

## THE HYDROGENATION OF CARBON DIOXIDE IN PARTS-PER-MILLION LEVELS

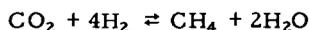
S. S. Randhava and A. Rehmat

Institute of Gas Technology  
Chicago, Illinois 60616

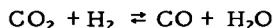
### INTRODUCTION

In recent years the development of the fuel cell, a device that converts chemical energy directly into electrical energy, particularly the low-temperature, acid fuel cell that uses reformed natural gas, made it necessary to design a process that can produce a reformat gas suitable for fuel cell application.

The process is well established, but the kinetics of some of the reactions that take place during the process are not very well known. One of the reactions that could take place during the process is



However, CO may be formed by the side reaction



Early investigations of the reaction between carbon dioxide and hydrogen were either primarily qualitative in nature or attempts to determine the equilibrium of the reaction; consequently, no data suitable for kinetic analysis were presented.

The first attempt to obtain rate data for this system was made by Nicolai, d'Hont and Jungers.<sup>1</sup> They studied the kinetics of carbon dioxide hydrogenation on a nickel catalyst at low pressures (0.10-1.0 atm) and temperatures of 180°-300°C. Binder and White<sup>2</sup> made an extensive study of this system for the first time. The rate of the reaction was correlated by a mechanism which assumes that the major resistance to the overall process is offered by the reaction of an adsorbed carbon dioxide molecule with at least two adsorbed hydrogen molecules; thus, the surface reaction appeared to be rate-controlling. This study was extended by Dew, White and Slipevich,<sup>3</sup> who studied the effect of total pressure and postulated a mechanism which assumes that the reaction takes place between four adsorbed molecules of hydrogen and an adsorbed molecule of carbon dioxide on the catalyst's surface.

In a search for a source of synthetic hydrocarbons, Fischer and Pichler<sup>4</sup> studied the reaction between carbon dioxide and hydrogen, and carbon monoxide and hydrogen over a ruthenium catalyst. Only high-molecular-weight hydrocarbons were obtained at 100 atmospheres; methane at one atmosphere. Pichler also reported that ruthenium could not be improved by promoters or carriers. For this reason and because of its high cost, this catalyst was not tried by other investigators for the hydrogenation of carbon dioxide or carbon monoxide until a later date.

In its search for better catalysts, the Bureau of Mines<sup>5,6</sup> found that ruthenium can be used on alumina in concentrations of 0.5%, at a cost no greater than commercially successful catalysts made from platinum. Ruthenium can also compete with nickel, considering the small quantities required (0.5% Ru vs. 48% Ni), and when compared to commercial nickel hydrogenation catalysts and the complexity of nickel pretreatment.

The purpose of this investigation was to obtain data over a range of temperatures, compositions, and space velocities, using a gas mixture containing carbon dioxide

(ppm) in hydrogen. Using a ruthenium catalyst impregnated on an alumina support for data at atmospheric pressure would yield an expression for the kinetics of the hydrogenation of carbon dioxide.

## EXPERIMENTAL

The basic description of the experimental apparatus has been presented elsewhere.<sup>7</sup> The reactor was fabricated from a 22-in.-long, stainless steel, Type-304 tube, having a 1/2-in. ID and a 1-in. OD. The thickness of the wall ensured longitudinal isothermality. A multipoint thermocouple was placed inside the bed, with three thermocouples observing temperatures at intervals of 1/4 in. A perforated screen, functioning as a catalyst support, was welded to the thermocouple rod 1 in. from the tip. A premixed mixture of carbon dioxide and hydrogen was passed through a pressure regulator and control valve to a calibrated rotameter. Then the gases entered the top of the reactor and flowed downward through the catalyst bed.

The catalyst used in this investigation was furnished by Englehard Industries, Inc., and consisted of 0.5% ruthenium impregnated on 1/8 x 1/8-in. cylindrical alumina pellets. Catalyst pellets (2 cc) dispersed in an equal volume of alumina pellets were used for every run. The catalyst was activated prior to a run sequence by passing H<sub>2</sub> over it at 450°C for approximately 2 hours. Because of the dispersed nature of the catalyst and the low gas concentrations, the reactor behavior was isothermal, with the temperature variance in three thermocouples never exceeding 1°C, even under conditions of maximum conversion. Steady-state conversions were achieved within 30 minutes for all variations of temperature and gas flow rate.

The product gases, after leaving the reactor, flowed through a condenser and were continuously monitored until a steady state was achieved. Two nondispersive, infrared analyzers (MSA Lira Model 300) were used to determine the concentrations of carbon monoxide and methane. The infrared analyzers were calibrated to read in the ranges of 0-100, 0-500, and 0-3500 ppm of CO and CH<sub>4</sub> and were never permitted to drift beyond 5 ppm on the 0-3500 ppm scale. The units were calibrated at the beginning of each run sequence (constant temperature with varying space velocities) with hydrogen used as the zero calibration gas. Five different gas mixtures were used to check the calibration scale of each of the Liras. The calibration gases were mixed and analyzed by The Matheson Co. and were accurate to within 2 ppm. All of the premixed and analyzed gases containing 1150, 2060, and 3580 ppm carbon dioxide in hydrogen were also supplied by The Matheson Co.

## RESULTS

In this investigation, the runs are grouped into three different sets, each having a different feed composition: 1150, 2060, and 3580 ppm CO<sub>2</sub> in H<sub>2</sub>. For each set five runs were made with varied flow rates and at constant temperature. The temperature range investigated was 200°-450°C; the gas flow rates used were 10, 30, 50, 70, and 100 cu cm/s, corresponding to the variation of residence time from 0.2 to 0.02  $\frac{\text{cu cm catalyst}}{\text{cu cm gas/s}}$ . The pressure was maintained at 1 atmosphere for all the runs. Selected runs were repeated to check reproducibility and for catalyst deactivation. All the data taken were reproducible to  $\pm 2\%$ ; no noticeable decrease in the catalytic activity was observed over the runs' durations.

Each run was obtained under steady-state conditions and consisted of an analysis of effluent gases at a given feed rate, temperature, pressure, and the quantity of the catalyst: The duration of each run was approximately 40 minutes. The quantity of the catalyst was kept constant throughout all the runs. The effects of the variables involved are discussed below.

Effect of Temperature. The number of moles of carbon dioxide converted per mole of carbon dioxide in the feed gas for all gas mixtures, and the corresponding number of moles of methane and carbon monoxide formed for selected gas mixtures at different temperatures are shown in Figures 1-5.

The production of methane per mole of CO<sub>2</sub> fed is maximum for the gas mixture containing 1150 ppm CO<sub>2</sub>: The ratio reaches 1 at temperatures around 450°C and a residence time of  $0.2 \frac{\text{cu cm catalyst}}{\text{cu cm gas/s}}$ . The conversion of carbon dioxide and the production of methane and carbon monoxide exhibited characteristic S-shaped curves, showing an increase in conversion with an increase in temperature.

The formation of carbon monoxide is favored by an increase in temperature; however, at temperatures below 350°C there is negligible formation. Above this temperature, the amount of carbon monoxide in the effluent progressively increases.

At higher temperature ranges note that all three gases exhibit asymptotic behavior regarding conversions. It is apparent that the selection of a temperature range for this experiment almost spans the entire range for carbon dioxide methanation at these concentrations.

Effect of Feed Gas Composition. The effect of feed gas composition on hydrogenation reactions is significant over the ruthenium catalyst. The carbon dioxide conversion increases with decreasing amounts of carbon dioxide in the feed gas at any temperature and for all residence times. The asymptotic values of conversion decreased from ~1 for 1150 ppm CO<sub>2</sub> to about 0.8 for 3580 ppm CO<sub>2</sub>. The amount of methane produced per mole of carbon dioxide in the feed also increases with the decrease in amount of carbon dioxide in the feed gas. It was interesting to note that the formation of carbon monoxide increases with an increase in the concentration of carbon dioxide in the feed. Consequently, the conversions may be increased by either raising the temperature to ~450°F, or by decreasing the amount of carbon dioxide in the feed gas.

Effect of Residence Time. In each case the conversion of carbon dioxide increases with an increase in residence time. At any given temperature, the production of methane also increases with an increase in the residence time. This would naturally indicate conventional reactor behavior.

However, the effect of residence time on the formation of carbon monoxide displayed a rather unconventional characteristic. Figure 5 shows an increase in the formation of carbon monoxide with a decrease in residence time over the entire range of temperatures and concentrations investigated.

## DISCUSSION

It appears possible that the following reactions are taking place:



Several investigators have shown<sup>2,3</sup> that, at higher concentrations of carbon dioxide in the feed, the methanation of carbon dioxide takes place directly by Reaction 1; carbon monoxide is formed by the side reaction, Reaction 2. It appears from our results that the methanation of ppm concentrations of carbon dioxide does not occur directly by Reaction 1, since we found that at any particular temperature carbon monoxide is produced by increasing the flow rate. This would mean that the reverse shift reaction (Reaction 2) reaches equilibrium almost instantaneously; the

methanation of carbon monoxide proceeds with time. More carbon monoxide is produced (Reaction 2) as the methanation of carbon monoxide takes place until the steady-state condition is reached. Nicolai, d'Hont and Jungers<sup>1</sup> pointed out that carbon dioxide does not react in the presence of carbon monoxide. In one of the studies at the Institute of Gas Technology<sup>10</sup> on the selective methanation of carbon monoxide using a gas mixture containing hydrogen, carbon dioxide, and carbon monoxide, it was also pointed out that ruthenium is the best selective methanation catalyst and that the reaction of carbon dioxide does not proceed in an appreciable amount until the level of carbon monoxide in the mixture reaches a certain minimum level. In the present investigation this is indeed the case. As soon as the carbon monoxide methanation reaches a steady state, leaving the concentration of carbon monoxide in the reacting mixture above this minimum, the conversion of carbon dioxide ceases completely, as indicated by Figures 1-3.

For finding the overall empirical rate expression valid for the change of conversion and corresponding rate constants at various temperatures for these reactions, an expression of the type

$$-r_{\text{CO}_2} = kC_{\text{CO}_2}^n$$

was tried for reasons given by Levenspiel,<sup>8</sup> who suggested the use of simple empirical rate expressions in chemical reactor design work. The use of such a power law rate equation is also supported by catalytic combustion studies at U.C.L.A.<sup>9</sup> Although the reaction rate should depend upon the concentration of hydrogen in addition to the concentration of carbon dioxide in the system, this term has been omitted from the rate expression used here, since hydrogen is in excess and is treated essentially as a constant.

The rate expression can also be stated in a different form

$$-r_{\text{CO}_2} = -\frac{dC_{\text{CO}_2}}{\left(\frac{V}{V_0}\right)} = kC_{\text{CO}_2}^n$$

which, when integrated, yields the expression -

$$k(n-1) \frac{V}{V_0} = C_{\text{CO}_2}^{1-n} + (C_{\text{CO}_2})_0^{1-n} \text{ for } n \neq 1$$

$C_{\text{CO}_2}^{1-n}$  was plotted against  $\frac{V}{V_0}$  for various values of  $n$ . The value of  $n$  giving the best straight line was used as the reaction order for the hydrogenation of the carbon dioxide reaction. The rate constants could then be calculated from the slopes of the lines. The best value of  $n$  was found to be 1.5. A typical plot of  $C_{\text{CO}_2}^{1-n}$  versus  $\frac{V}{V_0}$  for this value of  $n$  is shown in Figure 6 for a feed of 1150 ppm  $\text{CO}_2$ .

The reaction velocity constant is related to the reaction temperature in accordance with the Arrhenius equation

$$k = k_0 e^{-E/RT}$$

The Arrhenius plots for this reaction are given in Figure 7. The empirical frequency factor,  $k_0$ , and the activation energy for this reaction are tabulated in Table 1. All of the Arrhenius plots are linear in the temperature range considered.

Table 1. ACTIVATION ENERGIES AND SPECIFIC REACTION RATE CONSTANTS AS A FUNCTION OF THE INLET-GAS COMPOSITIONS

Concentration of CO <sub>2</sub> in Feed, ppm	E, kcal/ mole	k <sub>0</sub> , $\frac{\text{cu cm gas (ppm CO}_2\text{)}^{-0.5}}{\text{cu cm catalyst/s}}$
1150	10.8	5700
2060	11.4	4250
3580	11.5	2800

Unlike the methanation of carbon monoxide on ruthenium,<sup>7</sup> where only one Arrhenius plot was obtained for all the concentrations of carbon monoxide, three different plots are obtained for the three concentrations of carbon dioxide considered. This can be explained by the way in which the methanation of carbon dioxide takes place. Since it occurs by the reverse shift reaction, all we are dealing with is the methanation of carbon monoxide and the effect of the various amounts of carbon dioxide on such a reaction. Thus the decrease in k values, due to an increase in the concentration of carbon dioxide in the feed, can be compared to Cohen and Nobe's<sup>11</sup> work dealing with the effect of an increasing concentration of water vapor on the catalytic oxidation of carbon monoxide on nickel oxide. (This phenomenon is explained below.)

Every catalyst has a number of active sites where the reaction takes place. In the case of the hydrogenation of carbon dioxide these sites are occupied by carbon monoxide, which is reacting with hydrogen to form methane, and by carbon dioxide, which remains unreacted. As the concentration of carbon dioxide is increased, more of the sites are occupied by unreacted carbon dioxide, thus making fewer sites available for the reaction of carbon monoxide. Therefore, one would expect a decrease in the reactivity of carbon monoxide with hydrogen to form methane when carbon dioxide is present in the reacting mixture. This effect of increasing the amount of carbon dioxide is reflected in the decreasing values of the reaction constant, k.

### CONCLUSION

The hydrogenation of carbon dioxide at very low concentrations over a 0.5% ruthenium catalyst was studied. The empirical rate expression, valid for the change of conversion of CO<sub>2</sub> in the overall reaction, was found to follow the simple expression

$$-r_{\text{CO}_2} = k \text{CO}_2^{1.5}$$

where k obeyed the Arrhenius temperature dependence for each concentration at all temperatures.

The methanation of carbon dioxide took place in two steps: the formation of carbon monoxide and the subsequent hydrogenation of carbon monoxide to methane. The effect of an increasing amount of carbon dioxide in the feed was reflected in the decreasing values of the reaction constant, k.

### ACKNOWLEDGMENT

The authors wish to thank the Institute of Gas Technology which sponsored this work through its basic research program.

NOMENCLATURE

- $C_A$  = concentration of species A in effluent, ppm
- $(C_{A_0})$  = concentration of species A in feed, ppm
- E = activation energy, cal/g-mole
- k = reaction rate constant,  $\frac{(\text{cu cm gas})(\text{ppm CO}_2)^{-0.5}}{(\text{cu cm catalyst})(\text{s})}$
- $k_0$  = Arrhenius frequency factor,  $\frac{(\text{cu cm gas})(\text{ppm CO}_2)^{-0.5}}{(\text{cu cm catalyst})(\text{s})}$
- n = reaction order
- $r_A$  = rate of change of conversion of species A,  $\frac{(\text{cu cm gas})(\text{ppm CO}_2)}{(\text{cu cm catalyst})(\text{s})}$
- R = gas constant, cal/mole - °K
- T = temperature, °K
- $v_0$  = volumetric flow rate of gas, cu cm/s
- V = volume of catalyst, cu cm
- $x_A$  = moles of A converted or produced per mole of CO<sub>2</sub> in feed

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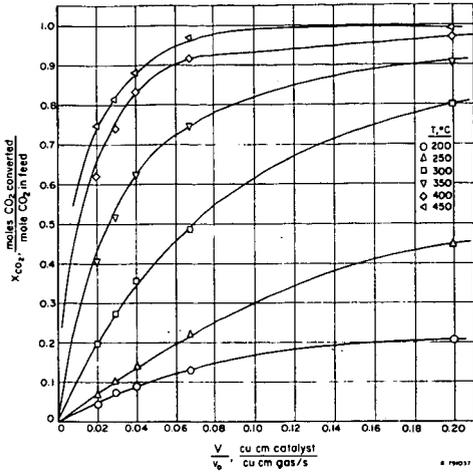


Figure 1. CONVERSION OF CO<sub>2</sub> AS A FUNCTION OF RESIDENCE TIME FOR 1150 ppm FEED GAS

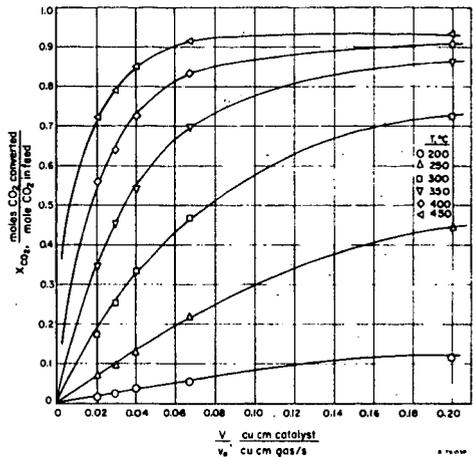


Figure 2. CONVERSION OF CO<sub>2</sub> AS A FUNCTION OF RESIDENCE TIME FOR 2060 ppm FEED GAS

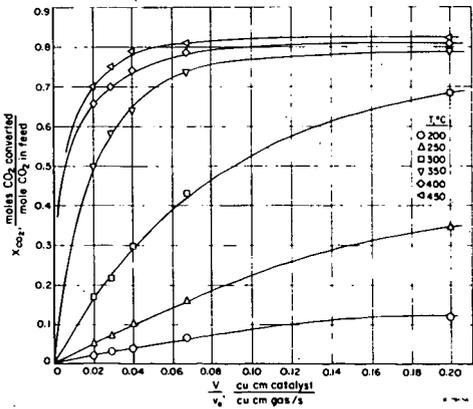


Figure 3. CONVERSION OF CO<sub>2</sub> AS A FUNCTION OF RESIDENCE TIME FOR 3580 ppm FEED GAS

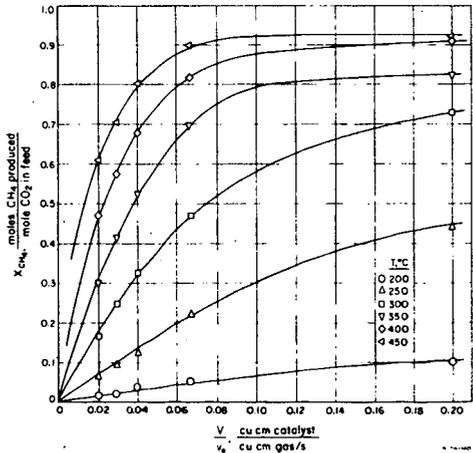


Figure 4. PRODUCTION OF CH<sub>4</sub> AS A FUNCTION OF RESIDENCE TIME FOR 2060 ppm FEED GAS

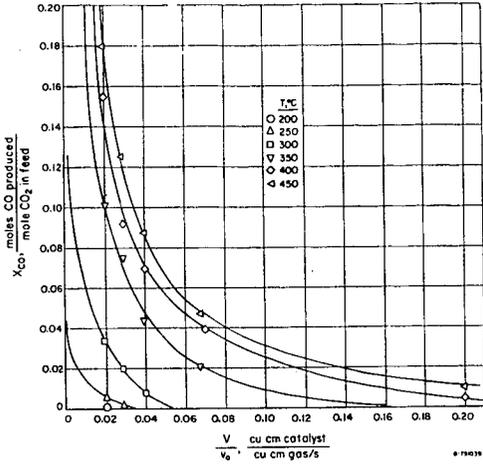


Figure 5. CO PRODUCTION AS A FUNCTION OF RESIDENCE TIME FOR 3580 ppm FEED GAS

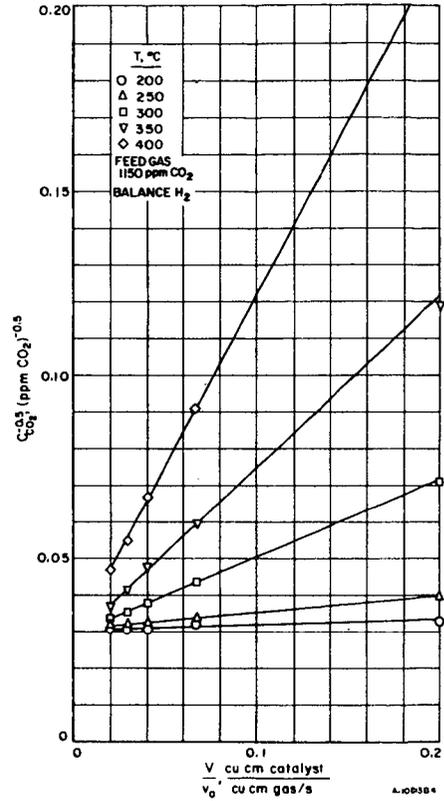


Figure 6. VARIATION IN  $C_{CO_2}^{-0.5}$  WITH RESIDENCE TIME FOR 1150 ppm FEED GAS

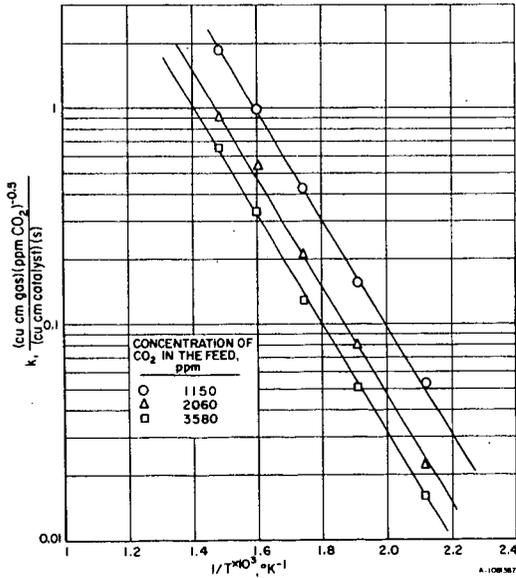


Figure 7. ARRHENIUS PLOT FOR HYDROGENATION OF  $CO_2$