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TITLE: C_1 Chemistry for Liquid Fuels (Task 1)

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OBJECTIVE: To produce methanol from syngas via methyl formate. The goal is to evaluate the feasibility of combining in one reactor the carbonylation of methanol to form methyl formate with the hydrogenolysis of methyl formate to form methanol. In addition, one aim is to discover a hydrogenolysis catalyst which will give an overall methanol production rate comparable to that of the current ICI process. The kinetics will be studied of the reactions individually and together.

TECHNICAL APPROACH: There is a current interest in improving the efficiency and economics of the methanol synthesis from syn gas. Several commercial processes produce methanol from mixtures of hydrogen, carbon monoxide and carbon dioxide. One process shown here employs a copper, zinc oxide, alumina catalyst and operates at approximately 250°C and one hundred atmospheres. The percentage conversion er pass is low, less than 20%, and so a large recycle is needed. The LaPorte liquid phase methanol process provides better control of the exothermic process and may avoid the necessity of shifting the syn gas to a higher hydrogen to carbon monoxide ratio. It would also operate at a similar temperature and pressure as that shown on the first slide.

This project examines a lower temperature synthesis of methanol via methyl formate suggested in 1919 by J. Christiansen of Denmark (1). The first reaction involved is the carbonylation of methanol by carbon monoxide to produce methyl formate, an ester of formic acid. This reaction is catalyzed by an alkali alkoxide. This could be sodium methoxide, or potassium methoxide. A higher alcohol could be used in place of methanol, thus producing the corresponding alkyl formate. This reaction proceeds fairly rapidly at 80°C and 30 atmospheres. The second reaction is the hydrogenolysis of methyl formate or an alkyl formate by hydrogen to produce the original alcohol plus a molecule of methanol. This reaction proceeds at 110°C to 180°C with one to thirty atmospheres of hydrogen. It is catalyzed by a copper catalyst.

Each reaction is very selective so few by-products would be made. The overall reaction is of 2:1 syn gas to methanol. Higher conversions can be attained here compared with the current commercial process. This could save the cost of using high pressure recycle compressors and perhaps allow cheaper materials of construction. Also, no water is formed in this reaction which could eliminate the cost of distilling water from the product methanol. A techno-economic study (2) comparing this alternative process with the ICI and LaPorte processes showed that the process would need to be conducted in one reactor rather than in two reactors to compete in the area of construction costs.

The work shown will be aimed at combining these two reactions and two catalysts in one reactor. First, these reactions are being studied individually. Most of the recent published work has been done in Australia by Trimm and co-workers (3). They studied the hydrogenolysis reaction mostly in the vapor phase but found some favorable results in the liquid phase (4). With methyl formate as the starting liquid, dissolved hydrogen reacts over the solid heterogeneous catalyst, namely Girdler copper chromite. We also chose a liquid phase reactor for the hydrogenolysis study since the carbonylation reaction is performed with a homogeneous catalyst in the liquid phase.

Our objectives are shown on the next slide: that is to develop practical operating conditions for the low temperature methanol synthesis. The main problem with the first reaction is the cost of cleaning up CO_2 and water from the syn gas since they might react with the sodium methoxide catalyst. The influence of CO_2 and water on the carbonylation reaction was examined. Also, the first reaction has been studied mainly with pure CO, not syn gas. This reaction is used commercially in the synthesis of formic acid. The influence of hydrogen was examined. The hydrogenolysis reaction is inhibited by the presence of CO. This might be the main obstacle to the successful development of this process.

The next slide shows the system used for studying the carbonylation reaction. Carbon monoxide is bubbled through a solution of sodium methoxide in methanol in batch experiments. As the CO is used up to make methyl formate, the pressure drops. An on-line GC sampling system takes a fresh sample from the liquid and the vapor phases every half hour and analyzes for H_2, CO, CO_2, MeOH and methyl formate.

The next slide shows the rate equation for the carbonylation reaction. The forward reaction rate varies with the catalyst concentration, the methanol concentration, and the concentration of CO dissolved in the liquid. Although this CO in the liquid can be measured with the on-line GC, it is more accurate to measure the partial pressure of CO in the gas phase and multiply that times a solubility factor alpha (Henry's law coefficient) which is known or measured at various temperatures.

The reverse reaction proceeds more slowly and is proportional to catalyst concentration and methyl formate concentration. The methanol and methyl formate concentrations can also be expressed as a function of the change in pressure of CO. The rate equation can be rewritten in the form shown on the next slide. The equilibrium constant can then be measured at various temperatures. When equation 2 is integrated the result is equation 4 which is simplified by defining A, B, delta, and lambda in this way. If just the forward reaction is involved, as during the first few minutes of the reaction, the rate equation simplifies to: the natural log of PCO divided by PCO initial equals kt.

The next slide shows a typical carbonylation run where the CO partial pressure drops with time as methyl formate is made. The CO dissolved in the liquid eventually drops low enough to stop the reaction. In the next slide the log of PCO/ PCO^o is plotted versus time. The forward rate constant can be obtained from the first few minutes of time. Then as the reverse reaction becomes significant a non-linear regression was used to fit the data. On this slide the open circles show pure CO as the reactant gas. The filled circles show the same partial pressure of CO with an equal pressure of hydrogen. Apparently, hydrogen simply acts as a diluent and does not inhibit this reaction.

In the next slide we see the influence of CO_2 and H_2O on the carbonylation catalyst, sodium methoxide. CO_2 reacts with sodium alkoxide to give the salt of the semiester of carbonic acid. Water can react with the catalyst to yield sodium hydroxide and alcohol. The reverse reaction also can occur.

In the next slide we see the ln of CO pressure over initial CO pressure plotted versus time. The triangles show CO alone. It has the steepest slope since it is the fastest reaction. The circles show CO_2 and CO bubbled into the reactor. The CO_2 at this temperature reacted stoichiometrically with the sodium methoxide. The squares show the addition of water and CO to the reactor. Not all of the sodium methoxide was converted to sodium hydroxide since there is some equilibrium reached between the forward and reverse reactions. Since it is more expensive to scrub CO_2 from syn gas than to remove water, the poisoning effect of CO_2 on the two reactions run concurrently will be important to study.

The next slide shows the Arrhenius plot for the log of the rate constant k_1, or k_{-1} plotted versus 1/T. E activation is calculated for the forward reaction, 16.3 kcal/mol, in the filled circles and for the reverse reaction in the open circles, 19.8 kcal/mol.

The next slide shows these activation energies: for sodium methoxide measured at this lab in column 1, for sodium methoxide measured by Tonner et al. in Australia in column 2, and for potassium methoxide measured by Liu et al. at the University of Pittsburgh in column 3. All three agree on the forward rate and Liu's data differs from ours for the reverse rate possibly because he worked at a point much closer to equilibrium by running semi-batch experiments for over 24 hours (5) while ours were batch experiments lasting one hour. The forward rates were all measured in the first few minutes.

The next slide shows the scehmatic for the hydrogenolysis reaction. Methyl formate is heated to the reaction temperature, then the pre-reduced copper catalyst is shot into the reactor by pressurizing with hydrogen. At that point the run begins. This is a semi-batch reaction in which hydrogen is constantly fed in as it is used, to keep the total pressure constant. The on-line GC then measures the mole percents of hydrogen, methanol and methyl formate. No reverse reaction is seen under these conditions. The next slide shows how the rate constant is measured from the experimental data. The rate is equal to the rate constant times the concentration of methyl formate. When this first order rate is integrated from time zero to time t, we obtain : minus the natural log of the methyl formate concentration over initial concentration is equal to kt.

Alpha, the conversion, is defined as the concentration of the methyl formate consumed divided by the initial methyl formate concentration. This can be rearranged to give 1-alpha equals $[MeF]/[MeF]^{o}$. When this is substituted into the integrated equation, we get -ln (1-alpha) = kt. Experimentally we have from the GC : moles of Methanol divided by moles of methyl formate. From this we can calculate alpha, the fraction converted. The next slide shows the rate equation where rate is proportional to the rate constant times the methyl formate concentration times the catalyst concentration times the partial pressure of hydrogen times the pressure of CO raised to some power. This empirically fits the drop in rate with the inhibition by CO. The next slide shows a possible reason for the inhibition of the hydrogenolysis reaction by CO is that the adsorption strength on the copper active sites is greatest for methyl formate, next for CO and least for H_2. So perhaps CO is competing with H_2 for adsorption on the same sites. One way to obtain some great improvement in this process would be to find a catalyst where H_2 adsorbs more strongly than CO. It seems important to measure this inhibition since there will be plenty of CO present. Fortunately, some work by the Australians and by those at Pitt shows that the inhibition by CO is reversible in the liquid phase. This is fortunate, in that, if there were an upset in the process and a lot of CO was present, activity could be regained.

An example of our tests for the hydrogenolysis reaction in the liquid phase is shown in the next slide. The catalyst used was Girdler copper chromite at a temperature of 110°C. We plotted -ln (1-alpha) versus time. The reaction progressing without CO is shown by the circles. In a second run shown by the squares, we start with just hydrogen then 44 PSI of CO was added at about 165 minutes and the reaction rate dropped off but continued to be first order. The next slide shows two more experiments where 100 PSI of CO was added, as shown by the circles or 145 PSI of CO was added, as shown by the squares. The lines bend over farther as more CO is added. From this data a power law can be derived which expresses the change in rate as a function of CO partial pressure. The next slide shows some data where Raney copper was used for the first time in the liquid phase as the catalyst. Here, the overall conversion is greater for the same grams of reduced catalyst injected, as seen on the y-axis. The CO inhibition occurs to the same extent as with copper chromite. The next slide compares three catalysts, each run several times with different pressures of CO added. The rate for 20 grams of catalyst per liter of methyl formate is fastest for Raney copper, next for Raney copper chromite, and last for Girdler copper chromite. The inhibition by CO is roughly the same for all the catalysts tested. Some surface area measurements by CO adsorption have shown that Raney copper simply has a higher copper surface area per gram of catalyst than does the Girdler copper chromite.

The next slide shows some modeling work which has been started to predict the rate of the two reactions combined in one autoclave. The optimum temperature will probably be between 140°C and 160°C. This is a complicated system to model since there is a homogenous reaction, and a heterogenous reaction. We assume that the reactants will behave as ideal gases and that the methanol and methyl formate going from liquid to vapor can be neglected in the material balance. Also, we assume that the amount of CO and H_2 dissolved in the liquid methanol and methyl formate remains constantly resupplied from the gas phase and that the dissolved gases can be neglected in the material balance. The catalysts, particularly the copper catalyst, will deactivate with time on stream and so some decay constant is used to simulate this deactivation.

The next slide shows the beginning mole balance for this modeling work. "Fg,in" is the flow of syn gas into the reactor in moles per time. "Fg,out" is the flow of syn gas and more correctly also of methanol vapor out of the reactor. Eventually, these two reactions will be run concurrently, first in a semi-batch process and later in a flow process as shown by the model. Mg is the total moles in the gas phase and Ml is the total moles in the liquid phase. The kinetic equations for the two reactions will be written as a function of the variables shown for the carbonylation and the hydrogenolysis reactions. The first reaction is assumed to go faster and is in equilibrium. The second reaction is slower and is the rate determining step. An equilibrium value of MeOH to methyl formate will be reached in the reactor.

This process will show some accumulation of products in the reactor and this accumulation is equal to the reactants in, plus methanol and methyl formate produced, minus components consumed, minus syn gas and vapors out. In the real experiments, some methanol vapor will come ver with the unreacted syn gas and some methanol liquid will accumulate in the reactor. Four equations showing the change in mole fraction of each component per change in time are shown. These are integrated and solved simultaneously. For example, the change in methanol per time is one mole lost for each occurrence of reaction one and two moles of methanol produced for each occurrence of reaction two.

In summary, the next slide shows the conclusions. The rate constants for the forward and reverse carbonylation reaction have been determined and may be used in modeling the two reactions run in a single, slurry phase reactor. CO_2 and H_2O have a negative influence on the reaction rate. CO_2 forms an insoluble salt at 70°C. H_2O reacts with sodium methoxide and produces sodium hydroxide which can then convert back to the methoxide. Thus the carbonylation rate is affected to a lesser extent. Raney copper was tested as the hydrogenolysis catalyst for the first time in the slurry phase. It is also inhibited by CO to the same extent as copper chromite. This inhibition will next be tested at higher temperatures, before running the two reactions concurrently.

FOOTNOTES:

1. Christiansen, J.E., U.S. Patent 1,302,011 (1919).
2. A Technical and Economical Evaluation of the Two-Stage, Low Temperature Methanol Process, by Burns and Roe Services Corporation,

under Contract No. DE-AC22-84PC72571, Subtask 4.01 (FY 86), October 1986.

3. Evans, J.W., Tonner, S.P., Wainwright, M.S., Trimm, D.L. and Cant, N.W., 11th Aust. Conf. on Chem. Eng. (1983).

4. Monti, D.M., Kohler, M.A., Wainwright, M.S., Trimm, D.L. and Cant, N.W., Appl. Cata. 22, 123 (1986).

5. Liu, Z., Tierney, J.W., Shaw, Y.T. and Wender, I., Fuel Proc. Tech. 18, 185 (1988).

SIGNIFICANT ACCOMPLISHMENTS: A Raney copper catalyst was tested for hydrogenolysis activity at 110°C. This is the first time such a catalyst has been tested in the liquid phase although Australian workers tested it successfully in the vapor phase. The Raney copper had two times the activity per gram of catalyst as that of the Girdler copper chromite.

The overall rate of methanol production needs to be raised by increasing the hydrogenolysis reaction rate, since it is the slower of the two reactions. Therefore, this improvement is an important one for raising the overall rate.

PUBLICATIONS: R.J. Gormley, A.M. Giusti, S. Rossini, and V.U.S. Rao, Kinetic Parameters in the Carbonylation Step of the Low Temperature Synthesis of Methanol, Proceedings of the 9th International Congress on Catalysis, Calgary (1988), p. 553.

C_1 CHEMISTRY FOR LIQUID FUELS (TASK 1)
(Low Temperature Synthesis of Methanol)

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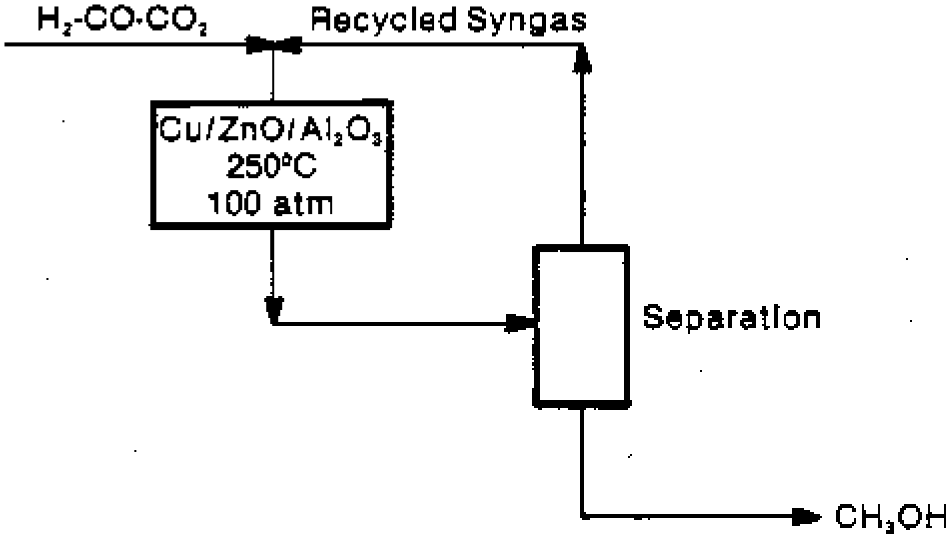
METHANOL SYNTHESIS

$$2H_2 + CO = CH_3OH$$

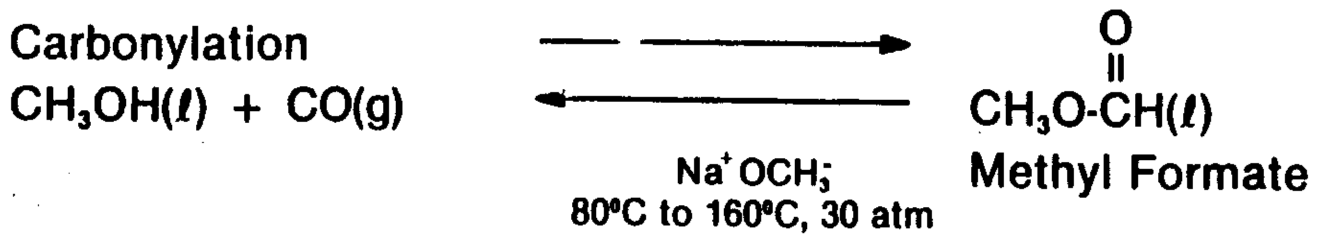
$$3H_2 + CO_2 = CH_3OH + H_2O$$



Problems:
- — Reaction exothermic ($\Delta H \sim -23$ kcal mol^{-1})
- — At T necessary for catalytic activity, an equilibrium limitation on conversion
  High P needed, large recycle
- — Lower P process , higher conversions desirable

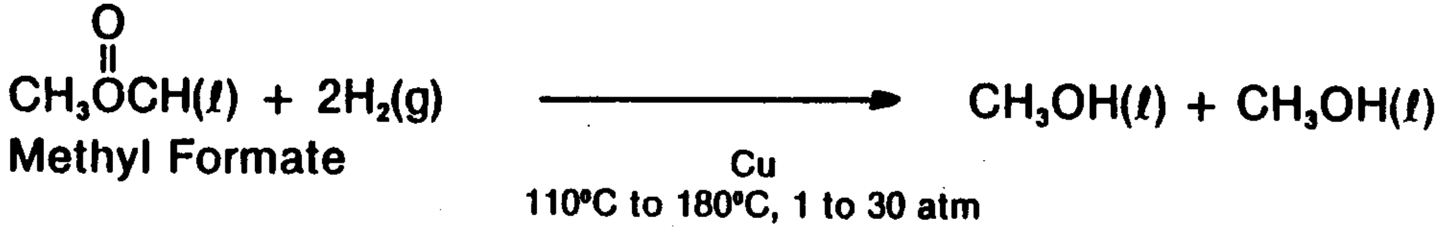
LOW TEMPERATURE SYNTHESIS OF CH_3OH

(A) Carbonylation



$$CH_3OH(\ell) + CO(g) \underset{80°C \text{ to } 160°C,\ 30 \text{ atm}}{\overset{Na^{+}OCH_3^{-}}{\rightleftarrows}} \underset{\text{Methyl Formate}}{CH_3O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}H(\ell)} \qquad (1)$$

(B) Hydrogenolysis



$$\underset{\text{Methyl Formate}}{CH_3\overset{\overset{\displaystyle O}{\|}}{O}CH(\ell)} + 2H_2(g) \xrightarrow[110°C \text{ to } 180°C,\ 1 \text{ to } 30 \text{ atm}]{Cu} CH_3OH(\ell) + CH_3OH(\ell) \qquad (2)$$

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(g) \qquad (3)$$

- Not thermodynamically limited
- Main advantage is lower T
- Lower T allows higher conversions, lower compression and recycling costs
- No water formation eliminates distillation

LOW TEMPERATURE METHANOL SYNTHESIS

DEVELOP PRACTICAL OPERATING CONDITIONS FOR THE LOW TEMPERATURE METHANOL SYNTHESIS

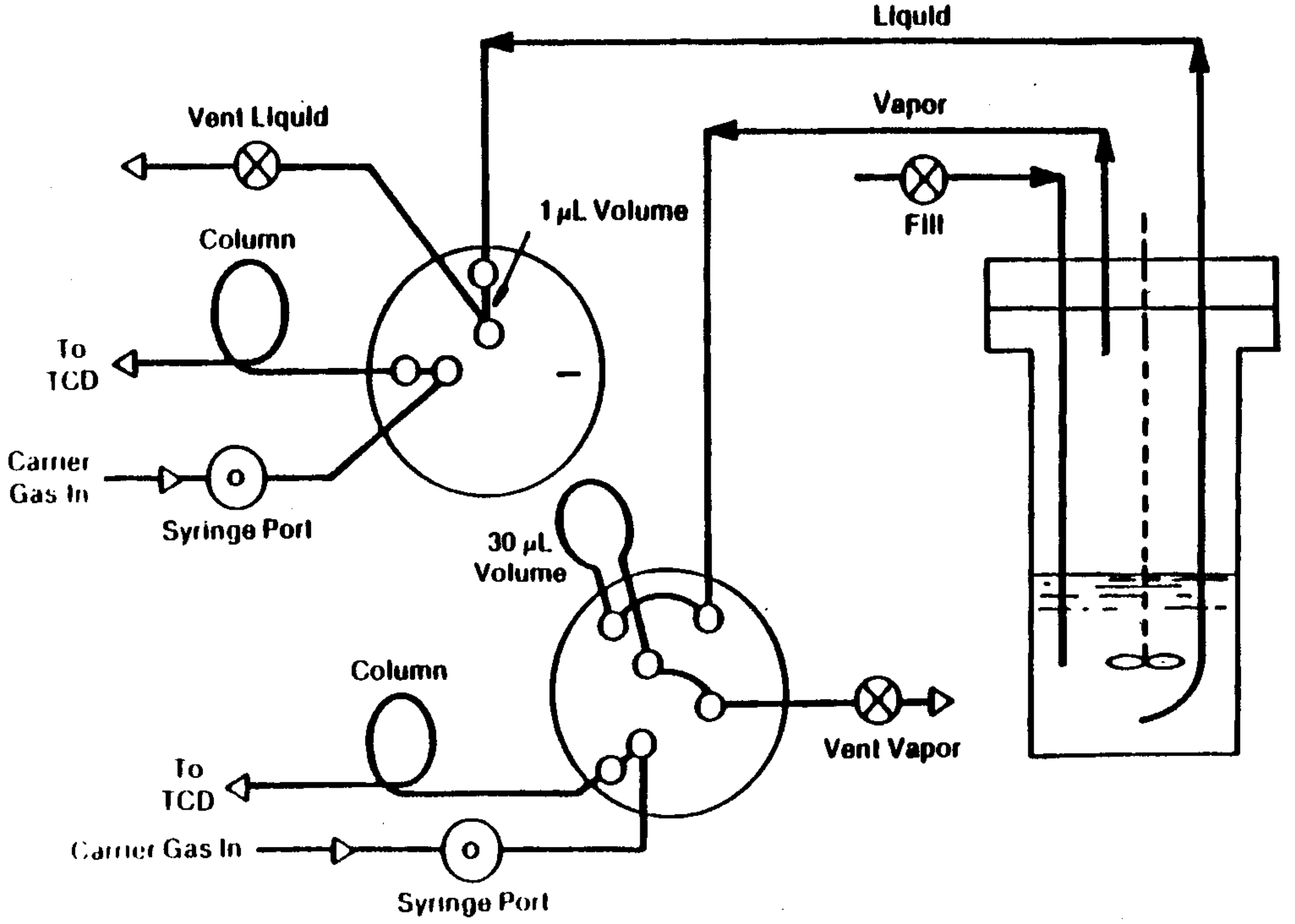
A) CARBONYLATION REACTION:

- EXAMINE THE INFLUENCE OF CO_2 AND H_2O IMPURITIES
- EXAMINE THE INFLUENCE OF H_2 WITH CO

B) HYDROGENOLYSIS REACTION:

- EXAMINE THE INFLUENCE OF CO WITH H_2
- EXAMINE THE STABILITY OF VARIOUS CATALYSTS

ALCOHOL TO FORMATE GC SAMPLING SYSTEM



RATE OF CARBONYLATION REACTION

$$CO + CH_3OH \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} CH_3OCHO$$

$$r = k_1 [cat]_\ell [CH_3OH]_\ell [CO]_\ell - k_{-1} [cat]_\ell [CH_3OCHO]_\ell \qquad (1)$$

It is assumed that $[CH_3OH]_\ell$, $[CH_3OCHO]_\ell$, and $[CO]_\ell$ are related to CO partial pressure in the gas phase according to the following equations:

$$\left[CO\right]_\ell = \alpha \left[CO\right]_g = \alpha \frac{p_{co}}{RT}$$

$$\left[CH_3OH\right]_\ell = \left[CH_3OH\right]_0 - \left(\frac{p^0_{co} - p_{co}}{RT}\right) \cdot \frac{V_g}{V_\ell}$$

$$\left[CH_3OCHO\right]_\ell = \left(\frac{p^0_{co} - p_{co}}{RT}\right) \frac{V_g}{V_\ell}$$

Equation (1) then becomes

$$r = -\frac{1}{RT}\ \frac{dp_{CO}}{dt} = \alpha\ k_1 \left[cat\right]_{\ell} \left(\left[CH_3OH\right]_0 - \frac{p^{\circ}_{CO} - p_{CO}}{RT}\ \frac{V_g}{V_{\ell}}\right)$$

$$\times\ \frac{p_{CO}}{RT} - k_{-1} \left[cat\right]_{\ell} \frac{V_g}{V_{\ell}} \left(\frac{p^{\circ}_{CO} - p_{CO}}{RT}\right) \qquad (2)$$

with

$$K_{eq} = \frac{k_1}{k_{-1}} \qquad (3)$$

Equation (2) may be integrated to give

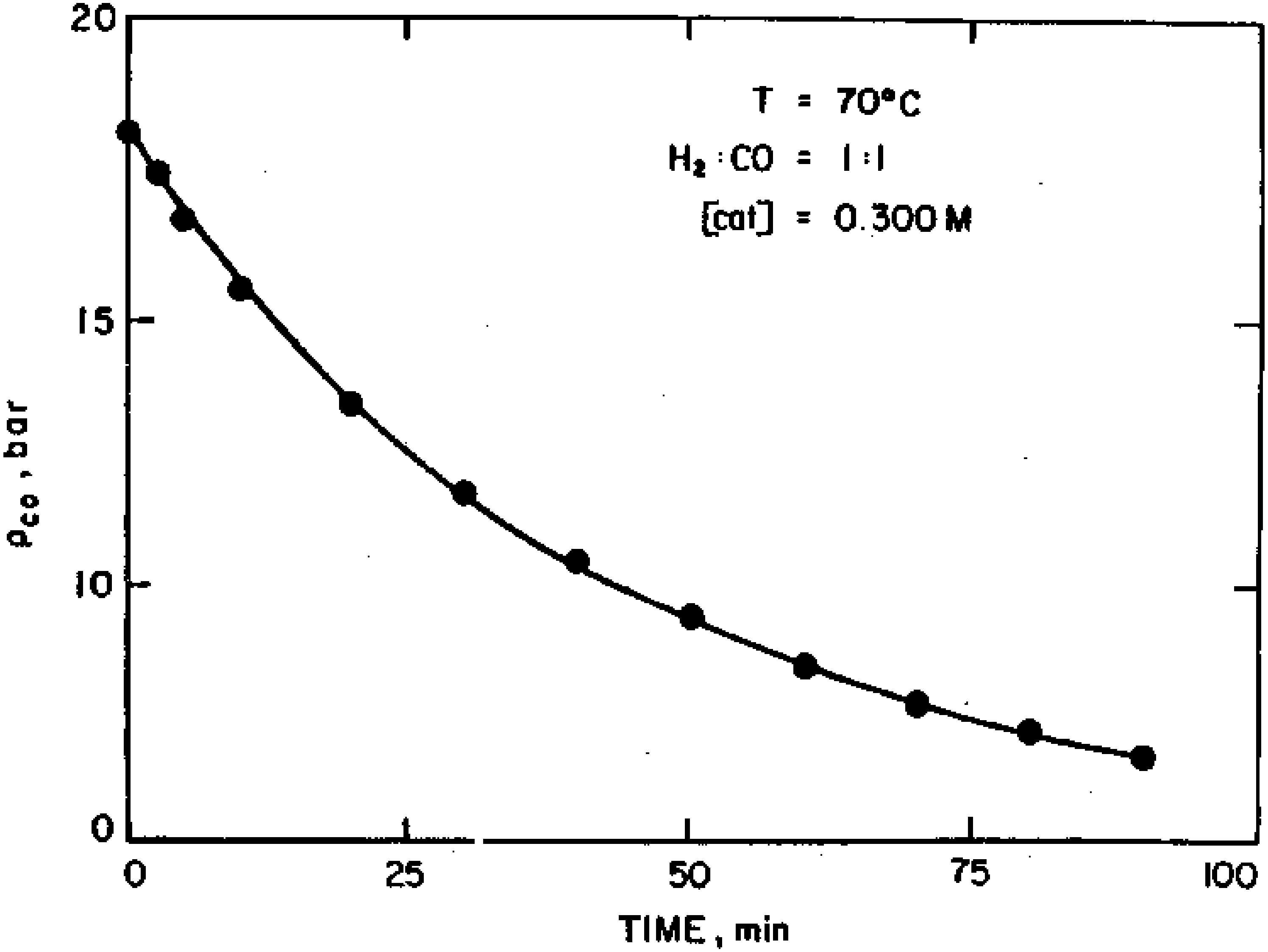
$$\ln\left(\frac{A-\Delta}{A+\Delta}\ \frac{p^{\circ}_{CO} - p_{CO}\ \frac{A+\Delta}{2}}{p^{\circ}_{CO} - p_{CO} - \frac{A-\Delta}{2}}\right) = \lambda\ k_1\ t \qquad (4)$$

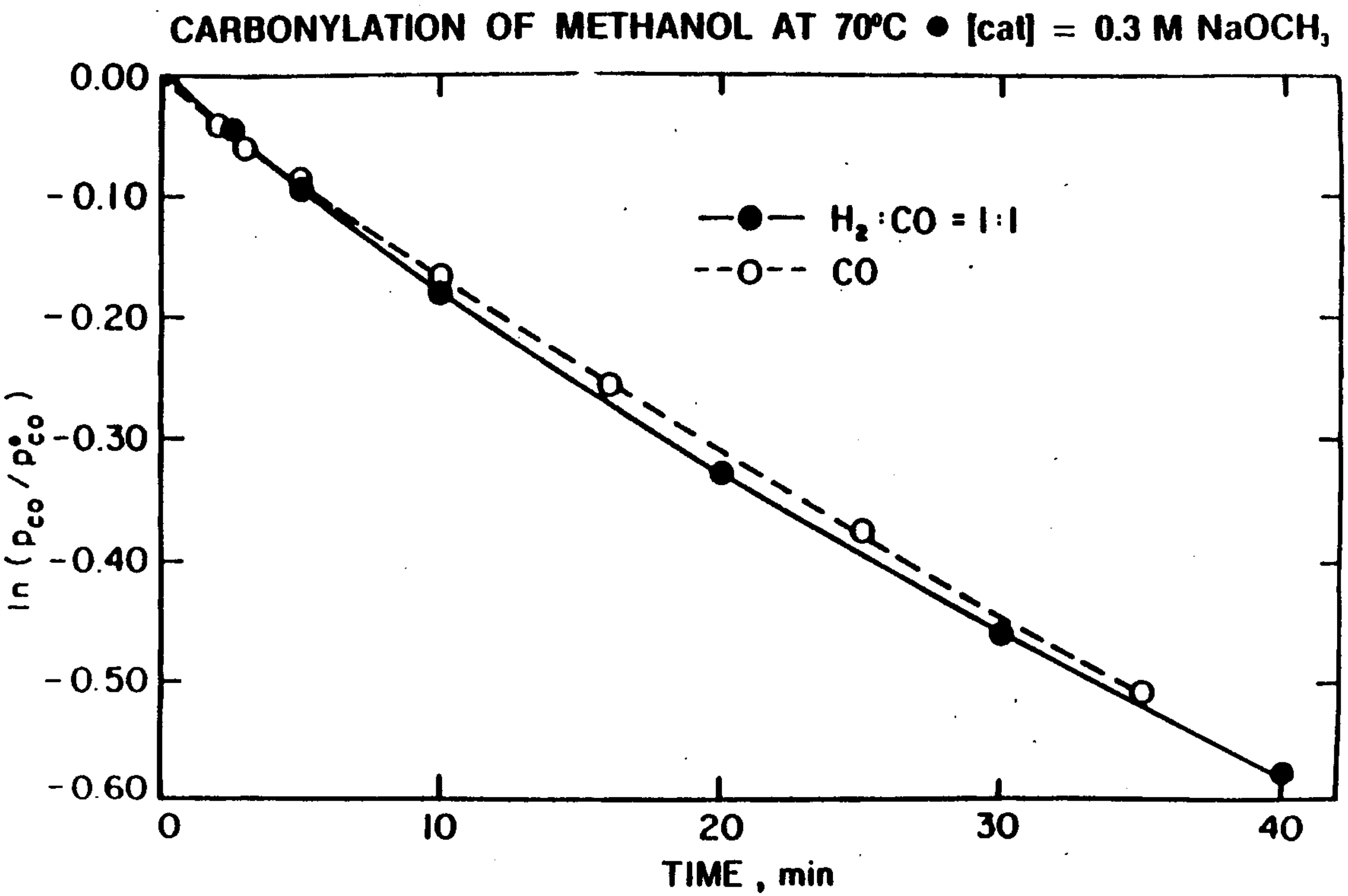
$$A = \frac{RT\ V_{\ell}}{V_g}\ \left[CH_3OH\right]_0 + \frac{RT}{\alpha\ K_{eq}} + p^{\circ}_{CO}$$

$$B = \frac{RT\ V_{\ell}}{V_g}\ p^{\circ}_{CO} \left[CH_3OH\right]_0$$

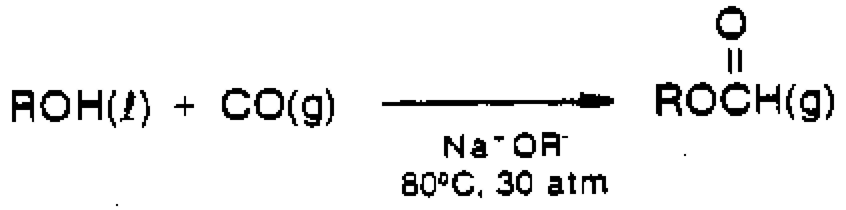
$$\Delta = (A^2 - 4B)^{\frac{1}{2}}$$

$$\lambda = \Delta\ \frac{\alpha V_g \left[cat\right]_{\ell}}{RT\ V_{\ell}}$$


T = 70°C
H_2 : CO = 1:1
[cat] = 0.300 M
p_{co}, bar
20
15
10
0
0
25
50
75
100
TIME, min


CARBONYLATION OF METHANOL AT 70°C • [cat] = 0.3 M NaOCH₃
—●— H₂:CO = 1:1
--o-- CO
0.00
-0.10
-0.20
-0.30
-0.40
-0.50
-0.60
ln (p_co / p°_co)
0
10
20
30
40
TIME , min

INFLUENCE OF CO_2 AND H_2O ON THE CARBONYLATION CATALYST

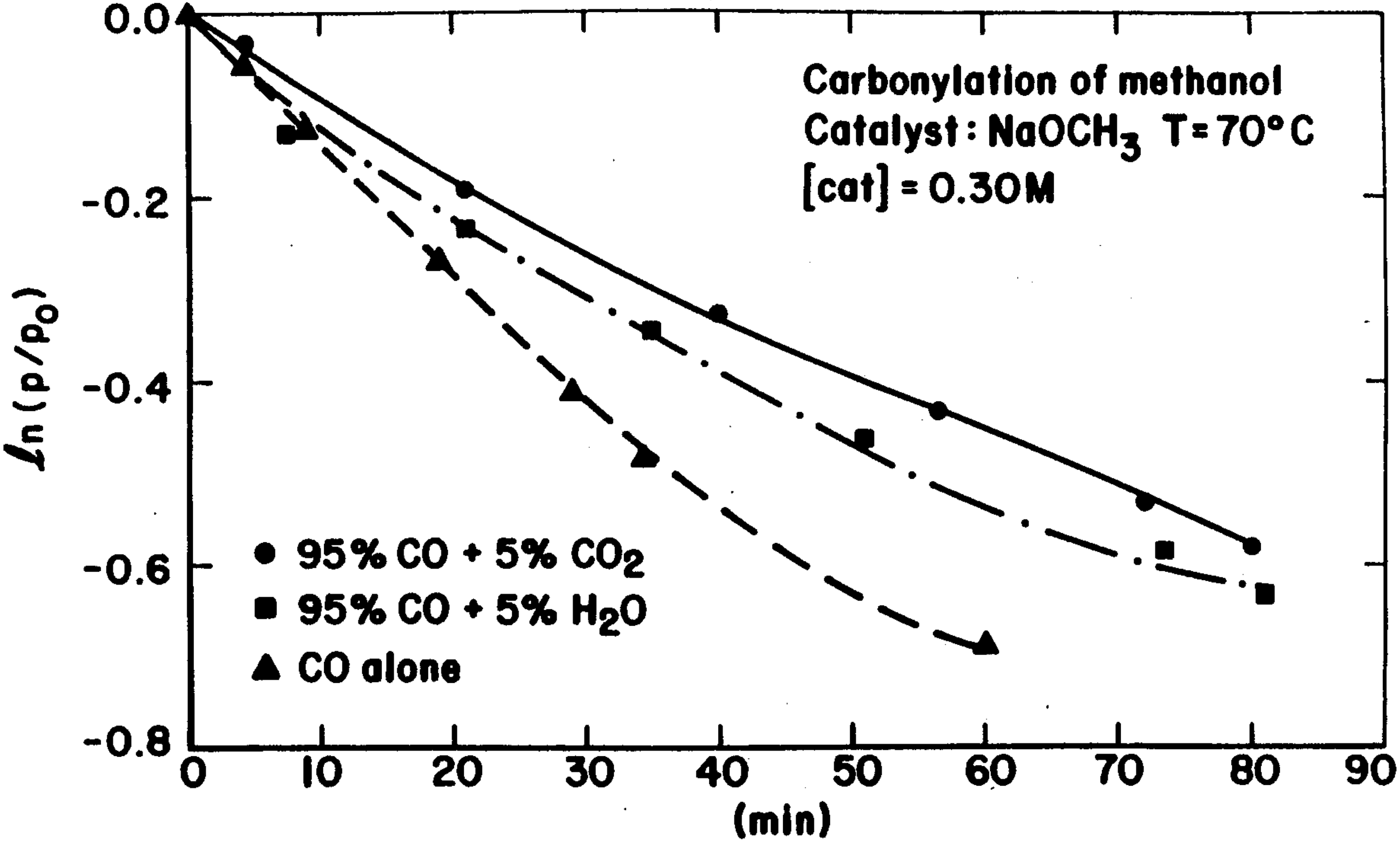


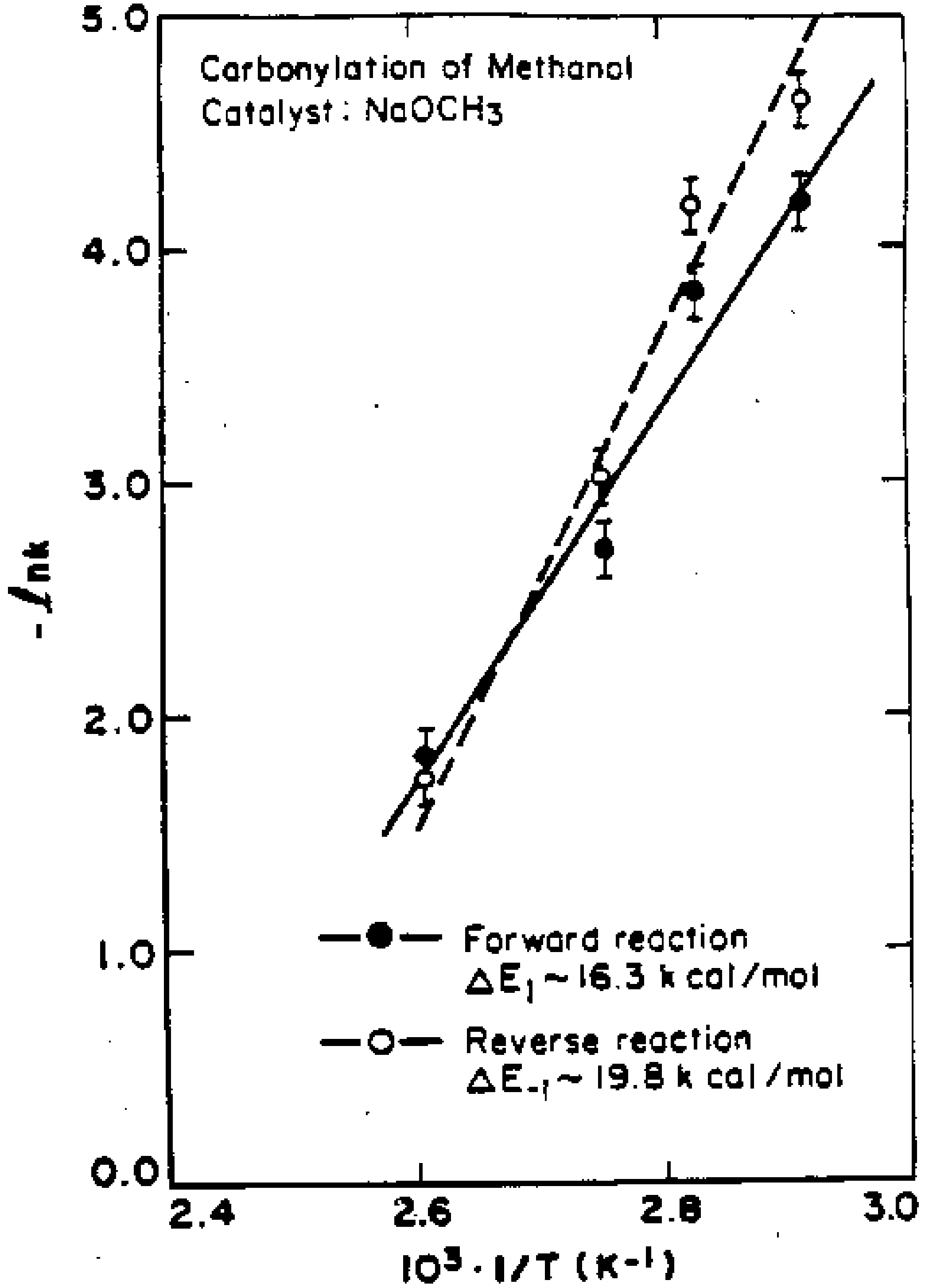
$$\mathrm{ROH}(l) + \mathrm{CO(g)} \xrightarrow[\substack{\mathrm{Na^+OR^-}\\ 80^\circ\mathrm{C},\ 30\ \mathrm{atm}}]{} \mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H(g)} \qquad (1)$$

CO_2 and H_2O may consume the catalyst (K^+OR^- or Na^+OR^-).

$$\mathrm{CO_2} + \mathrm{Na^+OR^-} \longrightarrow \mathrm{ROC}\begin{matrix}\!\!\nearrow\!\!\!\!\!/\ \mathrm{O}\\ \searrow\ \mathrm{ONa}\end{matrix} \qquad (2)$$

$$\mathrm{H_2O} + \mathrm{Na^+OR^-} \rightleftharpoons \mathrm{NaOH} + \mathrm{ROH} \qquad (3)$$


Carbonylation of methanol
Catalyst : $NaOCH_3$ T = 70° C
[cat] = 0.30M
● 95% CO + 5% CO_2
■ 95% CO + 5% H_2O
▲ CO alone
$\ell n\,(p/p_o)$
0.0
-0.2
-0.4
-0.6
-0.8
0
10
20
30
40
50
60
70
80
90
(min)


Carbonylation of Methanol
Catalyst: NaOCH3
5.0
4.0
3.0
2.0
1.0
0.0
-lnk
2.4
2.6
2.8
3.0
10³ · 1/T (K⁻¹)
—●— Forward reaction
ΔE1 ~ 16.3 k cal/mol
—○— Reverse reaction
ΔE-1 ~ 19.8 k cal/mol

ACTIVATION ENERGIES FOR THE FORWARD AND REVERSE REACTIONS $CO + CH_3OH \rightleftharpoons CH_3OCHO$

Catalyst	CH_3ONa	CH_3ONa	CH_3OK
ΔE^* forward (kcal/mol)	16.3 ± 0.1	16.0	16.2 ± 0.4
ΔE^* reverse (kcal/mol)	19.8 ± 0.1		27.6 ± 0.3
Temperature range (°C)	70-110	50-70	60-110
Reference	[1]	[2]	[3]

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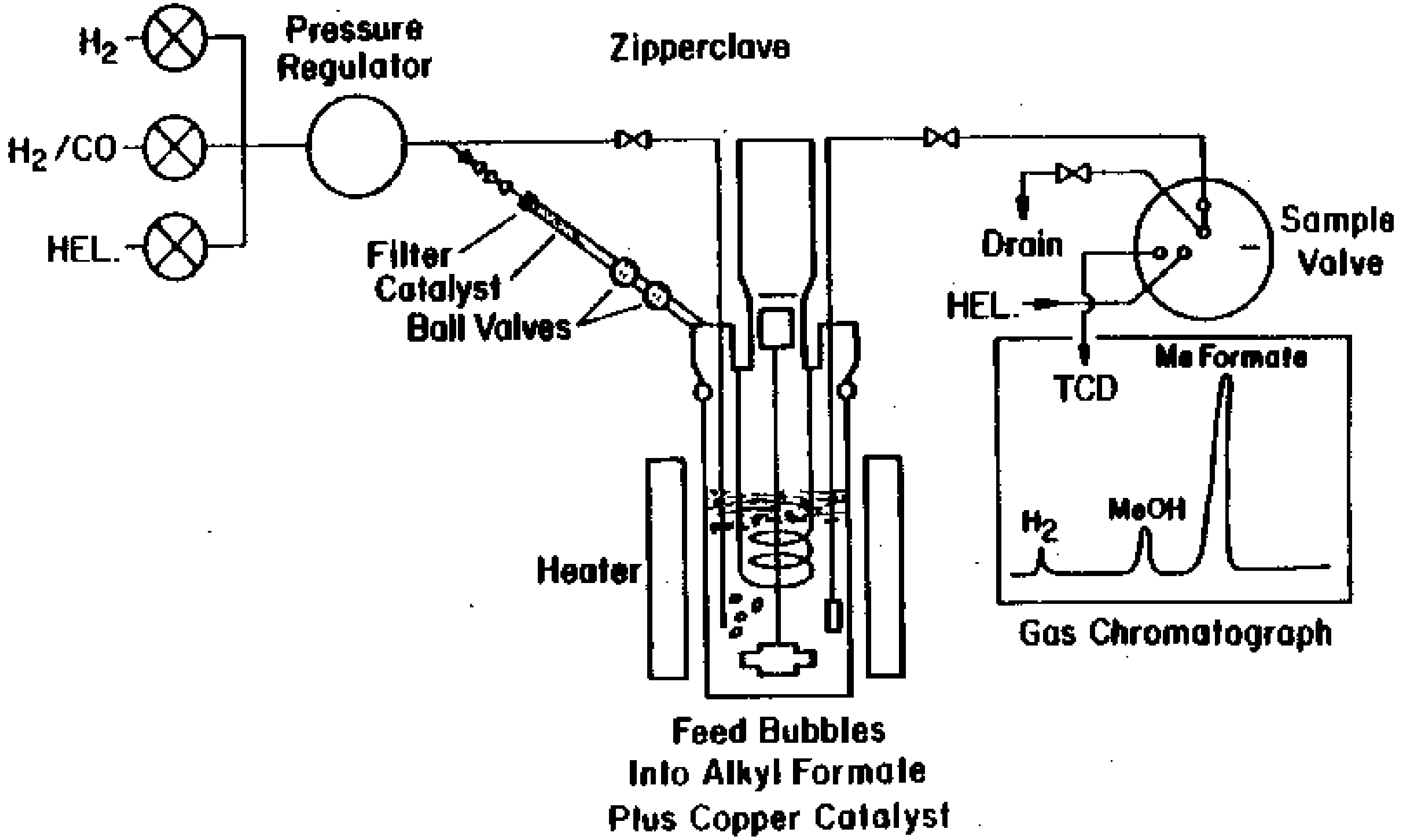
[1] Gormley et al., Proc. 9th Int'l. Congress on Cat., *553* (1988)

[2] Tonner et al., J. Mol. Catal. *18*, 215 (1983)

[3] Liu et al., Fuel Process. Tech., *18*, 185 (1988)

HYDROGENOLYSIS STEP SCHEMATIC

$$CH_3OCHO + 2H_2 \xrightarrow[\text{110°C, 50 atm}]{\text{Cu/Cr}} 2CH_3OH$$



$$CH_3OCHO + 2H_2 \xrightarrow[\text{Cu, 110°C}]{} 2CH_3OH$$

[MeF] = Methyl formate concentration (mol/L)

$$\text{rate} = -\frac{d\,[\text{MeF}]}{dt} = k\,[\text{MeF}]$$

$$-\ell n\ \frac{[\text{MeF}]}{[\text{MeF}]_0} = kt$$

$$\alpha = \text{conversion} = \frac{[\text{MeF}]_0 - [\text{MeF}]}{[\text{MeF}]_0}$$

$$1 - \alpha = \frac{[\text{MeF}]}{[\text{MeF}]_0}$$

$$-\ell n\,(1-\alpha) = kt$$

experimentally : have $\frac{\text{moles MeOH}}{\text{moles MeF}}$, calculate α

$$CH_3OCHO + 2H_2 \xrightarrow[\text{Cu, 110}^{0}\text{C}]{} 2CH_3OH$$

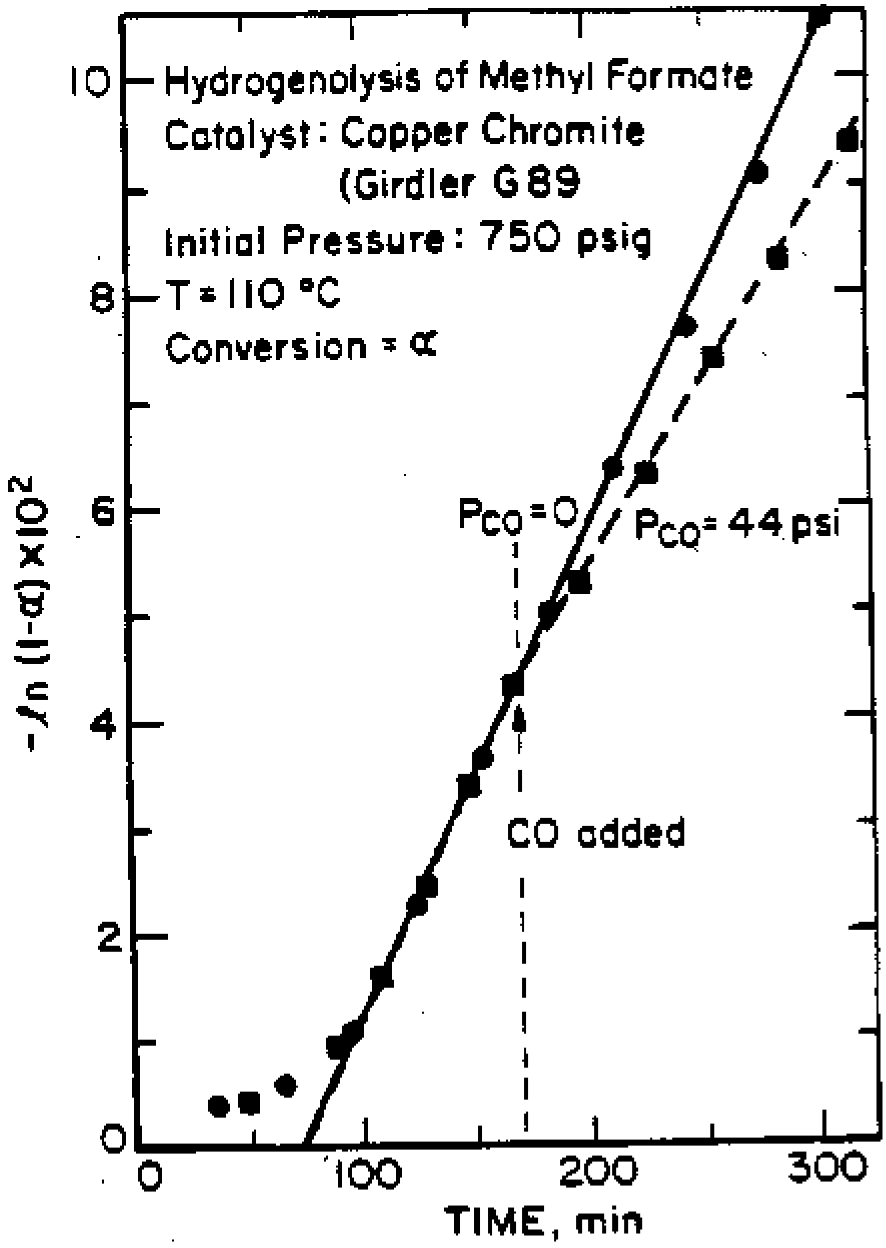
Hydrogenolysis reaction is inhibited by CO

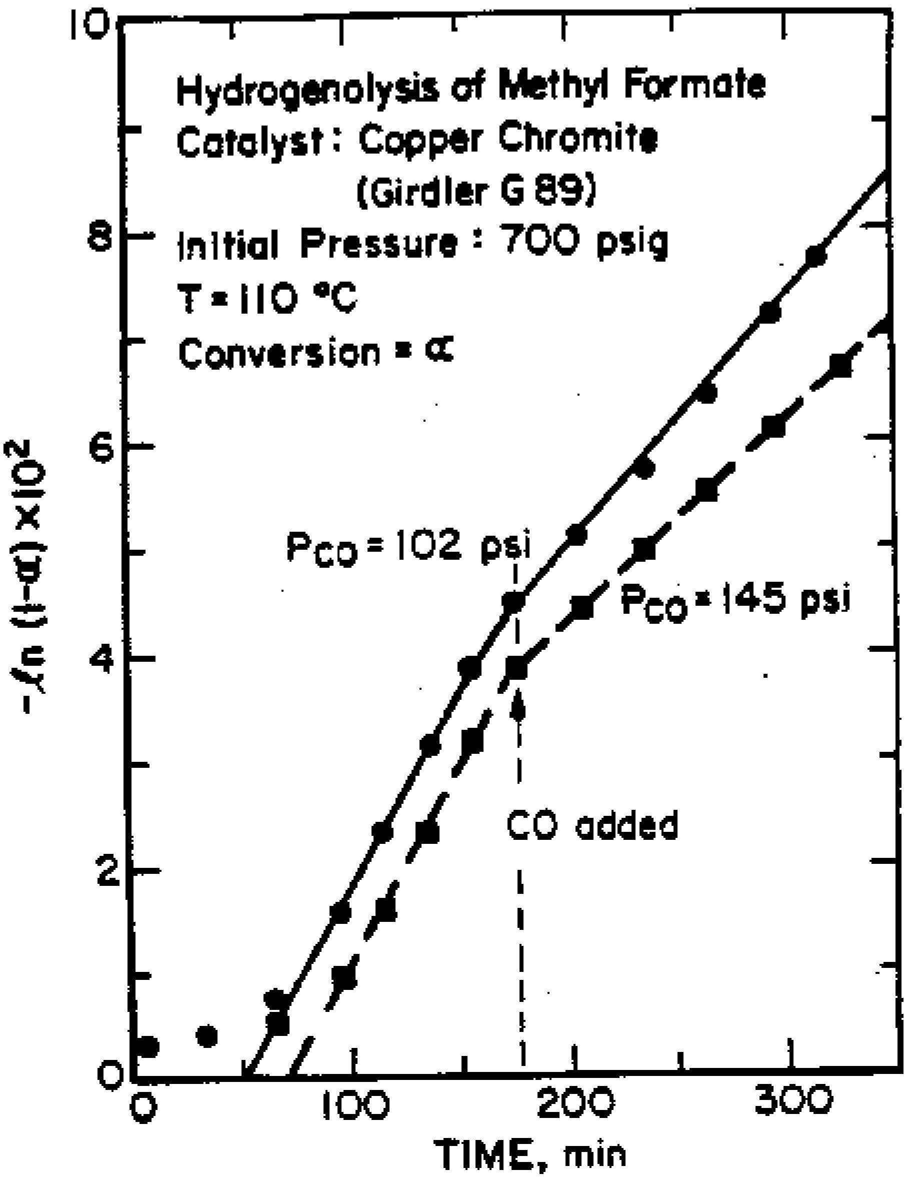
$$r = k\,[CH_3OCHO]\,[cat] \quad p_{H_2}\ p_{co}^{-x}$$

HYDROGENOLYSIS REACTION

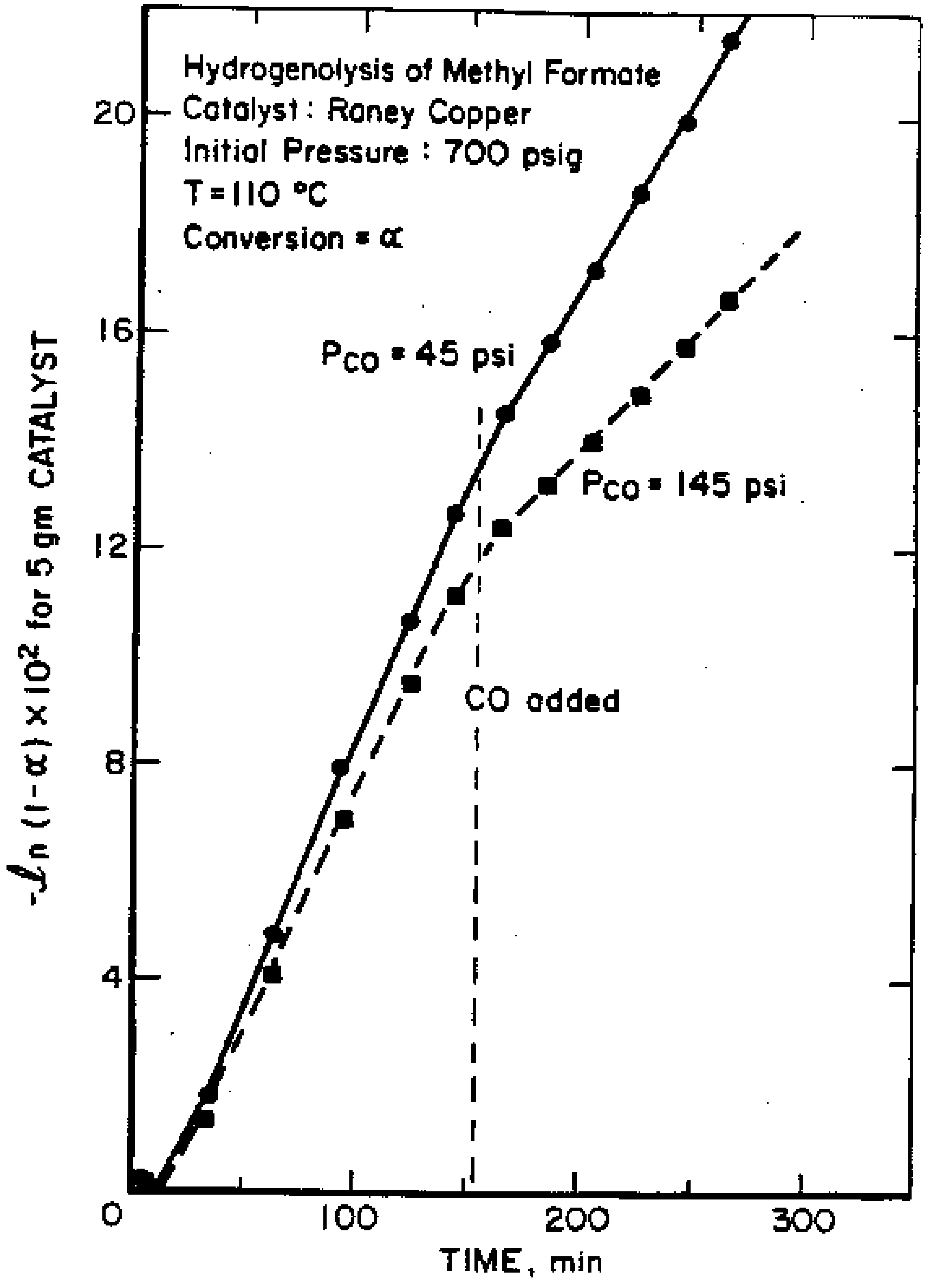
ADSORPTION STRENGTH ON COPPER

METHYL FORMATE > CO > H_2


Hydrogenolysis of Methyl Formate
Catalyst: Copper Chromite
(Girdler G89
Initial Pressure: 750 psig
T = 110 °C
Conversion = α
$P_{CO} = 0$
$P_{CO} = 44$ psi
CO added
$-\ln(1-\alpha) \times 10^2$
0
2
4
6
8
10
0
100
200
300
TIME, min



Hydrogenolysis of Methyl Formate
Catalyst: Copper Chromite
(Girdler G 89)
Initial Pressure: 700 psig
T = 110 °C
Conversion = α
P_{CO} = 102 psi
P_{CO} = 145 psi
CO added
$-\ln(1-\alpha)\times10^2$
TIME, min
0
2
4
6
8
10
0
100
200
300


Hydrogenolysis of Methyl Formate
Catalyst : Raney Copper
Initial Pressure : 700 psig
T = 110 °C
Conversion = α
P_{CO} = 45 psi
P_{CO} = 145 psi
CO added
$-\ln(1-\alpha) \times 10^2$ for 5 gm CATALYST
TIME, min
0
4
8
12
16
20
100
200
300

CATALYSTS SCREENED FOR THE HYDROGENOLYSIS OF METHYL FORMATE

Catalyst 20g/L	Rate $r \times 10^{-2}$ (mol/L min)	Inhibition by CO $\sim p_{co}^{-x}$
Raney Cu	1.6	$x = 0.30$ to 0.32
Raney Cu-Cr	1.2	$x = 0.21$ to 0.29
Copper Chromite (Girdler G-89)	0.8	$x = 0.22$ to 0.30

MODELING

Complicated System

1. Homogeneous Reaction

   $CH_3OH + CO \xleftrightarrow{1} CH_3OCHO$

2. Heterogeneous Reaction

   $CH_3OCHO + 2H_2 \xrightarrow{2} 2CH_3OH$

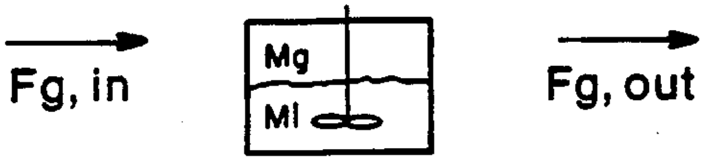
3. Nonideal Gas Condition (50 atm)
4. Vapor - Liquid Equilibrium

   $CH_3OH_{(l)} \longleftrightarrow CH_3OH_{(g)}$

   $CH_3OCHO_{(l)} \longleftrightarrow CH_3OCHO_{(g)}$

5. Solubility of CO, H_2 in methanol and Methyl Formate
6. Deactivation of the Catalyst

TWO STEP METHANOL SYNTHESIS IN A SLURRY REACTOR



Simplified System

Assumptions

1. The system can be represented by kinetic equations of carbonylation and hydrogenolysis
2. Ideal gas condition

$$CH_3OH + CO \overset{1}{\rightleftharpoons} CH_3CHO$$

$$\text{Carbonylation} = R_1 = f(T, C_{cat.1}, C_{MeOH}, P_{co}, C_{MeF})$$

$$2H_2 + CH_3CHO \xrightarrow{2} 2\,CH_3OH$$

$$\text{Hydrogenolysis} = R_2 = f(T, C_{cat.2}, C_{MeF}, P_{H_2}, P_{co})$$

Accumulation = in + produce — consume — out

Mole balance for MeOH, MeF, CO, H_2

$$\frac{d(M_l X_{MeOH})}{dt} = R_1 + 2R_2$$

$$\frac{d(M_l X_{MeF})}{dt} = R_1 - R_2$$

$$\frac{d(M_g Y_{co})}{dt} = F_{g,in} Y_{i,co} - R_1 - F_{g,out} Y_{co}$$

$$\frac{d(M_g Y_{H_2})}{dt} = F_{g,in} Y_{i,H_2} - 2R_2 - F_{g,out} Y_{H_2}$$

CONCLUDING REMARKS

1. The kinetic rate constants k_1 and k_{-1} for the forward and back reactions in the carbonylation of methanol have been determined and may be applied in modeling the low-temperature synthesis of CH_3OH in a single, slurry-phase reactor.

2. A negative influence of CO_2 and H_2O on the reaction was observed. The effect is more severe for CO_2, which removes the catalyst quantitatively by forming an insoluble sodium salt of the semiester of carbonic acid. Reaction of H_2O with CH_3ONa is equilbrium controlled and produces NaOH, which is slightly soluble in the reaction medium. Thus the carbonylation rate is affected to a lesser extent.

3. The hydrogenolysis of methyl formate over a Raney copper catalyst is inhibited by the presence of CO. The extent of inhibition by CO will be investigated at higher temperatures.

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