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Methanation of CO on Some Ni Catalysts

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The kinetics of methanating CO on a number of nickel catalysts was investigated in the range up to 10% or 20% CO in H_2 in a once-through differential reactor where the catalyst particles of size 0.3–0.5 mm were fluidized. The order with respect to CO was less than zero and approached -0.5 at higher CO concentrations. At low CO concentrations there was detected in most cases a maximum in rate, which could not be interpreted definitely as an intrinsic or a diffusion phenomenon. The measured rates at CO concentrations above the maxima were not influenced by diffusion; the rates in this region fitted well with the empirical, general rate equation

$$r = \frac{z_1 \exp(-E_1/RT) p_{\mathrm{H_2}}{}^n}{[1 + z_2 \exp(16\,650/RT)(p_{\mathrm{CO}}/p_{\mathrm{H_2}})]^{0.5}}.$$

Carrier and promoter oxides showed a significant effect on the kinetics, as z_2 and E_1 increased in the following order: γ- or η-Al_2O_3, $SiO_2 <$ $MgAl_2O_4$, α-Al_2O_3, $Co_2O_3 <$ $MgO \ll K_2O$. E_1 was in the 18–28 kcal/mole range and z_2 in the range of approximately 10^{-3} to 10^{-6}. For Ni on $MgAl_2O_4$ we found $n = 0.15$ by measurements in the pressure range of 1–15 atm.

A kinetic model is proposed with a step in the H_2 adsorption determining the rate. Methanation rates and the specific capacity for adsorption of H_2S are compared, showing that K_2O decreases the methanation activity without decreasing this capacity. The rates of methanation of CO, CO_2, and CH_3OH are compared.

INTRODUCTION

The purpose of this work was to elucidate the intrinsic kinetics of the methanation of CO

$$CO + 3H_2 = CH_4 + H_2O$$

taking place over some nickel catalysts. The effect on the rate equation of carrier composition and of promotion by potassium oxide was investigated, and the methanation activities were compared with the capacities of the different catalysts for adsorption of H_2S (at 500°C). Attention was devoted to the effects of diffusion restriction, which tend to modify the observed kinetics, especially at low concentrations of CO.

Since Sabatier invented the above process in 1902 only a little work on the intrinsic kinetics has been reported. White *et al.* (*1, 2*) studied the synthesis of methane from gases with about 20% CO in H_2 (integral conversions) in a fixed bed of commercial ⅛-inch pellets of a Ni-on-kieselguhr catalyst. The rates, however, must have been strongly influenced by gradients of concentration and temperature inside and outside the catalyst pellets, for which no corrections were made. Vlasenko *et al.* (*3*) studied methanation on a Ni-Cr_2O_3 catalyst of 100–1000 ppm CO in ammonia synthesis gas (pressures up to 300 atm) in the regime where film diffusion is the controlling parameter. In the only work known to the author in which intrinsic rates were measured, Vlasenko *et al.* (*4*) found methanation of CO on a Ni-Cr_2O_3 catalyst to be zero order with respect to CO, the activation energy being about 16.5 kcal/mole; the region investigated was 135–175°C and below 0.3% CO in H_2 at 1 atm. Below specific concentrations of CO the order increased due to internal and external diffusion restriction; the authors also found that the catalytic surface (in the kinetic regime) was ⅓ saturated with CO (compared to the adsorption capacity at 75°C) and concluded that the rate-determining step could be a reaction between adsorbed hydrogen and adsorbed CO. However, an infrared study (*5*) of the interaction of CO and H_2 on Ni on silica (up to 180°C) showed only bands from adsorbed CO and hydrocarbons. Another study (*16*) has shown that two-site adsorption of CO is predominant on Ni up to at least 65% coverage.

It is well known that only Ni, Co, Ru, and Fe are good catalysts for the formation of hydrocarbons from CO and CO_2. The large mass of data more than a few years old on tests of catalysts (*6*) is incomplete and the intrinsic kinetics are obscured by severe transport restrictions. However, there are many indications of a low order with respect to CO and only slight product inhibition (except on Fe catalysts). More recent studies (*7*, *8*) on the interaction between CO and H_2 on platinum group metals showed (a) the activity for the formation of hydrocarbons (the order of activity being Ru ≫ Rh,Ir > Pt,Pd) varied inversely with how strongly CO was bound to the surface; (b) with 0.5% Ru on alumina the intrinsic rate expression was $r = kp_{H_2}{}^{1.3 \text{ to } 2}p_{CO}{}^{-0.1 \text{ to } 0}$ with activation energy of 8–10 kcal/mole.

EXPERIMENTAL

The reactor was a once-through reactor consisting of an 8-mm id tube with preheater coil immersed in an externally heated salt bath stirred by bubbling air. The catalyst was (with a few exceptions) crushed to 0.3–0.5 mm particles and the amount used in the reactor was about 0.5 g. The catalyst was fluidized, the feed flow being about 100 Nl (normal liters)/hr. The feed gases were purified by Ascarite (NaOH on asbestos) and contained only H_2 and CO (except for the cases where the influence of CH_4, H_2O, and N_2 was examined). The conversions were kept below 1000 ppm CH_4 formed, the concentration of CH_4 being measured by a dispersed infrared analyzer (URAS, Hartmann & Braun) calibrated to full deflection for 1000 ppm CH_4. Thus the conversions were differential except for the lowest concentrations of CO. The effective concentration of CO was taken as $x_{CO,\text{inlet}} - x_{CH4,\text{exit}}/2$. The analyzer signals were corrected for the (small) sensitivity to the actual concentrations of CO. Temperatures were measured in the middle of the fluidized layer and in the salt bath and were controlled by a Thyristor controller. In no case did the difference between these two temperatures exceed 1°C.

In a blank test at 350°C and 1% CO, the reactor itself showed no significant methanation activity.

Catalysts

Cat no. 1. Tablets of $MgAl_2O_4$ spinel impregnated with NiO corresponding to 9–10% Ni. Reduced with H_2 at 420°C. $\rho_p = 1.8$ g/cm³.

Cat no. 2. No. 1 with a few percent K_2O added. Reduced at 570°C. $\rho_p = 1.8$ g/cm³.

Cat no. 3. A carrier of η-Al_2O_3 prepared from Al isopropoxide and impregnated with 12% Ni. Reduced at 420°C $\rho_p = 1.5$ g/cm³.

Cat no. 4. No. 3 with 2.5% K_2O added. Reduced at 450°C. $\rho_p = 1.5$ g/cm³.

Cat no. 5. A catalyst with 20% NiO, 55% MgO, and 25% Al_2O_3. Reduced at above 600°C. $\rho_p = 2.1$ g/cm³.

Cat no. 6. A Ni-Cr_2O_3 methanation catalyst with 50% Ni. Reduced at 350°C. $\rho_p = 1.9$ g/cm³.

All the catalysts were tested as 0.3–0.5 mm particles, if not otherwise stated.

RESULTS

Figures 1 to 7 present typical rate measurements for the six catalysts, of which no. 1 has been most completely investigated, including measurements on the pressure dependence (Fig. 2). Some additional effects studied more thoroughly with Cat. no. 1 should be mentioned:

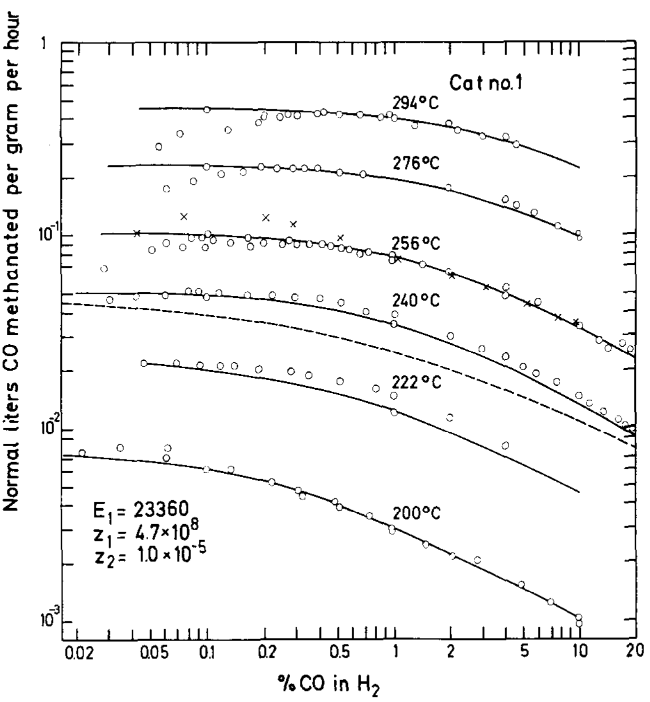

FIG. 1. Calculated and measured methanation rates on Cat no. 1. The circles are measurements after 2 weeks service, while the crosses are the rates measured less than 20 hr after the reduction of the catalyst *in situ*.

(a) The effect of adding 5% CH_4 and 5% H_2O to the feedgas was investigated in the range 0.3–2% CO at 240° and 256°C. The effect was essentially insignificant (as previously demonstrated (*2–4, 6*)). The effect of substituting 25% of H_2 by N_2 was also insignificant (compared to the uncertainty) and could be accounted for by the variation of p_{H_2} in the rate expression (see below).

(b) The catalyst activity was constant during the period of investigation (about

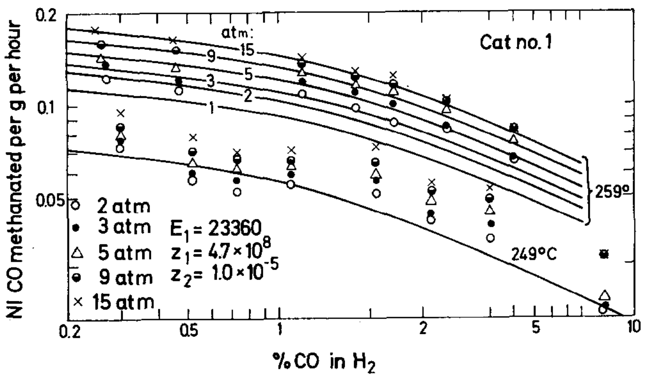

FIG. 2. Methanation rates of another sample of Cat no. 1 in our pressure reactor at 2, 3, 5, 9, and 15 atm. In the experiments at 259°C the pressure was kept constant for each sequence of measurements at different CO concentrations; in the experiments at 249°C the concentration was kept constant. By linear regression analysis on the rate equation modified as $\log r = n \log p_{H_2} + \text{constant}\ (T, x_{CO}/x_{H_2})$, we find $n = 0.15 \pm 0.02$ for the 75 measurements independently of temperature and CO concentration. The solid lines are the calculated rates at 1 atm and 249°C and at 1, 2, 3, 5, 9, and 15 atm and 259°C.

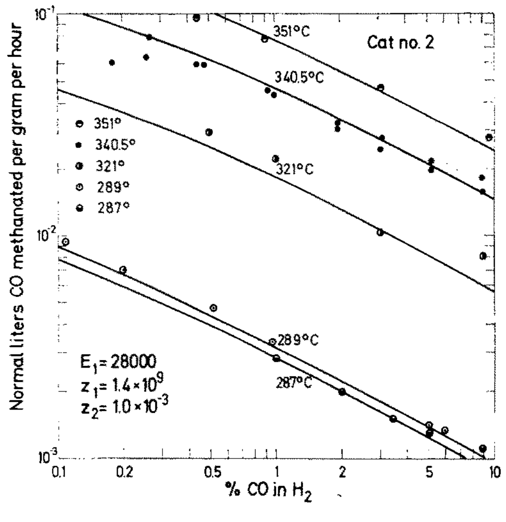

FIG. 3. Typical rate measurements for Cat no. 2.

2 weeks) except for the fact that the freshly reduced catalyst had a relatively higher activity at low x_{CO} (the crosses on Fig. 1); this slight increase of order regarding CO during the first days after reduction of Cat. no. 1 seems also to be the case for many nickel catalysts investigated by the author. For the other catalysts, the measurements presented here were made after an initiation period of at least 2 days.

(c) Heat treatment in H_2 up to 1000°C did not change significantly the shapes of the curves of rate versus x_{CO}.

(d) Hysteresis effects as to CO concentration and temperature were not very significant. The same stationary methanation rate seemed generally to be established no more than 30 min after change of conditions in any direction. However, reproducibility of measured rates on the same sample of catalyst was in many cases no better than ±20%, being best at the higher CO concentrations, and no explanation can be given for this; the uncertainties in the experimental technique at atmospheric pressure can only account for about ±5–10%.

Figure 2 shows how the methanation rate depends on total presures up to 15 atm. On Fig. 7 is illustrated the effect of decreasing the particle size to 0.15–0.25 mm; the dashed lines on the same figure illustrate (by repeated measurements) the effect of preventing fluidization of the 0.15–0.25 mm particles by a wad of glass

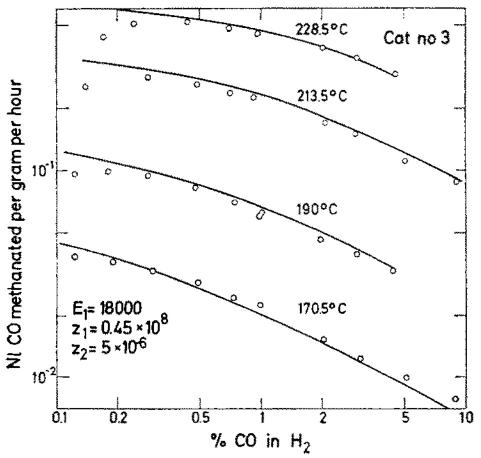

FIG. 4. Typical rate measurements for Cat no. 3.

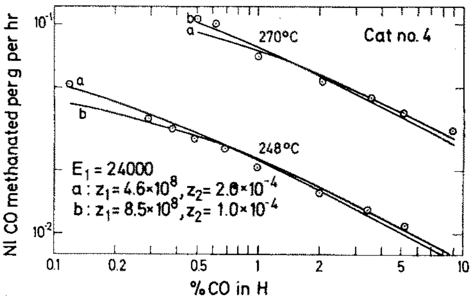

FIG. 5. Typical rate measurements for Cat no. 4.

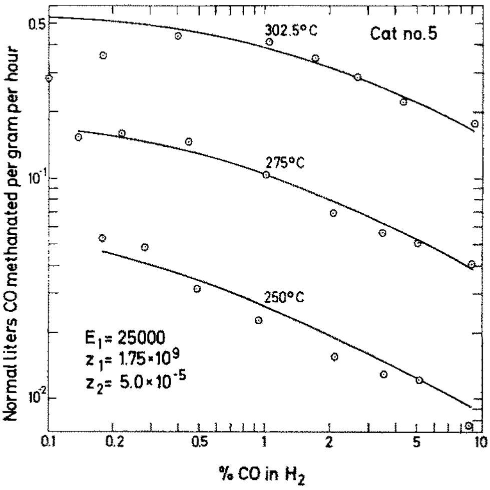

FIG. 6. Typical rate measurements for Cat no. 5.

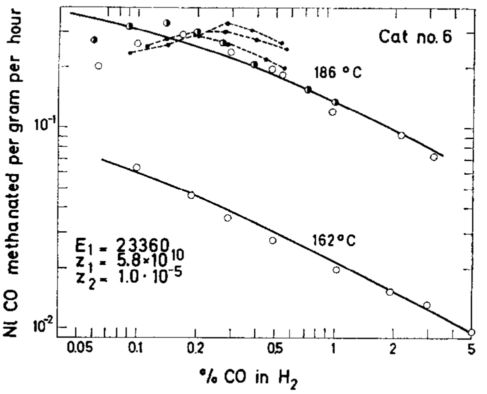

FIG. 7. The half-filled spheres are the rates measured on 0.15–0.25 mm powder of Cat no. 6; the filled spheres are repeated courses of measurements when fluidization of the same sample of 0.15–0.25 mm powder was hindered by a wad of glass wool.

wool. Apparently, the use of smaller particles moved the maximum slightly to the left, while prevention of fluidization moved the maximum substantially towards higher CO concentrations; these effects have also been found with Cat. no. 1 (and other catalysts), but not so distinctly.

ESTIMATION OF DIFFUSION RESTRICTION

It is well known that diffusion restriction tends to change a zero order reaction towards a reaction of the order ≥ 0.5 below a certain concentration of the restricted component depending on the actual zero order rate and the effective diffusion coefficient in the catalyst pores and in the external film (*4*, *8*). On the other hand, a reaction with negative order will have a *maximum* of rate at a certain concentration. Actually, we have found (*9*) that the methanation rates of Cat no. 1 in 4.5-mm cylinders and no. 3 in 5-mm cylinders exhibited such maxima, which could easily be explained by the theory set out below.

The problem here is to assess to what extent the drop-off in rate at the lowest x_{CO} (as detected for Cat nos. 1, 3, 5, and 6) was caused by diffusion restriction or reflects a quality of the intrinsic ("true") kinetics; theoretically, the intrinsic kinetics of a low order reaction has to approach first order at least at very low concentrations.

The effectiveness factor, E, of a sphere in which a zero order reaction, $r_0 = k$ g mole/cm³ sec, takes place, is a function of the modulus

$$\phi^2 = a^2(k/D_e c_s) \qquad (1)$$

where a is the radius of the sphere, D_e the effective diffusion coefficient (of CO) in the porous sphere, and c_s the molar concentration (of CO) at the surface of the sphere. For $\phi^2 \leq 6$, $E = 1$ and above $\phi^2 = 6$, E decreases.

Around the sphere there is a gas film causing a drop in concenrtation from the bulk gas phase to the surface of the sphere

$$p - p_s = (a/3)(r/k_g) \qquad (2)$$

where r is the actual rate and k_g (g mole/cm² sec atm) is the gas film coefficient.

The existence of a maximum as equivalent to an (apparent) zero order rate with respect to CO near this maximum. *If* a maximum is caused by diffusion, ϕ^2 has approximately to equal 6. Inserting $\phi^2 = 6$ in Eq. (1), using the fact that $r = k$, and combining with (2) yields the following condition for the fact that diffusion *cannot* have caused the maximum in rate versus p_{CO}:

$$\left(\frac{r}{p_{\text{CO}}}\right)_{\max} \ll \frac{6}{a_2(RT/D_e) + a(2/k_g)} \qquad (3)$$

The typical conditions are as follows: 0.4-mm particles ($=d_p$) in an 8-mm tube, 100 Nl H_2/hr at 300°C, and 1 atm, and void approximately 80%.

Estimation of k_g is as follows: $Re_p = d_pG/\eta = 0.04(3.9 \times 10^{-3})/1.48 \times 10^{-4} = 1$ (i.e., laminar region). From Zenz and Othmer (*10*), p. 473, we have $f_D \approx 1.3$ or or $Sh = j_D Sc^{1/3} Re_p \approx 1$; as theoretically (*8*, p. 47) $Sh = 2$ for a single particle in stagnant fluid, $Sh = 1$ seems not to be a very unreasonable figure. Thus we have

$$k_g = Sh \frac{D_b \rho_f}{MdpP} = 1.1 \times 10^{-3} \frac{\text{g mole}}{\text{cm}^2 \text{ atm sec}}$$

which inserted in (3) together with $a =$

0.02 cm yields the general condition for the absence of diffusion restriction in case of 0.4 mm catalyst particles

$$\left(\frac{r}{p_{\mathrm{CO}}}\right)_{\max} \ll \frac{6}{19/D_{\mathrm{e}} + 36} \quad \frac{\text{g mole}}{\text{atm cm}^3\text{ sec}} \tag{4}$$

By rate measurements on larger particles and by other means (*9*) we have estimated the values of D_e to be inserted; the results are presented in Table 1.

TABLE 1

Effective Diffusion Coefficients for CO in the Catalyst Particles under the Reaction Conditions—Values Inserted in the Right-Hand Side of Eq. (4)

Cat no.	D_e (cm²/sec)	$\left(\frac{r}{p_{\mathrm{CO}}}\right)_{\max}$, predicted by Eq. (4) (g mole/cm³ sec atm)
1	0.17	0.04
2	~0.15	0.04
3	0.03–0.05	0.01
4	0.03–0.05	0.01
5	0.01–0.02	0.005
6	~0.1	0.03

The experimental maxima are located approximately on the line $r = 2 \times 10^{-3} p_{\mathrm{CO}}$ g mole CO/cm³ sec (Cat nos. 1, 3, 5, and 6) independent of D_e, the locations being more or less affected by change in particle size and whether the bed was allowed to fluidize or not. These findings indicate some sort of external diffusion restriction corresponding to a value of k_g two orders of size below the expected value.

We can, therefore, only conclude that in the region of $dr/dp_{\mathrm{CO}} > 0$ the measured rates can reflect both intrinsic kinetics and some external diffusion restriction, while for at least Cat no. 6 some sort of external diffusion (perhaps channelling or cluster formation) is probably governing. More experimental work in this region is necessary.

Rate Equations

We shall confine the rate equations to the region of zero order or below (regarding CO), i.e.,

$$r/x_{\mathrm{CO}} > 4 \times 10^{-3}\ (\text{g mole CO/cm}^3\text{ sec}) \approx 300/\rho_{\mathrm{p}}\ (\text{Nl CO/hr g}) \tag{5}$$

together with $x_{\mathrm{CO}} < 0.1$ to 0.2.

At first, a rate equation must admit the following general conditions which easily can be derived directly from the measurements (most completely from Cat no. 1):

(1) The rates are independent of methane and water up to at least 5 volume % and independent of nitrogen.

(2) For all catalysts, the order regarding CO drops off to a constant value of −0.5 at high concentrations of CO.

(3) The pressure experiments (Fig. 2) showed that the shape of the plot of log r versus log x_{CO} is independent of the total pressures, which means that p_{CO} is only involved as the ratio between p_{CO} and $p_{\mathrm{H_2}}$ (or less likely the total pressure). A regression analysis of the 75 measurements of Fig. 2 using Eq. (7) (replace 0.15 by n) linearized by taking the logarithms showed that the rates are proportional to the total pressure to a power of 0.15 ± 0.02, independently of the CO concentrations.

Therefore, among all equations of the intuitively chosen general form

$$r = \frac{k_1 p_{\mathrm{CO}}{}^a p_{\mathrm{H_2}}{}^b}{(1 + k_2 p_{\mathrm{H_2}}{}^c + k_3 p_{\mathrm{CO}}{}^d / p_{\mathrm{H_2}}{}^e)^f} \tag{6}$$

the following rate equation is selected as the model fitting most adequately to the experiments, taking also into consideration that the number of parameters to be fitted should be kept at a minimum:

$$r = \frac{z_1 \exp(-E_1/RT) p_{\mathrm{H_2}}{}^{0.15}}{[1 + z_2 \exp(-E_2/RT)(p_{\mathrm{CO}}/p_{\mathrm{H_2}})]^{0.5}} \tag{7}$$

If 1 was not included in the denominator square root, the region of transition between 0′ and −0.5′ order would nearly without exceptions be significantly too broad (the dashed line on Fig. 1) to fit the experimental data.

The best fit of the four parameters of Eq. (7) for the six catalysts are given on the figures, where the corresponding calculated curves are also drawn. The values of z_2 are subject to rather large uncertainties. The values of E_2 for Cat nos. 2 and 7

TABLE 2
BEST FIT VALUES ON FIGS. 1–7[a]

Cat no.	z_1 (Nl CO/hr g)	E_1 (kcal/mole)	z_2	r_m (250°) (Nl CO/hr g)	S (ppm S)
1	0.47×10^9	23.36	1.0×10^{-5}	0.081	1000
2	1.4×10^9	28	10^{-3} ($>5 \times 10^{-4}$)	0.0028	850
3	4.5×10^7	18	5×10^{-6} ($3\text{–}7 \times 10^{-6}$)	1.35	5450
4	0.85×10^9	24	10^{-4} ($0.5\text{–}2 \times 10^{-4}$)	0.080	5400
5	1.75×10^9	25	5×10^{-5} ($3\text{–}10 \times 10^{-5}$)	0.063	2300
6	6.8×10^9	23	10^{-5} ($1\text{–}2 \times 10^{-5}$)	10	—

[a] $E_2 = -16\,650$ cal/mole. The intervals of z_2 in the parentheses are those which could fit as well for the chosen values of z_1, E_1, and E_2; r_m (250°) is the calculated rate at 250°C, 1 atm for unity of the denominator, and S is the sulphur capacity as explained in the text.

are taken equal to that of Cat no. 1 simply because no differences of E_2 can be detected with the present measurements. The results with estimated uncertainties are given in Table 2.

The rate equations are not obtained by a rigorous regression analysis, but only by a simple trial-and-error procedure. If a sufficiently sophisticated regression method had been used, a rather subjective choice would always have been involved in one way or another (weighting), so the author believes that such a rigorous method could probably not have given more "true" rate equations from these measurements.

It should be mentioned that for catalysts with not too high z_2 values the order (of CO) seems to approach a somewhat higher value than —0.5 at higher temperatures for large CO concentrations.

TENTATIVE MECHANISMS

Apparently, there is a strong rate inhibition by adsorption of CO. Among the many possibilities of combining adsorption of CO and adsorption of H_2 with adsorption rate or surface reaction rate controlling, using the Langmuir isotherm, we have found only one mechanism to fit fairly well the shapes of the experimental curves if this mechanism is to be both mathematically easy and physically reasonable. In this mechanism dissociative adsorption of H_2 through several steps determines the methanation rate, while adsorption on dual sites of CO and H_2 inhibits the rate.

We believe that the adsorption of hydrogen leading to the "active" state could take place in two ways:

$$H_2 + s \xrightarrow{k'} 2H'_{ads} \tag{8}$$

and/or

$$H_2 + 2s \underset{}{\overset{K_1}{\rightleftharpoons}} H_{2ads} \overset{K_2}{\rightleftharpoons} 2H_{ads} \xrightarrow{k''} 2H''_{ads} \tag{9}$$

where only H'_{ads} or H''_{ads} (which probably are physically identical) can react with the adsorbed CO

$$CO + 2s \overset{K_C}{\rightleftharpoons} CO_{ads} \tag{10}$$

Assuming that only H_{2ads} and CO_{ads} cover an appreciable part of the total concentration of sites, L, we have

$$\begin{aligned} L &= [s] + 2[CO_{ads}] + 2[H_{2ads}] \\ &= [s] + 2[s]^2\,(K_1p_{H_2} + K_Cp_{CO}) \end{aligned} \tag{11}$$

Assuming nearly all sites are covered, i.e., omitting [s], we have

$$[s] = (L/2)^{0.5}(K_1p_{H_2} + K_Cp_{CO})^{-0.5} \tag{12}$$

In the case of (8) determining the rate, the rate equation becomes

$$r = k'K_pp_{H_2}[s] = \frac{k'(L/2K_1)^{0.5}p_{H_2}{}^{0.5}}{[1 + (K_C/K_1)(p_{CO}/p_{H_2})]^{0.5}} \tag{13}$$

and in the case of (9) determining the rate

$$r = k''[H_{ads}] = \frac{k''(LK_2/2)^{0.5}}{[1 + (K_C/K_1)(p_{CO}/p_{H_2})]^{0.5}} \tag{14}$$

Equations (13) and (14) are identical with Eq. (7) except for the numerator dependency of H_2. Addition of these two rate equations, the total numerator rate constants being proportional in the ratio of about 1:4, gives a new equation which in the range of 1–15 atm is proportional to $p_{H_2}{}^{0.15}$ within ±6%, i.e., within the experimental error.

DISCUSSION OF MECHANISM AND CATALYST SURFACE PROPERTIES

Probably a large number of other more complicated mechanisms could lead to rate equations fitting the measured rates within the experimental errors. Even if the adsorption rate of hydrogen is determining the rate, detailed mechanisms other than (8) and (9) could possibly lead to suitable equations. The existence of several chemisorbed states of hydrogen on nickel and other metals is generally accepted (*11, 12, 13*), while no strong evidence of just exactly the sequence (9) can be derived.

If our proposed mechanism is true in principle, it should imply that the numerator rate expression (denominator is taken as unity) for methanation of CO would represent the upper possible rates of any hydrogenation process on a given catalyst at any given temperature and p_{H_2} *if* only the same number of atoms of activated hydrogen, H'_{ads} and H''_{ads}, had to be consumed by the hydrogenation of one molecule of the component in question; if the number were *n* times higher, the upper possible rate should be *n* times lower (we imagine that the intermediary compounds on the surface could possibly be hydrogenated by other states of hydrogen, H_{2ads} or H_{ads}). In Fig. 8 are compared the methanation rates of CO, CO_2, and CH_3OH on a catalyst not mentioned above, but similar to no. 1; CO_2 actually has the same maximum rates as CO, however at a much higher percent CO_2, while methanol only reaches about ⅔ of these maximum rates before an abrupt drop-off (for unknown reasons) below a certain percent methanol. However, the apparent accordance in rates could just as well be explained by a fast formation of CO (as an intermediary), the rate therefore being determined in principle by whatever the kinetics could be for the methanation of CO. Comparative measurements of the rates of hydrogenation of, say, ethylene would be more valuable.

Hydrogenation of ethylene and hydrogenolysis of hydrocarbons on Ni, Co, Fe, and Pt catalysts are generally believed to be governed by surface reactions (*11, 14*); we have found no examples of hydrogenations for which kinetics similar to our proposed mechanism or equations were postulated.

The value of the numerator rate constant of Eq. (7) is proportional to the specific area of nickel surface (m^2 Ni per g cat) of the catalyst considered [the *L* dependence of Eqs. (13) and (14) does

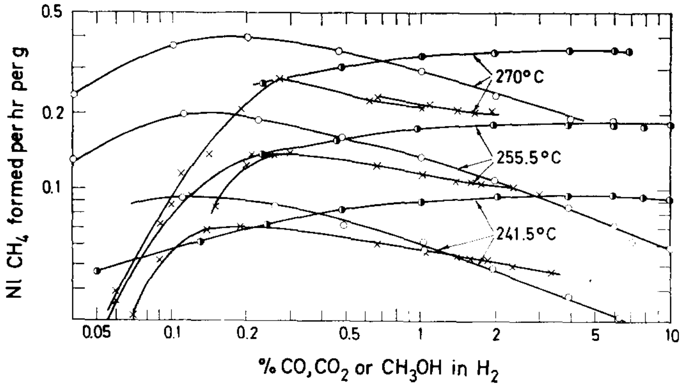

FIG. 8. Measured methanation rates of CO, CO_2, and CH_3OH on the same sample of a catalyst with 14% Ni on a carrier of composition: 4% K_2O, 11% SiO_2, and 85% Al_2O_3; the particles were 0.4–0.5 mm and the sample was fluidized. The rate equation for CO is similar to that of Cat no. 1 except for a higher value of z_1. The curves are the best connections through the measured rates.

not necessarily contradict this as L is a—somewhat speculative—concentration of sites on the Ni surface], while the denominator constant is only a function of the chemical properties of this surface. Apparently, the oxides in the carrier and especially the addition of potassium oxide have an effect on the denominator, the denominator constant, z_2 (E_2 constant), increasing in the order (see Table 2):

$$\gamma\text{- or }\eta\text{-Al}_2\text{O}_3,\ \text{SiO}_2 < \text{MgAl}_2\text{O}_4,\ \alpha\text{-Al}_2\text{O}_3,\ \text{Cr}_2\text{O}_3 < \text{MgO} \ll \text{K}_2\text{O}$$

Also the numerator activation energy, E_1, seems to increase in the same order. The sequential placing of α-Al_2O_3 and partly of MgO and SiO_2 is based on rate measurements not presented in this article. The sequence found suggests a connection with surface acidity which is, however, not confirmed by measurements on this quantity.

The last two columns of Table 2 compare the calculated activity at 250°C for unity of the denominator with the same catalyst sample's capacity in wt ppm S for adsorption of H_2S at 500°C using a method reported by J. Rostrup-Nielsen *(15)*. The sulfur capacity is believed to be proportional to the number of "exposed" nickel sites; apparently, addition of a few percent of K_2O does not greatly influence the sulfur capacity or the number of "exposed" nickel sites, while the methanation activity—even at low x_{CO}— is drastically decreased.

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