

## II. THE INTRINSIC KINETICS OF THE FISCHER-TROPSCH SYNTHESIS ON A COBALT CATALYST

### Abstract

The rate of synthesis gas consumption over the catalyst was measured at 220 to 240°C, 0.5 to 1.5 MPa, H<sub>2</sub>/CO feed ratios of 1.5 to 3.5 and conversions of 6 to 68% of hydrogen and 11 to 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:

$$-R_{H_2+CO} = \frac{a P_{CO} P_{H_2}}{(1 + b P_{CO})^2}$$

The apparent activation energy was 93 to 95 kJ/mol. Data from previous studies on cobalt-based Fischer-Tropsch catalysts are also well correlated with this rate expression.

### II. A. Introduction

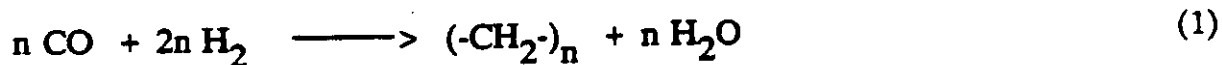
A number of kinetic studies of the Fischer-Tropsch synthesis over cobalt catalysts have been performed.<sup>1-8</sup> All of the expressions found to fit rate data on these catalysts show that carbon monoxide inhibits the rate of synthesis. However, a wide array of proposed forms for the rate expression 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 for this part of the study 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, one-liter, continuous-flow, slurry reactor was used. The reactor behaves as a CSTR, providing data at uniform temperature and composition which are easy to analyze.

## II. B. Background

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



Cobalt is not very active for the water-gas-shift reaction<sup>9</sup>; 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,  $-R_{\text{H}_2+\text{CO}}$ . Some previous studies report the rate of conversion of carbon monoxide only,  $-R_{\text{CO}}$ . If the extent of water-gas-shift is negligible, the two rate measures,  $-R_{\text{H}_2+\text{CO}}$  and  $-R_{\text{CO}}$ , 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 II-1. The rate expressions of Yang et al.<sup>3</sup>, Pannell et al.<sup>4</sup>, and Wang<sup>6</sup> were all developed by regression of a power-law equation of

the general form:

$$-R = aP_{H_2}^b P_{CO}^c \quad (2)$$

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

Anderson<sup>2</sup> found the equation developed by Brötz<sup>1</sup> to be inadequate for data over a wide range of inlet H<sub>2</sub>/CO ratios. From data taken in a fixed-bed at atmospheric pressure over a wide range of H<sub>2</sub>/CO ratios and temperatures, Anderson and co-workers at the Bureau of Mines<sup>10</sup> (Storch et al., 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, Anderson<sup>2</sup> (p. 270) and Storch et al. report that eq 4 does not satisfactorily fit the data at high values of  $P_{H_2}^2 P_{CO}$ . 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  $P_{H_2}^2 P_{CO}$ .

Rautavuoma and van der Baan<sup>5</sup> studied the rate of reaction 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 "-CH<sub>2</sub>-" surface intermediate. The formation of this surface intermediate is the rate determining step. The model also 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 H<sub>2</sub> in the denominator of the rate expression.

In the most recently-published work, Sarup and Wojciechowski<sup>7</sup> 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<sub>2</sub>O plus CO<sub>2</sub>. A wide range of values of P<sub>H<sub>2</sub></sub> and P<sub>CO</sub> 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 Wojciechowski<sup>7</sup> and reviewed by Wojciechowski<sup>8</sup>.

The general form of rate expression which they propose is:

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

In eq 11, k is a kinetic parameter, a and b are the reaction orders of the rate-controlling step, K<sub>i</sub> represents an adsorption parameter for the i<sup>th</sup> adsorption term, and c<sub>i</sub> and d<sub>i</sub> describe the dependence of surface coverage of the i<sup>th</sup> adsorption term on the reactant partial pressures. All of the possible reaction mechanisms considered by Sarup and Wojciechowksi involve a bimolecular surface reaction, 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<sub>i</sub>. 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 II-1) and eq 12 (Sarup and Wojciechowski's models 1, 5, and 6, respectively).

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

a, b, c, and d in eq 9, 10, and 12 are model-specific, temperature-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 the 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 re-regress the data, making the final form of the equation:

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

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

## II. C. Experimental Section

In this study, the experiments were performed in a continuous, mechanically-stirred, one-liter autoclave. The slurry reactor and ancillary equipment are described in detail elsewhere<sup>11</sup>. 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<sup>11,12,13</sup>, as indicated by the lack of effect of stirring rate and other variables<sup>12</sup>. Calculations as described by Satterfield<sup>14</sup> 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<sub>2</sub>. This catalyst was prepared for us by an outside laboratory and is of the approximate composition of the cobalt catalysts used at Ruhrchemie<sup>10</sup>. 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 to 92 μm (170 to 270 ASTM Mesh). Following sieving, 17 grams of the catalyst were placed in a tubular reduction vessel. The catalyst was held in this reduction unit with 7 μm stainless-steel sintered frits while hydrogen (prepurified, MedTech Gases, Inc.) was brought on-stream at a flow of 1.36 Nl/min (approximately 10,000 V/V/hr). At this flow rate, the pressure in the vessel was 0.79 MPa. The temperature of the reduction tube was increased steadily from 25°C to 330°C over 4 hours 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 hours 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 one-liter 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 NI/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 pass through a 13 X molecular sieve, an activated carbon trap, and a 2  $\mu$ 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 hours and then the reactor temperature was increased to 240°C over a period of 7 hours. The reactor was then kept at 0.79 MPa, 240°C, and  $H_2/CO=2.0$  at a flow rate of 2.0 NI/min for 72 hours 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 to 24 hours, with at least 12 hours allowed between material balances to ensure steady-state operation. When the reactor temperature or pressure was changed, at least 48 hours were allowed between material balances.

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 non-condensed 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<sup>12,15</sup>. Table II-2 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<sub>2</sub>/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 NI/min/g of catalyst (unreduced basis).

Products were analyzed with three gas chromatographs, as described by Huff et al.<sup>16</sup>. A Hewlett-Packard 5880 with a dimethyl silicone capillary column and flame ionization detector (FID) was used for hydrocarbon analyses of non-condensable gases and the organic phases from the hot and cold traps. Aqueous liquid samples from the hot and cold traps, and non-condensed 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 of non-condensable gases, particularly H<sub>2</sub>, CO, and CO<sub>2</sub>. Tie components, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub> and C<sub>3</sub> 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 H<sub>2</sub> 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 H<sub>2</sub>/CO usage ratio with reaction conditions. This averaged slightly above 2.

#### II. D. Results and Discussion

The forms of eq 3-13 all have subtle differences in their functional dependence on



$P_{H_2}$  and  $P_{CO}$ , so experiments were run over a broad range of  $H_2/CO$  ratios in an attempt to avoid a covariance between these two independent variables of regression.

Figures II-1 and II-2 are plots of  $P_{H_2}$  versus  $P_{CO}$  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. co-vary), for example  $bP_{CO}^n$  and  $dP_{CO}$  in eq 9. Thus, the addition 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<sup>17</sup>. There, it is shown that the inhibiting effects of  $H_2O$  on the synthesis had been incorrectly attributed to  $CO_2$  by previous researchers, as a result of the high degree of correlation between  $P_{H_2O}$  and  $P_{CO_2}$ .

Eq 4 and eq 7 both contain only two parameters and are thus examined as possible rate expressions without modification. Eq 9, eq 10, and eq 12 contain more than two adjustable parameters. In the case of eq 10 and eq 12, it was assumed that CO was the predominant surface species, which is justified by non-reacting, single-component adsorption data on cobalt surfaces<sup>18</sup>; these data indicate that 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 Wojciechowski<sup>7</sup> when they removed the constant d from eq 9 and re-regressed their data. The following equations represent the simplified, two-parameter forms of eq 9, 10, and 12:

$$-R_{\text{CO}} = \frac{aP_{\text{CO}}^{1/2}P_{\text{H}_2}^{1/2}}{(1 + bP_{\text{CO}}^{1/2})^2} \quad (14)$$

$$-R_{\text{CO}} = \frac{aP_{\text{CO}}P_{\text{H}_2}^{1/2}}{(1 + bP_{\text{CO}})^2} \quad (15)$$

$$-R_{\text{CO}} = \frac{aP_{\text{CO}}P_{\text{H}_2}}{(1 + bP_{\text{CO}})^2} \quad (16)$$

In eq 14-16,  $a$  and  $b$  are assumed to be temperature dependant constants,  $a$  representing a kinetic parameter and  $b$  an adsorption coefficient.

Eq 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 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 follows:

$$\frac{P_{H_2}^2 P_{CO}}{-R_{H_2+CO}} = \frac{1}{a} + \frac{b P_{H_2}^2 P_{CO}}{a} \quad (17)$$

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

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

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

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

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 II-3 through II-7 show plots of the data at 240°C according to the five linearized

forms given by eq 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 II-3 gives R-squared values for the fit of the data to the linearized forms of 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 II-4 shows the results of nonlinear regression of the data which confirms that eq 16 fits the data best. Table II-5 presents the parameter values and some related regression information for the fit of eq 16 to the data from this study. The parameters  $a$  and  $b$  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  $P_{H_2}$  and  $P_{CO}$  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 apparent activation energies reported previously: 102 kJ/mol calculated by Anderson<sup>2</sup> (p.266) from data of Fischer and Pichler<sup>19</sup>, 103 kJ/mol reported by Storch et al.<sup>10</sup> (p.530), 96 kJ/mol calculated by Anderson<sup>2</sup> (p.266) from data of Gibson and Hall<sup>20</sup>, and 84 kJ/mol reported by Anderson<sup>2</sup> (p.265). These apparent activation energies were calculated from the slope

of plots of the logarithm of the rate of reaction versus the reciprocal of absolute temperature for data collected at similar pressures, feed rates and feed compositions. Yang et al.<sup>3</sup> 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 to 103 kJ/mol. This is perhaps surprising considering the wide range of conditions that were studied.

Figure II-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.

## II. E. Comparison to Literature Data

Data from three of the studies listed in Table II-1 are available in the literature<sup>5,6,8</sup>. Having developed a two-parameter 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 examine goodness-of-fit and to look for outlying data points.

Figure II-9 shows the data of Rautavuoma and van der Baan<sup>5</sup>, Figure II-10 the data of Wang<sup>6</sup> (pp.100-101), and Figure II-11 the data of Sarup and Wojciechowski<sup>8</sup>. All three sets of data fit the linear relationship of eq 21 well and have positive slopes and intercepts, as would be expected.

## **II. F. 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. Eq 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 to 103 kJ/mol.

## II.G. Nomenclature

- a -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 hydrogen plus carbon monoxide or carbon monoxide, mmol/min/g of catalyst (unreduced basis).
- $-R_{H_2+CO}$  -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).

## II.H. Literature Cited

- (1) Brötz, W. Z. Elektrochem. 1949, 53, 301.
- (2) Anderson, R.B. In Catalysis; Emmett, P.H., Ed., Reinhold: New York, 1959; Vol. IV, pp. 257-283.
- (3) Yang, C.-H.; Massoth, F.E.; Oblad, A.G. Adv. Chem. Ser. 1979, 178, 35.
- (4) Pannell, R.B.; Kibby, C.L.; Kobylinski, T.P. Proc. 7th Int. Cong. on Catal. Tokyo, 1980, p. 447.
- (5) Rautavuoma, A.O.I.; van der Baan, H.S. Appl. Catal. 1981, 1, 247.
- (6) Wang, J., Ph.D. Thesis, Brigham Young University, Provo, Utah, 1987, p. 99.
- (7) Sarup, B.; Wojciechowski, B.W. Can. J. Chem. Eng. 1989, 67, 62.
- (8) Wojciechowski, B.W. Catal. Rev.-Sci. Eng. 1988, 30, 629.
- (9) Newsome, D.S. Catal. Rev.-Sci. Eng. 1980, 21, 275.
- (10) Storch, H.H.; Golumbic, N.; Anderson, R.B. The Fischer-Tropsch and Related Syntheses, Wiley, New York, 1951, p. 529.
- (11) Huff, G.A., Jr.; Satterfield, C.N. Ind. Eng. Chem. Fundam. 1982, 21, 479.
- (12) Huff, G.A., Jr., Sc.D. Thesis, M.I.T., Cambridge, Massachusetts, 1982.
- (13) Huff, G.A., Jr.; Satterfield, C.N. Ind. Eng. Chem. Process Des. Dev. 1984, 23, 696.
- (14) Satterfield, C.N., Mass Transfer in Heterogeneous Catalysis, reprint edition, Krieger Publishing Company, Inc., Malabar, Florida, 1981.
- (15) Donnelly, T.J.; Yates, I.C.; Satterfield, C.N. Energy Fuels 1988, 2, 734.



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

(17) Yates, I.C.; Satterfield, C.N. Ind. Eng. Chem. Res., 1989, 28, 9.

(18) Vannice, M.A. Catal. Rev.-Sci. Eng. 1976, 14, 153.

(19) Fischer, F.; Pichler, H. Brennstoff-Chem. 1939, 7, 97.

(20) Gibson, E.J.; Hall, C.C. J. Appl. Chem. 1954, 4, 49.