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Kinetics of the Methanation of CO and CO_2 on a Nickel Catalyst

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The kinetics of the methanation of CO_2 in H_2 on a supported nickel catalyst have been measured at partial pressures of CO_2 below 0.02 atm and at atmospheric pressure and at temperatures between 200 and 230°C. The methanation of CO was studied in the same concentration range, between 170 and 210°C.

The results can be described by rather simple Langmuir-type rate equations:

$$r_{CO_2} = \frac{1.36 \times 10^{12} \cdot \exp(-25\,300/RT) \cdot p_{CO_2}}{(1 + 1270 \cdot p_{CO_2})} \text{ mol hr}^{-1}\text{ g}^{-1}$$

and

$$r_{CO} = \frac{2.09 \times 10^{5} \cdot \exp(-10\,100/RT) \cdot p_{CO}}{(1 + 4.56 \times 10^{-4} \cdot \exp(+12\,400/RT) \cdot p_{CO})^2} \text{ mol hr}^{-1}\text{ g}^{-1}$$

Experiments at 200°C show that CO poisons the methanation of CO_2 in concentrations larger than 200 ppm. Water and methane in small concentrations have no effect on the reaction rate.

The results of this study are in good agreement with data published previously. Some mechanistic implications of the kinetic data are discussed.

INTRODUCTION

Crude hydrogen or ammonia synthesis gas produced by, e.g., hydrocarbon/steam reforming or partial oxidation of hydrocarbons, followed by CO shift and absorption of CO_2, still contains about 0.5%* of carbon oxides. These impurities are usually removed by hydrogenation to methane on a supported nickel catalyst to avoid poisoning of catalysts used in subsequent processes such as the synthesis of ammonia. The stoichiometric equations involved are:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (\Delta H_r^0 = -49 \text{ kcal/mol CO}),$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (\Delta H_r^0 = -39 \text{ kcal/mol } CO_2).$$

Several papers have been published on the kinetics of the above reactions (*1–8*). Most of these [e.g., (*1, 2*)] deal with the methanation of carbon oxides in concentrations between 20 and 70%, where the object is to produce methane-rich fuel gases. Very little is known, however, about the rates of hydrogenation of traces of CO and CO_2 such as practiced for hydrogen production. When hydrogenating CO on nickel Vlasenko, Yuzefovich, and Rusov (*3*) found a zero order dependency of the rate on the partial pressure of carbon monoxide between 135 and 175°C and at concentrations below 0.3% in hydrogen. The total pressure was always 1 atm. Schoubye (*4*), on the other hand, found a negative order in CO which decreases from

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* In this paper concentrations in % refer to vol %.

zero to −0.5 with increasing CO concentration. His experiments were carried out under the following conditions: 0.1–20% CO in hydrogen, 160–300°C and a total pressure of 1–15 atm. He described his results with the equation:

$$r = \frac{k_\infty \cdot \exp(-E/RT) \cdot p_{H_2}{}^n}{(1 + K_\infty \cdot \exp(16\,650/RT) \cdot p_{CO}/p_{H_2})^{0.5}},$$

E varies from 18 to 28 kcal; a typical value for n is 0.15.

Vlasenko, Rusov, and Yuzefovich (*5*) also studied the kinetics of hydrogenating low concentrations of carbon dioxide. They found a first order dependency in CO_2, varying the temperature from 125 to 325°C and the concentration from 0.05 to 0.4% CO_2 in hydrogen. Again, all the experiments were performed at a total pressure of 1 atm.

Vlasenko *et al.* have published data on the hydrogenation of mixtures of the oxides on nickel (*6*). Their qualitative conclusion is that CO_2 does not influence the hydrogenation of CO whereas CO is a strong poison for the hydrogenation of CO_2. This is confirmed by Campbell, Graven, and Young (*9*) who report that concentrations of carbon monoxide above 200–300 ppm inhibit the hydrogenation of carbon dioxide. Rehmat and Randhava (*7*) use this fact to methanate CO selectively in the presence of CO_2.

In this study, the hydrogenation kinetics of the separate carbon oxides are first examined and then the behavior of mixtures is compared with these kinetics. This work is part of a more extensive investigation into the dynamic behavior of tubular fixed-bed catalytic reactors. Since the experiments on reactor dynamics will be carried out at atmospheric pressure, the kinetic work reported in this paper also relates to that pressure. The results can, therefore, not be used at hydrogen partial pressures other than approximately 1 atm.

THEORY

The methanation of CO or CO_2 in hydrogen has some special features which make it possible to describe beforehand what type of kinetic equation might be expected. We have used the assumption of localized Langmuir chemisorption which leads to kinetic equations known as Langmuir-Hinshelwood kinetics, as Eley-Rideal mechanisms and also as Hougen-Watson models. Following the approach of Yang and Hougen (*10*) the general form of the kinetic equation can be written as:

$$r = \frac{k_\infty \cdot \exp(-E/RT) \cdot g(\mathbf{p}) \cdot (1 - \beta)}{(1 + f(\mathbf{p},T))^m}. \quad (1)$$

In this equation, $g(\mathbf{p})$ is the pure kinetic term which is followed by a correction for the deviation from thermodynamic equilibrium, $(1 - \beta)$. In the denominator, $f(\mathbf{p},T)$ originates from the coverage balance over the active sites and m is the number of sites involved in the rate-determining step.

Calculation of the equilibrium compositions shows that for CO as well as for CO_2 the conversion is complete up to 400°C (*2*). This means that the value of β is so small that it can be neglected. Similarly, $g(\mathbf{p})$ is only a function of the partial pressures of hydrogen and the carbon oxide, provided that the effects of the reaction products in the numerator need not be taken into account. Furthermore, the partial pressure of hydrogen is very large compared to that of the carbon oxide and as a consequence $g(\mathbf{p})$ is a function of the carbon oxide concentration only. For the same reason the contribution of hydrogen to the denominator can be neglected. When one supposes that dissociative adsorption of CO, CO_2, CH_4 or H_2O does not occur, a simplified rate equation is obtained. For the methanation of CO one finds:

$$r = \frac{k_\infty \cdot \exp(-E/RT) \cdot p_{CO}}{(1 + K_{CO} \cdot p_{CO} + K_{H_2O} \cdot p_{H_2O} + K_{CH_4} \cdot p_{CH_4})^m}. \quad (2)$$

When reactants only are present this equation becomes:

$$r = \frac{k \cdot p_{CO}}{(1 + K_{CO} \cdot p_{CO})^m}. \quad (3)$$

For CO_2 a similar equation is obtained. The adsorption constants in the equations depend on the temperature.

We have applied Eq. (3) to data produced with the aid of the technique of measuring initial reaction rates. This method combines the advantages of the differential method and the integral method by measuring several points of the curve of the conversion ξ versus the space time, W/F, followed by extrapolation of this line to the origin. The slope of the curve in the origin, i.e., the reaction rate corresponding to the feed conditions, was determined by fitting a straight line through the origin to those points which, by visual inspection, were still in the linear region. The reciprocal space velocity, W/F, is defined as the quotient of the catalyst weight W divided by the molar flow F of the carbon oxide. The necessary calculations were performed with the aid of the criterion of least squares. For the best slope for a straight line through the origin one can derive:

$$r = \frac{\Sigma \xi_i (W/F)_i}{\Sigma (W/F)_i^2}. \qquad (4)$$

After a kinetic equation had been found for the reaction rates of CO or CO_2 in hydrogen, measurements were carried out using a feed containing a mixture of CO and CO_2. The possible influence of the reaction products, CH_4 and H_2O, on the rate of hydrogenation were also studied.

EXPERIMENTAL METHODS

Materials. The nickel on carrier catalyst was G-65 obtained from Girdler-Südchemie, Munich. It was deduced from the X-ray pattern that its carrier material is γ-alumina. The catalyst contains 33.6 wt % NiO and has a BET surface area of 40 m^2/g. For each run 2.4 g crushed commercial catalyst of particle size 0.35–0.42 mm was mixed with 0.5 g quartz of the same size. The gases used were of commercially available "chemically pure" quality. They were dried separately over molecular sieve 3A.

Equipment. Figure 1 shows a flow sheet of the equipment. Application of Brooks ELF precision flow controllers for CO and CO_2 makes it possible to mix a few ml/min of these gases with a hydrogen stream of 1000 to 1500 ml/min without any measurable fluctuations in the concentrations. The flows were measured by means of the pressure drop over a capillary placed in thermostat (*1*). The mixed gases were then led over a B.T.S. catalyst to remove traces of oxygen (*2*). The tubular reactor (volume, 4 ml) was placed in a fluid bed acting as a thermostatic bath (*3*). The length of the reactor was about 125 times the particle size and the diameter about 25 times, which ensured a good approach to plug flow. With sampling valve (*4*) samples of feed and product gases could be injected into gas chromatograph (*5*) which separated the components over a 6 m active carbon column using hydrogen as the carrier gas.

The conversion to methane was calcu-

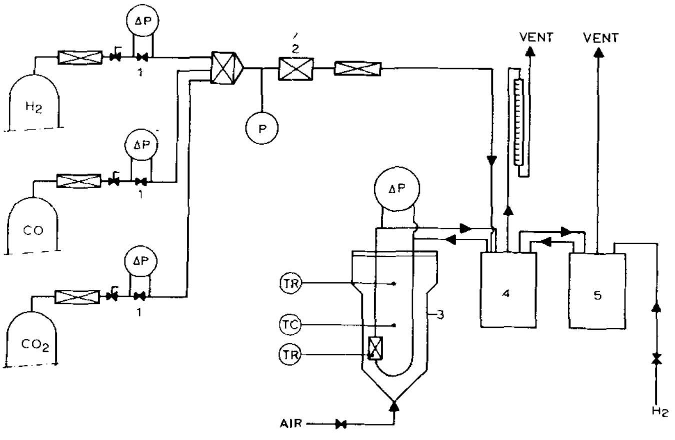

FIG. 1. Simplified flow sheet of the equipment.

lated from the CO/CH_4 and/or the CO_2/CH_4 ratio in the product gas. The mass balance was checked by analysis of the feed.

Procedure. The catalyst was reduced with hydrogen at 350°C for 16 hr and then deactivated until a constant activity was reached. Deactivation was accomplished with either 1% CO in hydrogen at 200°C or 1.4% CO_2 in hydrogen at 220°C. The conversion as a function of time shown in Fig. 2 became constant within a few hours when hydrogenating CO_2 but in the case of CO the catalytic activity continued to decrease. However, after 70 hr the changes became very small so that it was possible to correct for the deactivation by occasional measurements under the standard conditions mentioned above.

RESULTS

Hydrogenation of CO_2

The rate of hydrogenation of carbon dioxide was measured at 200, 215 and 230°C in the concentration range 0.22–2.38% in hydrogen; the total pressure was 1 atm. The graph of conversion versus the reciprocal space velocity W/F_{CO_2} shows a definite curvature for large conversions (cf. Fig. 3). Therefore only points below 60% were used when calculating the initial rate according to Eq. (4).

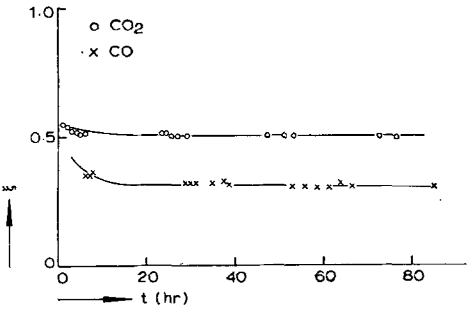

FIG. 2. Conversion, ξ, as a function of time during deactivation with 1% CO in hydrogen at 200°C or 1.4% CO_2 in hydrogen at 220°C.

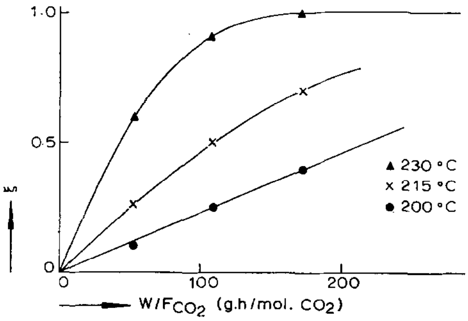

FIG. 3. Example of measured conversions as a function of the reciprocal space velocity ($x_{CO_2} = 0.015$).

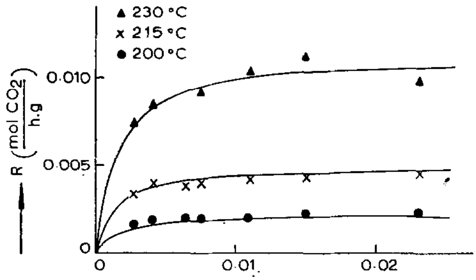

FIG. 4. Initial rates of CO_2 methanation. Points represent measured values. Lines are calculated values from model I with the parameter values in Table 2.

In Fig. 4 the rates are given as a function of the partial pressure of CO_2. The results show a change from first order dependency below 0.004 atm to zero order dependency at partial pressures above 0.015 atm. They can be described with the Langmuir isotherm, which means that Eq. (3) holds, with m equal to 1. Transformation of this equation gives:

$$1/r = 1/kp_{CO_2} + K_{CO_2}/k. \qquad (5)$$

To test the applicability of Eq. (5) a polynomial regression analysis was made for $1/r$ as a function of $1/p_{CO_2}$. It appears that the first degree polynomial gives the best description at the three temperatures (see Fig. 5). From the slope of the lines and the intercepts the values of k and K_{CO_2} can be calculated:

T (°C)	k [mol/(g hr atm)]	K_{CO_2} (atm^{-1})
200	2.00	844
215	4.35	936
230	7.65	669

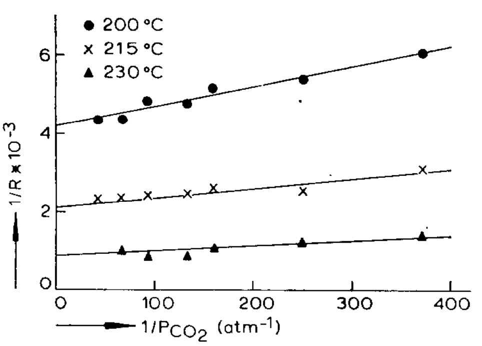

FIG. 5. Langmuir plot of $1/r_{CO_2}$ against the reciprocal partial pressure, $1/p_{CO_2}$.

It follows that rate constant k is strongly temperature dependent but that K_{CO_2} can be constant. Therefore the equation used to describe all the data points is:

$$\text{I} \qquad r = \frac{k_\infty \cdot \exp(-E/RT) \cdot p_{CO_2}}{1 + K_{CO_2} \cdot p_{CO_2}}. \tag{6}$$

With a nonlinear regression routine the best values of the parameters were then determined, minimizing the sum of squares of the deviations between the measured and the computed values.

Apart from the model described by Eq. (6) more complicated models were tested. The first extension was the introduction of temperature dependency of the adsorption constant K_{CO_2}:

$$\text{II} \quad r = \frac{k_\infty \cdot \exp(-E/RT) \cdot p_{CO_2}}{1 + K_\infty \cdot \exp(-\Delta H/RT) \cdot p_{CO_2}}. \tag{7}$$

In a third model the value of the exponent of the denominator was allowed to vary:

$$\text{III} \quad r = \frac{k_\infty \cdot \exp(-E/RT) \cdot p_{CO_2}}{(1 + K_\infty \cdot \exp(-\Delta H/RT) \cdot p_{CO_2})^m}. \tag{8}$$

The use of this model can give some idea about the sensitivity towards m. Of course only integer values can have a physical meaning.

The results of the regression calculations on these three models are given in Table 1. Since the differences in the variances are not significant it must be concluded from a statistical point of view that it is impossible to say that one of the models describes the data best. Therefore model III will be discarded because apparently a variable value for m does not improve the regression significantly and, moreover, the value found is close to unity.

The calculation for the initial rate involved an arbitrary maximum conversion level of 60%, which can cause low estimates of some reaction rates, especially for the measurements at 230°C. In order to eliminate these errors another regression analysis was made on the measured conversion points for the analytically integrated models I and II. The minimum was sought of the sum of squares of the differences between calculated and measured conversions. From these calculations it follows that, although model II has the smallest variance, the difference between s_I^2 and s_{II}^2 is again not significant.

Model I is preferred because of its physical simplicity and, since the regression on

TABLE 1
RESULTS OF THE REGRESSION ON THE REACTION RATES FOR CO_2

Parameter	Model I	Model II	Model III	Dimensions
k_∞	1.71×10^{12}	3.96×10^{10}	9.58×10^{10}	mol CO_2/(hr g atm
E	26.1	22.3	23.5	kcal/mol
K	7.02×10^2	—	—	atm^{-1}
K_∞	—	8.58	18.1	atm^{-1}
ΔH	—	-4.37	-3.10	kcal/mol
m	1	1	1.11	—
Sum of squares of residuals	2.79×10^{-6}	2.75×10^{-6}	2.61×10^{-6}	
Variance about regression	1.64×10^{-7}	1.72×10^{-7}	1.74×10^{-7}	

TABLE 2
RESULTS OF THE REGRESSION ON THE CONVERSIONS FOR CO_2

Parameter	Model I	Model II	Dimensions
k_∞	1.36×10^{12}	7.87×10^{14}	mol CO_2/(hr g atm)
E	25.3	31.6	kcal/mol
K	1.27×10^{3}	—	atm^{-1}
K_∞	—	2.51×10^{6}	atm^{-1}
ΔH	—	7.45	kcal/mol
Sum of squares of residuals	1.07×10^{-1}	1.04×10^{-1}	
Variance about regression	1.56×10^{-3}	1.53×10^{-3}	

the measured conversions is more realistic than the regression on the initial rates, we choose as the best description of the kinetics:

$$r = \frac{1.36 \times 10^{12} \cdot \exp(-25\,300/RT) \cdot p_{CO_2}}{(1 + 1270 \cdot p_{CO_2})} \quad \text{mol hr}^{-1}\,\text{g}^{-1}. \quad (9)$$

The calculated rates are shown in Fig. 4.

Finally, we tested whether the values for the apparent activation energy E_a calculated from the models agree with the values found from the measured rates. The apparent activation energy is defined (*11*) as:

$$E_a(\mathbf{p}) = -R \cdot \left.\frac{\partial \ln(r(\mathbf{p}))}{\partial 1/T}\right|_{\mathbf{p}}.$$

When this operation is applied to Eq. (8) a relation between the apparent activation energy and the surface coverage is found:

$$E_a = E - \frac{K_\infty \cdot \exp(-\Delta H/RT) \cdot p_{CO_2}}{1 + K_\infty \cdot \exp(-\Delta H/RT) \cdot p_{CO_2}} \times m \cdot \Delta H = E - m \cdot \theta_{CO_2} \cdot \Delta H. \quad (10)$$

For model I, which can be interpreted as model III with ΔH equal to zero and m equal to 1, E_a must be independent of coverage and therefore independent of temperature and pressure. The apparent activation energy was calculated from the measurements for one value of the partial pressure of carbon dioxide by finding the values of A and E_a that minimize

$$Q = \sum_{j=1}^{3} [r_j(\mathbf{p}) - A \cdot \exp(-E_a/RT_j)]^2. \quad (11)$$

Since only three points are used for each calculation a high accuracy cannot be expected. The results of these calculations are shown in Fig. 6 along with the lines obtained from models I and II. It follows that the activation energy does not depend very strongly, if at all, on the experimental conditions.

Hydrogenation of CO

The initial rates of carbon monoxide hydrogenation were determined in the temperature range 170–210°C at atmospheric pressure. The conversion ξ was determined as a function of the reciprocal space velocity for 17 concentrations in the range 0.22–2.38% CO in hydrogen. As an example the results are given in Fig. 7 for 0.65% CO. The lines shown in Fig. 7 are straight up to 95% conversion; such excellent linearity was found at all concentrations which sug-

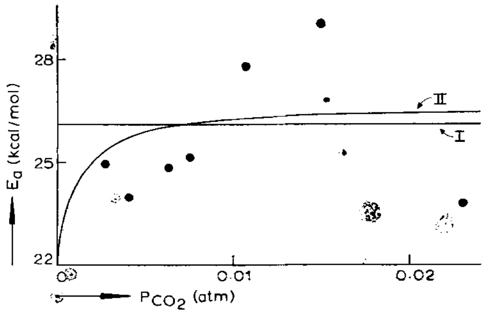

FIG. 6. Apparent activation energy E_a as a function of p_{CO_2}. Points: values calculated from initial rates. Lines: correspond to models I and II, with parameter values in Table 1.

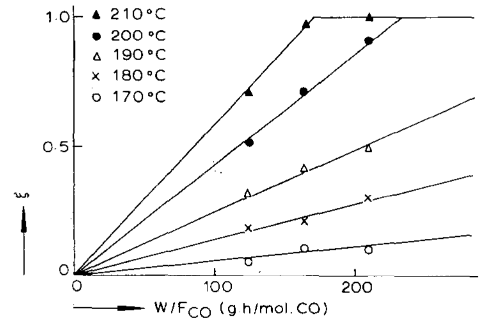

FIG. 7. Example of measured conversions as a function of W/F_{CO} ($x_{CO} = 0.0065$).

gests zero order kinetics. If, however, the slopes of the lines are plotted as a function of p_{CO} it appears that the rate varies with the partial pressure of CO. The presence of a maximum at CO pressures between 0.002 and 0.005 atm is quite evident (Fig. 8). Regression of $1/r$ as a function of $1/p_{CO}$ does not give satisfactory results because a polynomial of at least the third degree is needed to describe the measured rates.

The appearance of a maximum rate is rather intriguing and the question arises whether Eq. (3) can indeed describe the presence of this extremum. There are two conditions that must be fulfilled:

$$\frac{\partial r}{\partial p_{CO}}\bigg|_T = 0 \quad \text{for} \quad \begin{cases} p_{CO} = p_{CO_{max}} \\ p_{CO} \to \infty \end{cases}. \tag{12}$$

Differentiation of Eq. (3) leads to:

$$\frac{\partial r}{\partial p_{CO}}\bigg|_T = \frac{k}{(1 + K_{CO}\cdot p_{CO})^m} \cdot \left(1 - \frac{m \cdot K_{CO}p_{CO}}{1 + K_{CO}p_{CO}}\right) = 0.$$

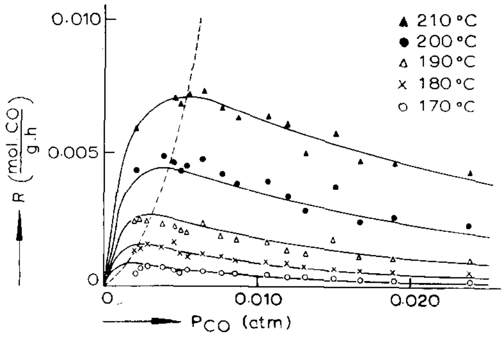

FIG. 8. Initial rate of methanation of CO. Lines were calculated from model I. Broken line represents calculated maximum rates.

The second condition of Eq. (12) is invariably satisfied since m is always positive. The first condition produces a relation for $p_{CO}{}^{max}$:

$$p_{CO_{max}} = \frac{1}{(m - 1)\cdot K_{CO}}. \tag{13}$$

It appears from Eq. (13) that a maximum occurs only when $m \neq 1$. This is in line with the fact that neither the rate data nor the rate equation for CO_2 hydrogenation, where 1.0 was found to be the right value for m, show a maximum.

Apart from one, two is an obvious choice for m, which means that a dual-site step should control the reaction rate:

$$r = \frac{k \cdot p_{CO}}{(1 + K_{CO}\cdot p_{CO})^2}. \tag{14}$$

This relation can be written as:

$$\left(\frac{p_{CO}}{r}\right)^{1/2} = \frac{1}{(k)^{1/2}} + \frac{K_{CO}}{(k)^{1/2}} \cdot p_{CO}$$

Regression analysis of the left side as a function of p_{CO} showed that, for three of the five temperatures, a first degree polynomial gives the best fit and that the other two are described quite satisfactorily by a first degree polynomial. The values for k and K_{CO} can be calculated from the coefficients. K can also be calculated from the position of the maximum rate with Eq. (13), although this procedure gives less accurate results.

	From linear regression		From maximum rate	
T (°C)	k [mol/(g hr atm)]	K_{CO} (atm^{-1})	K_{CO} (atm^{-1})	$p_{CO_{max}}$ (atm)
170	0.94	403	333	0.003
180	1.89	365	333	0.003
190	2.92	314	500	0.002
200	4.66	252	250	0.004
210	4.32	166	160	0.006

It is concluded from these calculations that the rates can be described by Eq. (14) and that both parameters are strongly temperature dependent. This points to a model like:

$$\text{I} \quad r = \frac{k_\infty \cdot \exp(-E/RT) \cdot p_{\mathrm{CO}}}{(1 + K_\infty \cdot \exp(-\Delta H/RT) \cdot p_{\mathrm{CO}})^2}. \qquad (15)$$

Two adjacent models were also tested:

$$\text{II} \quad r = \frac{k_\infty \cdot \exp(-E/RT) \cdot p_{\mathrm{CO}}}{(1 + K_{\mathrm{CO}} \cdot p_{\mathrm{CO}})^2}, \qquad (16)$$

and

$$\text{III} \quad r = \frac{k_\infty \cdot \exp(-E/RT) \cdot p_{\mathrm{CO}}}{(1 + K_\infty \cdot \exp(-\Delta H/RT) \cdot p_{\mathrm{CO}})^m}. \qquad (17)$$

The results of the regression calculations are shown in Table 3 in which the three models are placed in the order of increasing complexity. The difference in the variances of model II and model I being significant at a 90% level, model II is excluded as it is too simple. Since the difference in variances between model I and model III is not significant in a statistical sense, model I is selected as the best model on physical grounds. The fact that the value of the power in model III is very close to 2 supports this choice. The predicted rates calculated from this model are shown as lines in Fig. 8; the agreement between calculated and measured rates is satisfactory. The calculated position of $p_{\mathrm{CO}_{\max}}$ is indicated by the broken line.

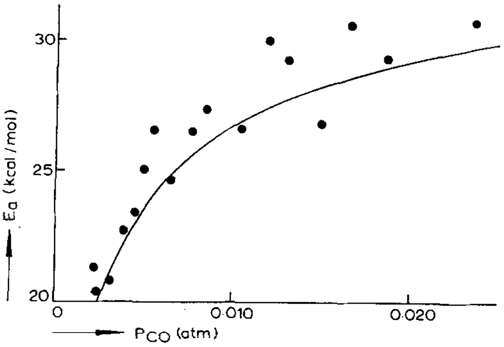

FIG. 9. Apparent energy of activation E_a as a function of p_{CO}. Points are calculated from the initial rates. Line corresponds to model I.

The apparent activation energy was calculated both from the models and from the experimental data, with Eqs. (10) and (11), respectively. The results (Fig. 9) show that E_a varies quite strongly with p_{CO}. Nevertheless, model I describes this variation quite well.

Hydrogenation of Mixtures of CO and CO_2

The feed to an industrial methanator always contains carbon oxides as well as hydrogen; typical concentrations are 0.1% CO and 0.3% CO_2. Some exploratory experiments were carried out at 200°C to study the rate of hydrogenation in mixtures. Three CO/CO_2 ratios were used, viz, 0.22, 0.50, and 1.90. The total concentration of carbon oxides in hydrogen varied from 0.67 to 3.75%. It soon became clear

TABLE 3
RESULTS OF THE REGRESSION ON THE REACTION RATES OF THE HYDROGENATION OF CO

Parameter	Model II	 I	 III	Dimension
k_∞	2.66×10^{12}	2.09×10^{5}	8.26×10^{4}	mol CO/(hr g atm)
E	25.6	10.1	9.17	kcal/mol
K	2.28×10^{2}	—	—	atm^{-1}
K_∞	—	4.56×10^{-4}	2.31×10^{-4}	atm^{-1}
ΔH	—	−12.4	−13.2	kcal/mol
m	2	2	1.93	—
Sum of squares of residuals	8.11×10^{-6}	5.83×10^{-6}	5.81×10^{-6}	
Variance about regression	1.05×10^{-7}	7.68×10^{-8}	7.75×10^{-8}	

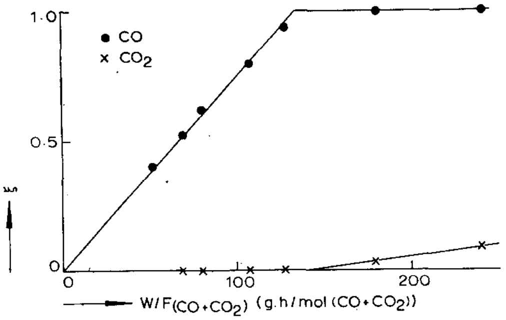

FIG. 10. Conversion of CO and CO_2 in a mixture as a function of the total reciprocal space velocity ($x_{CO} = 0.0069$, $x_{CO_2} = 0.0306$).

that the methanation of carbon dioxide does not start until a very high conversion of CO is attained. An example of the measured conversion curves is given in Fig. 10. Often cases were encountered where, at CO concentrations of but 200 ppm, the rate of methanation of CO_2 was not yet measurable. Thus, one may conclude that the first part of the catalyst bed almost exclusively converts carbon monoxide to methane and that only the second part of the bed causes hydrogenation of carbon dioxide. If this is true, the initial rates for both reactions should be equal to the rates measured with single feeds. The rate for the hydrogenation of CO can be calculated as the quotient $\xi_{CO}/(W/F_{CO})$. For carbon dioxide a corrected space velocity must be used, because a fraction of the bed is not active for this reaction. The weight of this part of the bed should be subtracted from the total weight of catalyst to find the corrected space velocity. The experiments were not accurate enough to permit exact calculation of the rate of CO_2 hydrogenation. From Table 4 it appears that the values from the mixed feed correspond reasonably well with those of a single feed.

The rates for the pure feed were calculated from the rate equations.

TABLE 4

COMPARISON OF REACTION RATES IN FEEDS CONTAINING MIXED CARBON OXIDES WITH THOSE IN SINGLE FEEDS

C_{CO} %	C_{CO_2} %	r_{CO} mixture	r_{CO} pure	r_{CO_2} mixture	r_{CO_2} pure
0.37	0.72	0.0047	0.0042	0.0030	0.0018
0.45	0.92	0.0047	0.0043	0.0026	0.0019
0.55	2.30	0.0048	0.0043	0.0045	0.0020
0.69	3.10	0.0043	0.0040	0.0021	0.0021

Effect of Reaction Products

With our apparatus it was feasible only to investigate possible effects of methane on the rate of hydrogenation of CO and CO_2. Methane was added to the feed in the following ratios:

CO/CH_4: 0.24 and 0.31,

CO_2/CH_4: 0.55 and 0.61.

The reaction rates of these mixtures corresponded to the rates for the "pure" feeds within 5% so that we may conclude that methane has no effect. This is in agreement with results of other investigators (*3*, *4*).

The following remarks can be made about the effect of water:

i. When hydrogenating CO the reaction rate is very constant up to high conversions, which indicates that the products have very little influence on the rate, if any.

ii. Although the agreement between the rates of hydrogenation of CO_2 alone and in mixtures with CO as shown in Table 4 could be better, these data at least suggest that the water formed by conversion of CO does not affect the rate of CO_2 hydrogenation. Moreover the measured conversion could be described rather well by an equation in which the presence of methane and water is not taken into account.

Other authors who added water to the feed have come to the conclusion that water has no effect on the reaction rate (*3*, *5*), at least in the small concentrations encountered in the present work.

DISCUSSION

After a discussion of the results for the CO_2 and CO hydrogenation some possibilities will be put forward for the mechanism for the hydrogenation of mixtures of the gases. First, however, it must be stated that a kinetic study of a reaction gives only overall information on that reaction and, therefore, the results can only be used to exclude mechanisms that lead to kinetics contradictory to those found experimentally. Critical examination of the kinetic relations may lead to the formulation of well-defined hypotheses about the mechanism which can be tested in other ways, e.g., on a thermobalance or by a spectro-kinetic study.

A comparison between the rate of reaction for the hydrogenation of CO_2 found by Vlasenko, Rusov, and Yuzefovich (*5*) and our data shows that the rates per gram of catalyst agree very well for the smaller particle size which they used. Since their experiments above 200°C were conducted below 0.002 atm CO_2, a first order relation can be expected as is shown in Fig. 4. An experiment by Vlasenko *et al.* on a thermobalance gave no weight increase of the catalyst within experimental error. From this they concluded that $\Theta \leq 0.03$ for the nickel surface. This experiment has been reproduced by us under well-defined conditions. Contact of the activated catalyst at 215°C with 2.4% CO_2 in hydrogen gave an increase in weight corresponding to a coverage of the BET surface area of 8–10%. The conclusion is that the nickel surface area which is active for CO_2 methanation is small compared to the total surface area. A selective determination of the nickel surface area by chemisorption has not been made; therefore, the size of the nickel surface which is active for the methanation of CO_2 is also unknown.

Furthermore, it can be stated that the rate-determining step involves only one site and that the presence of CO almost completely poisons the hydrogenation of CO_2. These findings could mean that the adsorption of CO_2 on the clean surface is rate-determining under these conditions. At high concentrations of CO_2, surface reaction or a desorption step probably controls the rate.

The results for the hydrogenation of CO are also in agreement with the experiments reported in the literature. Vlasenko, Yuzefovich, and Rusov (*3*) found an approach to zero order kinetics with increasing partial pressure. Their measurements are located at $p_{CO} \leq 0.003$ atm and $T \leq 175°C$, conditions at which the maximum in the reaction rate is almost not observable (Fig. 8). Again the reaction rates found by Vlasenko *et al.* agree extremely well with our data. Schoubye (*4*) found maxima in his experimental data and he ascribes their presence to mass transfer restrictions which, however, could not be predicted by correlations. In order to explain the negative slope of R versus p_{CO} he introduces a dissociative, poisoning adsorption of CO which slows down the rate of adsorption of hydrogen which should be rate determining. When comparing his catalyst No. 3, which is 12% Ni on η-alumina, with our catalyst it appears that the positions of the maxima agree very well. The reaction rates at the positions of the extrema differ by a factor of 2 which can be caused by a higher intrinsic activity of Schoubye's catalyst. The calculated value of the apparent activation energy at the maximum rate found from Schoubye's data and our own agree satisfactorily, as shown in Table 5. No comparison can be made on the effect of hydrogen as the partial pressure of hydrogen was almost constant and equal to 1.0 in our experiments.

The physical idea behind our model

TABLE 5

COMPARISON BETWEEN THE EXPERIMENTAL RESULTS OF SCHOUBYE AND THIS STUDY

	Schoubye [Ref. (*4*)]	Present results
Catalyst:	No. 3 12% Ni on Al_2O_3	G 65 34% NiO on Al_2O_3
Temp (°C):	190	190
Maximum rate		
Position p_{CO} atm	0.002	0.0025
Rate mole/(g hr)	4.5×10^{-3}	2.5×10^{-3}
E_A kcal/mole	20.8	22.0

equation is a rate-determining reaction between two adsorbed species, one of which is CO or a complex formed by CO. In this case the rate is highest when both reactants have a coverage of 0.5. Increase of the partial pressure of CO increases the coverage of the CO-derived species but the coverage of the other reactant decreases so that the rate also diminishes. This property of the Langmuir kinetic models was recognized and found for the hydrogenation of ethylene before 1925 (*12*). A possible rate-determining step is the reaction between an adsorbed enol complex and adsorbed hydrogen, since a reaction involving two CO-containing complexes is rather unlikely. Moreover, infrared spectral data indicate that an enol-type complex, $(H_2 \ldots CO)$, can be formed on metal surfaces from mixtures of CO and hydrogen (*13*). Therefore the reaction on the surface might be:

$$(H_2 \ldots CO)_s + H_{2,s} \rightarrow H_2O_s + CH_{2,s}.$$

It is followed by the formation of methane from the methylene fragment and hydrogen. This hypothetical mechanism can be tested by experiments in which the partial pressures of CO and hydrogen are varied by dilution with an inert gas. If it applies, a maximum rate must be found at a hydrogen partial pressure corresponding to a coverage of 0.5, just as was observed for CO in the present work.

Vlasenko *et al.* found zero order dependency at a coverage of 0.3. Since their zero order region corresponds to the maximum of our model, the agreement between our value 0.5 and their value 0.3 for the coverage is acceptable. Moreover, it can be estimated from the data of Schoubye, after having made certain assumptions, that the expected value for the coverage of a CO-containing complex at the maximum rate at 200°C is 0.43.

Calculations show that film diffusion did not limit the rate of a conversion and that the calculated value for the effectiveness factor for internal diffusion limitation is in the worst case equal to 0.98.

It must be concluded that our data agree very well with the data of Vlasenko and Schoubye and that our kinetic equation is in agreement with all experimental observations.

From the picture given above the behavior of mixtures of the carbon oxides can be explained as follows. The rate of adsorption of carbon dioxide is rate determining for its methanation, which means that its rate is proportional to the fraction of the surface which is free from adsorbate. On the other hand, hydrogen and CO adsorb very fast, which implies that in the presence of CO no sites will be available for carbon dioxide. Nevertheless, this explanation cannot explain all the data because it does not predict that CO must be removed to such a deep level as was observed before CO_2 hydrogenation sets in. Vlasenko *et al.* found that even 160 ppm inhibits the hydrogenation of carbon dioxide. Also the statement by Vlasenko *et al.* that the CO hydrogenation should become mass transfer limited before CO_2 reacts seems very likely from our calculations.

The assumption of a definite heterogeneity in the active sites seems inevitable to explain these facts. This assumption is supported by the fact that only 8–10% of the surface seems active for the conversion of CO_2. Apparently, coverage by CO of these most active sites suffices to prevent completely the hydrogenation of CO_2.

However, to arrive at an exact description of these kinetic phenomena, more detailed studies on the adsorption of CO and CO_2 in the presence of hydrogen need to be conducted on this catalyst, combined with spectro-kinetic and microbalance studies.

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