.0	2.67	5.08	20.5
3A	200	6.0	8.0	6.0	1.33	4.66	38
4A	200	4.0	8.0	8.0	2.00	4.98	27
1B	200	4.0	14.0	2.0	3.50	3.54	20
2B	200	4.0	13.0	3.0	3.33	3.25	18
3B[f]	200	4.0	8.0	8.0	2.00	2.60	14
4B[g]	200	4.0	8.0	8.0	2.00	2.66	14
5B	200	6.0	8.0	6.0	1.33	2.39	19
6B	200	3.0	8.0	9.0	2.67	3.08	12
7B	200	4.0	4.0	12.0	1.00	1.37	7.4
8B	200	3.0	8.0	11.0	2.67	4.38	18
9B	200	2.0	8.0	10.0	4.00	3.51	9.4
10B	200	6.0	8.0	6.0	1.33	2.33	19
1C	180	4.0	8.0	8.0	2.00	1.32	7.1
2C	192	4.0	8.0	8.0	2.00	2.07	11
3C	200	4.0	8.0	8.0	2.00	2.69	14.5
4C	213	4.0	8.0	8.0	2.00	4.63	25
5C	225	4.0	8.0	8.0	2.00	7.76	42
6C	238	4.0	8.0	8.0	2.00	17.65	95

[a] Single sample of 1.50 g (1.538 cm^3).

[b] Series A runs were conducted on the fresh catalyst at 200°C; after Run 4A, the catalyst was apparently deactivated. Series B runs were conducted on the same catalyst at 200°C; the catalyst was regenerated in H_2 at 400°C for 5 h and then at 350°C for 12 h Before Runs 4B and 5B, respectively. Series C runs were conducted on the same catalyst at different temperatures.

[c] Inlet molar H_2/CO ratio.

[d] CO conversion; $X_{CO} = (F^\circ_{CO} - F_{CO})/F^\circ_{CO}$, where F°_{CO}=molar flow rate of CO at the inlet and F_{CO}=outlet molar flow rate; $F_{CO}=v_0C_{CO}=v_0P_{CO}/RT$, where v_0=volumetric flow rate (cm^3/min).

[e] Turnover frequency, i.e., CO molecules converted per catalytic site per second, based on H_2 chemisorption (10.5 μmol/g); valid at 200°C and partial pressures and conversions shown.

[f] Following regeneration in H_2 at 400°C for 5 h; activity was apparently not significantly changed.

[g] Following a second regeneration in H_2 at 350°C for 12 h; activity was essentially the same as before treatment.

SiC (Buehler, No. 40 6410 AB, 400 mesh) to moderate temperature gradients in a differential, fixed-bed tubular reactor (FBR). Tests were conducted at a total pressure of 20 bar, 180–238°C, H_2/CO feed ratios of 1.0–4.0, H_2 and CO partial pressures ranging from 2–6 and 4–14 bar, respectively, and space velocities of 3000–5000 h^{-1}. Conditions for each test (run) and the order in which runs were conducted are listed in Table 1. CO conversions were generally 3–5% for tests at 200°C to ensure the absence of pore diffusional mass transfer and heat transfer disguises of rate. The Weisz–Prater number was estimated to be 0.1–0.3 (based on conservatively low estimates of the bulk diffusivity for CO in liquid oil of 5×10^{-5} cm^2/s and of the effective diffusivity of 1×10^{-5} cm^2/s), confirming that effects of pore diffusional resistance on rate were negligible (since the Weisz–Prater number should be less than 1 for negligible pore resistance [17]).

The catalyst sample temperature was monitored during activity tests to ±1°C using a calibrated, movable, stainless-steel, shielded Type K thermocouple fed through a fitting at the top of the reactor such that its tip was in direct contact with the catalyst bed outlet. The temperature gradient across the catalyst bed of about 3 cm in length was found (by varying the position of the thermocouple) to be 2–3°C, with or without reaction taking place at 5% CO conversion. Thus, the temperature gradient was probably principally due to a temperature gradient across the length of the furnace.

Reaction products were passed directly from the reactor through heated lines to a Hewlett Packard gas chromatograph (5890A) for analysis; the oven temperature was programmed from 50 to 235°C; non-condensable gases were separated in a column packed with 60/80 mesh Carboxen 1000 and detected by thermal conductivity, while C_1–C_{15} hydrocarbons were separated in a 10 m fused silica capillary column coated with SP 2100 and detected by flame ionization. The catalyst sample was initially reduced in situ, cooled in H_2 to 200°C and operated under synthesis conditions shown for Run 1 (Table 1) for a period of 15–20 h before collection of rate data to ensure that "steady-state" conditions were achieved with respect to the C_1–C_{15} hydrocarbons. Subsequent changes in temperature or partial pressure were followed by reaction for 10–12 h before collection of rate data. Multiple gas samples (4–8) were analyzed at each steady-state condition.

3. Results

The 11.7% Co/TiO_2 was found to have a H_2 chemisorption uptake at 25°C of 10.5 μmol/g, an extent of reduction of cobalt to the metal of 77.4% and a dispersion 1.4%.

Rate data (CO conversions and CO turnover frequencies) obtained in 20 different activity tests of the 11.7% Co/TiO_2 catalyst in the FBR reactor at 20 bar and a space velocity of 5000 h^{-1} after 10–20 h of reaction are summarized in Table 1. Three series of runs are listed in Table 1: (1) Series A runs obtained on the fresh catalyst at different CO concentrations (H_2 concentration held constant), (2) Series B runs obtained at different concentrations of CO and H_2 on the same catalyst at 200°C after an apparent 40–45% loss of activity (apparent by comparing CO conversion for Runs 4A and 4B obtained under the same conditions), and (3) Series C runs obtained on the same catalyst (following Series B) over a range of temperatures (180–238°C) at fixed concentrations of CO and H_2.

The reason for the change in activity after Run 4A is uncertain; it is unlikely that the catalyst was poisoned by an impurity, since activity was stable during Series B and C runs (apparent by comparing CO conversions for Runs 4B and 3C); catalyst deactivation by sintering is also unlikely at this low reaction temperature. Loss of activity due to formation of a carbon deposit or oxidation of the cobalt surface was suspected. However, since attempts to regenerate the catalyst following Runs 2B and 3B did not change activity, oxidation of the cobalt surface can also be ruled out. The formation after Run 4A and before Run 1B of a graphitic carbon not removable in H_2 at 350–400°C is suspected; formation of very stable carbon deposits during FTS on Co and Fe catalysts which cause activity loss have been observed in previous studies [18,19].

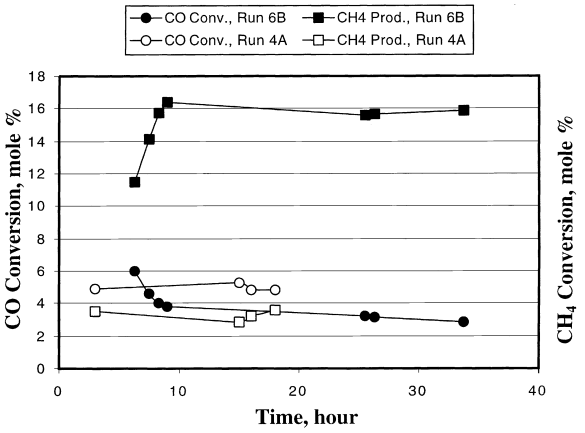

Fig. 1. CO conversion and methane selectivity as functions of time at 200°C for Runs 4A and 6B (see Table 1 for conditions).

Typical CO conversion and methane selectivity vs. time data are shown in Fig. 1 for Runs 4A and 6B. It is evident that steady-state data are obtained after 10–20 h of reaction; moreover, a significantly higher methane selectivity for the 6B run is evident — a feature that is generally associated with the lower activity in the Series B runs. This is also apparent from the selectivity data for the A and B runs listed in Table 2; moreover the propagation probabilities are lower for the Series B runs. The product distributions summarized in Table 2 are only approximate (i.e., ±20–30%), since CO conversions were only 1–5%; nevertheless, the high selectivities for liquid/waxy hydrocarbons and propagation probabilities (α values) in the range of 0.9 are typical of those previously observed [20–22] for FTS on supported cobalt catalysts.

While catalyst activity for Series A was significantly higher than for Series B and C, it was nevertheless possible to analyze the kinetic data separately for Series A, B, and C to obtain kinetic parameters with

Table 2
Hydrocarbon selectivity data for CO hydrogenation on 11.7% Co/TiO$_2$ at 20 bar, GHSV=5000 h^{-1}, and 200°C

Run	P_{CO} (bar)	H$_2$/CO	CO conversion	Mol % C of hydrocarbon product				
				CH$_4$	C$_2$–C$_4$	C$_5$–C$_{11}$	C$_{12+}$	α[a]
2A	3.0	2.67	5.08	3.9	2.8	10	82	0.98
4A	4.0	2.00	4.98	3.3	2.7	9.9	84	0.98
2B	4.0	3.00	3.33	16	11	30	42	0.89
7B	4.0	1.00	1.32	9.2	12	29	48	0.92

[a] Propagation probability based on a least squares fit of log (mole fraction) vs. carbon number for n=3–12.

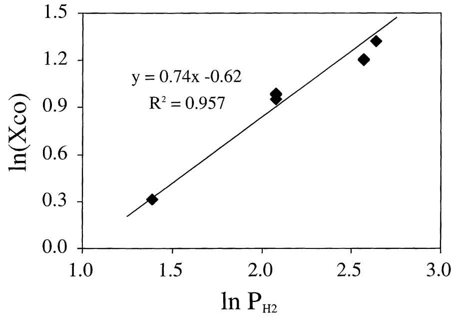

Fig. 2. CO conversion vs. P_{H_2} (bar) at 200°C and at a P_{CO} of 4 bar plotted on a natural log scale.

reasonably high precision. For example, Fig. 2 shows a plot of ln(X_{CO}) vs. ln P_{H_2} data from Series B in which P_{H_2} was varied, while P_{CO} was held constant; from this plot having a high correlation coefficient, the H$_2$ concentration dependence was found to be 0.74. Fig. 3 shows similar separate plots of data from Series A and B runs in which P_{CO} was varied and P_{H_2} was held constant, from which concentrations dependencies of −0.12 and −0.37 were obtained; in both sets of data the correlation coefficients are high. Nevertheless, there is a significant difference in concentration dependence between the two series, possibly due to the differences in activity.

The temperature dependence of the reaction rate on 11.7% Co/TiO$_2$ was obtained from an Arrhenius plot of CO turnover frequency (TOF) data obtained in the Series C runs at temperatures ranging from 180 to 238°C, a H$_2$/CO ratio of 2 (P_{CO}=4 and P_{H_2}=8 bar), and a space velocity of 5000 h^{-1} (see Fig. 4). From this highly linear plot involving six points, the apparent activation energy is found to be 83.2±6.4 kJ/mol and log A (A is the pre-exponential factor) is 7.38±0.5.

Incorporating the reaction orders, 0.74 for H$_2$ and −0.24 for CO (average of values for Series A and B), into a simple power law expression and applying this rate law to the TOF data in Table 1, rate constants were calculated for each of the runs at 200°C. The average value of these rate constants with its standard deviation is summarized in Table 3. Values of E, log A and reaction orders for H$_2$ and CO are also listed along

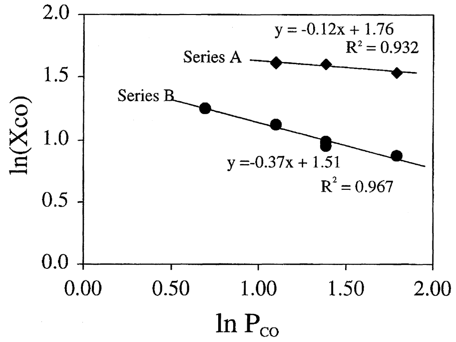

Fig. 3. CO conversion vs. P_{CO} (bar) at 200°C and at a P_{H_2} of 8 bar plotted on a natural log peak.

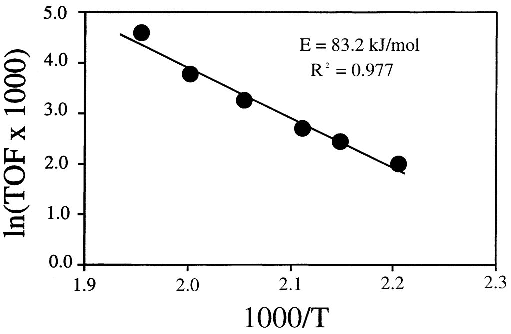

Fig. 4. Arrhenius plot of CO conversion at H$_2$/CO=2 (P_{CO}=4 and P_{H_2}=8 bar) and 5000 h^{-1}.

Table 3
Summary of kinetic parameters based on a simple power law fit[a] of the rate (TOF) data in Table 1

$k\times10^3$ (s^{-1}) at 200°C[b]	E^c (kJ/mol)	$\log A^d$	Reaction order	
			x=H_2	y=CO
5.1±2.4	83.2±6.4	7.38±0.5	0.74±0.06[e]	−0.24[f]

[a] $-r_{CO}\ (\mathrm{TOF}) = kP_{H_2}{}^{x}P_{CO}{}^{y}$.

[b] Average rate constant based on all data in Table 1 obtained at 200°C.

[c] Activation energy based on Series C data.

[d] Log (base 10) of pre-exponential factor based on Series C data.

[e] Based on Series B data in Table 1; valid at 200°C.

[f] Average reaction order for Series A and B data.

with their standard deviations. The standard deviations for the rate constant of 47% of the mean indicates that it was obtained with an acceptable degree of precision (since a precision of ±25–50% for rate data for a catalytic reaction is typical, even state-of-the-art); the acceptably low standard deviations for the rate constants, activation energy, pre-exponential factor and reaction orders along with their correlation coefficients of 0.93–0.98 in Figs. 2–4 indicate that these parameters represent the data well. Moreover, F-statistic analysis indicates that these parameters represent the data within a confidence interval of better than 95 or 99%.

4. Discussion

4.1. Comparison of the activity and kinetic parameters with previous studies

It is fundamentally important to report activity/selectivity and kinetic data for a reaction study in the context of previous work, in order to establish the accuracy of such data. While previously reported activity and kinetic parameters for Co/TiO_2 catalysts are limited, they nevertheless allow such a comparison (see Table 4). The TOF data in Table 4 from different studies have been normalized to the same conditions of temperature and reactant partial pressures using reaction orders of 0.74 and −0.24 for H_2 and CO and E=83 kJ/mol thereby allowing a valid comparison; rate constants were calculated from TOF data of this and the other studies shown using the simple power rate law developed in this study.

It is evident that TOF data from this study are in very good to excellent agreement with (i.e., within 8–50%) and within experimental precision of those

Table 4
Comparison of activity and kinetic parameters for FT synthesis on Co/TiO_2 and supported cobalt catalysts (including Co/TiO_2) at 200°C, 10 atm, H_2/CO=2

Study	$\mathrm{TOF}^a\times10^3$ (s^{-1})	$k^b\times10^3$ (s^{-1})	E (kJ/mol)	Reaction order		Comments
				H_2	CO	
This work	15.4±7.4[c]	5.1±2.4	83.2±6.4	0.74±0.06	−0.24±0.03	12% Co/TiO_2, 20 atm, X_{CO}=0.05
[20]	28	8	96			3 and 10% Co/TiO_2
	42	12	142			Low pressure, X_{CO}<0.05, 3–6 h reaction (not at steady state)
[22]	18	5.8				10% Co/TiO_2; 10 atm, X_{CO}=0.36
[21]	17	5.6				20 atm, X_{CO}=0.5; Co on Al_2O_3, SiO_2, TiO_2
[16]	17±14	5.7	102±19	0.7	−0.2	Compilation of 12 studies of Co on Al_2O_3, SiO_2, TiO_2, and other supports. Range of T, P, and X_{CO}

[a] TOF data normalized to 200°C, P_{H_2} =6.67 bar, P_{CO}=3.33 bar using reaction orders of 0.74 and –0.24 for H_2 and CO and E=83 kJ/mol.

[b] Calculated from TOF data at 200°C using reaction orders of 0.74 and –0.24 for H_2 and CO.

[c] All runs at 200°C.

reported in other studies conducted on similar catalysts at 10–20 atm total pressure, i.e., those reported by Duvenhage and Coville [22], Iglesia et al. [21], and Ribeiro et al. [16]. Indeed, TOF data from different laboratories can be considered to be in good agreement if they agree within a factor of two. Accordingly, the TOF data of this study appear to be of high accuracy. It should be emphasized that the comparison of TOF data for Co/TiO_2 with those for Co/Al_2O_3 and Co/SiO_2 is valid, since Iglesia et al. [21] have shown that specific activities of these different catalysts on a site basis are the same within experimental error, if the catalysts are of moderate to high cobalt loading (10–25 wt.%) and well reduced. It is evident that the TOF rates from the study of Reuel and Bartholomew [20] are higher than those obtained in the other studies at high pressure, probably since Reuel and Bartholomew's data were obtained at low partial pressures and early in the reaction before steady state had been reached.

It is remarkable that TOF rates obtained on cobalt catalysts in different laboratories at significantly different temperatures, reactant and product partial pressures, and conversions (see Table 4) agree so closely when properly normalized by temperature and reactant partial pressures. This confirms the validity of using TOF comparisons and strongly supports the concept of TOF for CO hydrogenation on cobalt being structure-insensitive as previously proposed [21,23]. It further suggests that CO conversion and water partial pressure (P_{H_2O} is a function of conversion) have negligible effects on activity within the conditions of these studies. Indeed, the reported activity from this study at 5% CO conversion is the same within experimental error as that reported by Duvenhage and Coville [22] at 36% conversion and those reported by Iglesia et al. [21] at 50% conversion. This is in contradiction to experimental observations reported by Iglesia [5] indicating that the TOF of supported cobalt increases about a factor of two with increasing CO conversion from about 5 to 60%. This increase in activity was reported to be concurrent with increasing partial pressure of product water and was attributed to receding of support films decorating the metal surface at high partial pressures of water or filling of small pores with water [5]. It is possible that the remarkable agreement of TOF rates in Table 4 occurs because most of these rates were measured at steady state for which effects of support decoration and water partial pressure were washed out. It should be emphasized that the effects of metal decoration by reduced TiO_x species are expected to be small for the data in this study, since the catalysts were reduced at only 400°C, a temperature low enough to cause relatively little decoration of metal crystallites in 10% Co/TiO_2 [24].

The activation energy of 83.2 ± 6.4 kJ/mol from this study is the same within experimental error as those obtained in other studies of cobalt catalysts, i.e., 102 ± 19 [16]. Nevertheless, it is substantially lower than the value of 142 kJ/mol reported by Reuel and Bartholomew [20] for FTS on a 10% Co/TiO_2. However, Reuel and Bartholomew's value was obtained at a significantly lower reactant partial pressure and was based on only two data points, while that in this study was based on six data points. It should be emphasized that apparent activation energies based on rate can vary significantly with reactant partial pressures and temperature range. The best comparison would be in terms of rate constants, where available.

The reaction orders of 0.74 and -0.24 for H_2 and CO obtained in this study are consistent with those reported in previous kinetic studies of FTS on supported cobalt [4,14,16]. They agree remarkably well with those found by Ribeiro et al. [16] of 0.7 and -0.2 for H_2 and CO.

4.2. Kinetic models (rate equations) for CO hydrogenation on cobalt

It is widely recognized that simple power law expressions have somewhat limited application to catalytic reactions, i.e., they typically predict rate well over a narrow range of reaction conditions, while Langmuir–Hinshelwood (LH) expressions, because of their fundamental origin, predict rate over wider range of conditions. However, it is unclear which of a number of rate expressions proposed for CO hydrogenation on cobalt (Table 5) provide the best representation of available data. In the most thorough kinetic analysis to-date, Yates and Satterfield [14] fitted their rate data obtained on $Co/MgO/SiO_2$ at 220–240°C as well as rate data obtained by previous investigators on other cobalt catalysts to various LH expressions, finding that these data were best fitted by a relatively simple LH expression, $-r_{CO} = aP_{CO}P_{H_2}/(1+bP_{CO})^2$. Whether this or another expression would best fit data at lower

Table 5
Summary of kinetic studies of the FTS on cobalt catalysts

Study	Catalyst	Reactor type	Operating conditions[a]			Intrinsic kinetic expression[b]
			T (°C)	P (bar)	H_2/Co	
[6]	Co/MgO/ThO_2/kieselguhr	FBR[c]	185–200	1	2	$-r_{H_2+CO} = \frac{aP_{H_2}^2}{P_{CO}}$
[7]	Co/ThO_2/kieselguhr	FBR	186–207	1	0.9–3.5	$-r_{H_2+CO} = \frac{aP_{H_2}^2 P_{CO}}{(1+bP_{H_2}^2 P_{CO})}$
[8]	Co/CuO/Al_2O_3	FBR	235–270	1.7–55	1.0–3.0	$-r_{H_2+CO} = aP_{H_2} P_{CO}{}^{-0.5}$
[9]	Co/La_2O_3/Al_2O_3	Berty (low conversion)	215	5.2–8.4	2	$-r_{H_2+CO} = aP_{H_2}{}^{0.55} P_{CO}{}^{-0.33}$
[10]	Co/Al_2O_3	FBR (low conversion)	250	1	0.2–4.0	$-r_{CO} = \frac{aP_{H_2} P_{CO}{}^{0.5}}{(1+bP_{CO}{}^{0.5})^3}$
[11]	Co/B/Al_2O_3	FBR (low conversion)	170–195	1–2	0.25–4.0	$-r_{CO} = aP_{H_2}{}^{0.68} P_{CO}{}^{-0.5}$
[12]	Co/kieselguhr	Berty	190	2–15	0.5–8.3	$-r_{CO} = \frac{aP_{CO}{}^{0.5} P_{H_2}{}^{0.5}}{(1+bP_{CO}{}^{0.5}+cP_{H_2}{}^{0.5}+dP_{CO})^2}$
[13]						$-r_{CO} = \frac{aP_{CO} P_{H_2}{}^{0.5}}{(1+bP_{CO}+cP_{H_2}^{0.5})^2}$
[14]	Co/MgO/SiO_2	Slurry	220–240	5–15	1.5–3.5	$-r_{CO} = \frac{aP_{CO} P_{H_2}}{(1+bP_{CO})^2}$
[15]	“Co catalysts”	FBR	200–210	1–30	1–10	$-r_{CO} = \frac{aP_{H_2}^{0.6} P_{CO}^{0.65}}{(1+bP_{CO})}$
This study	Co/TiO_2	FBR	200	8–16	1–4	$-r_{CO} = \frac{aP_{H_2}^{0.74} P_{CO}}{(1+bP_{CO})^2}$
This study	Co/TiO_2	FBR	200	8–16	1–4	$-r_{CO} = aP_{H_2}^{0.74} P_{CO}^{-0.24}$

[a] These ranges of operating conditions are estimated from the experimental data provided.
[b] a, b, c, and d in these equations are temperature-dependent constants.
[c] Fixed bed reactor.

reaction temperatures and specifically the data of this study was a question considered further in this study.

Rate expressions proposed in kinetic studies of FTS on cobalt catalysts (Table 5) range from simple power law expressions to fairly complex LH expressions of different forms. A set of six simplified but representative rate models shown in Table 6 (four simplified LH expressions based on previous studies, one LH expression based on this work, and the simple power law expression obtained in this study) were tested against 10 representative data points (Runs 1B, 7B, 9B–10B, and 3C of Table 1): since Run 8B was clearly a statistical outlier it was omitted from this study.

These data were fitted, after the fashion of Yates and Satterfield [14], to these models (Table 6) using a nonlinear optimization least squares fitting routine to obtain values of the constants a and b and the residual sum of squares. Two different nonlinear optimization approaches were explored and found to give comparable results, i.e., the Simplex searching method, the results of which were refined by a modified Powell’s optimization algorithm, and Microsoft’s Excel Solver; the results shown in Tables 7 and 8 and in Fig. 5 were obtained by the last of these methods.

Table 6
Models tested in fitting kinetic data for 11.7% Co/TiO_2

Model	Rate equation	Study
1	$-r_{CO} = \frac{aP_{H_2} P_{CO}}{(1+bP_{CO})^2}$	[14]
2	$-r_{CO} = \frac{aP_{H_2}{}^{0.5} P_{CO}{}^{0.5}}{(1+bP_{CO}{}^{0.5})^2}$	[12]
3	$-r_{CO} = \frac{aP_{H_2}{}^{0.5} P_{CO}}{(1+bP_{CO})^2}$	[13]
4	$-r_{CO} = \frac{aP_{H_2}{}^{0.6} P_{CO}{}^{0.65}}{(1+bP_{CO})}$	[15]
5	$-r_{CO} = \frac{aP_{H_2}{}^{0.74} P_{CO}}{(1+bP_{CO})^2}$	This study
6	$-r_{CO} = aP_{H_2}{}^{0.74} P_{CO}{}^{-0.24}$	This study

Table 7
Calculated kinetic and statistical parameters for six rate models[a]

Model	$a \times 10^3$	$b \times 10^2$	RSS[b] $\times 10^6$	Comments
1	0.50	2.4	2.7	
2	1.9	−6.6	9.7	Negative *K*
3	1.8	4.8	11.1	
4	2.0	7.1	9.8	
5	1.1	4.0	6.7	Best fit to data
6	4.0	–	13.7	Fair non-linear fit

[a] Models listed in Table 6.
[b] Residual sum of squares.

Values of the calculated constants *a* and *b* and residual squared sums (residual sum of squares) or RSS values for the nonlinear optimization fits for each of the six models are listed in Table 7. It is evident that the RSS is lowest for Model 5, the LH rate equation proposed in this study, indicating that this rate form provides the very best fit to the selected data. The RSS values for Models 2–4 are all approximately 50% larger than that for Model 5 indicative of lower precision in fitting the data; the negative value of *K* for Model 2 suggests this is not a physically mean-

Table 8
Comparison of experimental and calculated TOF data for 11.7% Co/TiO$_2$

$(\mathrm{TOF})_{\mathrm{exptl}} \times 10^3$ (s^{-1})[a]	Calculated TOF data from models $\times 10^3$ (s^{-1})[b]					
	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
20.1	23.2	19.1	19.3	20.3	20.9	20.3
17.9	19.9	17.6	17.8	18.5	18.8	18.1
14.0	13.3	14.4	14.6	14.5	14.1	13.4
14.3	13.3	14.4	14.6	14.5	14.1	13.4
19.3	18.3	18.9	18.7	17.6	18.5	12.7
12.4	10.4	12.0	11.9	12.5	11.4	15.0
7.4	6.6	10.2	10.3	9.6	8.7	8.0
9.4	7.2	9.3	8.6	9.9	8.2	15.8
14.5	13.3	14.4	14.6	14.5	14.1	13.4
18.8	18.3	18.9	18.7	17.6	18.5	12.2

[a] Experimental data.
[b] Models are shown in Table 6.

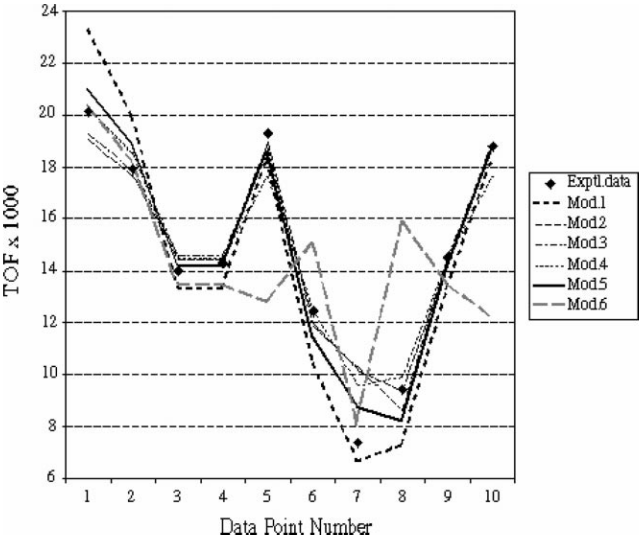

Fig. 5. Comparison of calculated and experimental TOF rate data for disappearance of CO at 200°C; conditions correspond to those listed for Runs 1B through 10B (Run 8B excepted) and 3C in Table 1.

ingful representation of the data. The factor of four larger RSS values for Model 1 relative to Model 5 indicates the former is a significantly less reliable model. The RSS for Model 6 (simple power law expression), however, is the highest (20 times higher than that for Model 5), indicating that this form is not a reliable representation of the data (especially for Data Points 5, 8, and 10). Indeed, these differences in goodness of fit among Models 1–6 in comparison with the experimental data of this study are evident in Fig. 5 and in the comparison of experimental and calculated TOF data in Table 8. Since the data of this study are best fitted by the Model 5 rate expression and since it is similar to Model 1 which also provides a good fit of the high temperature data of Yates and Satterfield [14] and of data from three other investigations over a range of conditions including a wide range of P_{CO} [14], we conclude that Model 5 is capable of fitting rate data for FT synthesis on cobalt catalysts over a wide range of conditions.

5. Conclusions

1. Rates of CO hydrogenation on a well-characterized 11.7% Co/TiO_2 catalyst measured after 20 h of reaction in a differential fixed-bed reactor at 20 atm, 180–240°C, and 5% conversion, over a range of reactant partial pressures, can be used to model precisely and accurately the kinetics of this reaction.
2. Turnover frequencies and rate constants determined from this study are in very good to excellent agreement with those obtained in previous studies of Co/TiO_2 and other cobalt-support combinations, when the data are normalized to the same conditions of temperature and partial pressures of the reactants. Based on this comparison it is concluded that CO conversion and the partial pressure of product water have little effect on specific rate per catalytic site.
3. The data of this and other studies are fitted fairly well by a simple power law expression of the form $-r_{CO} = kP_{H_2}{}^{0.74}P_{CO}{}^{-0.24}$, where k=5.1×10^{-3} at 200°C, P=10 atm, and H_2/CO=2/1.
4. The data of this study are best fitted by the simple LH rate form $-r_{CO} = aP_{H_2}^{0.74}P_{CO}/(1 + bP_{CO})^2$ in comparison to fits of the same data by several other representative LH rate forms proposed in previous studies.

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