

Hydrogenation of CO₂ on Group VIII Metals

I. Specific Activity of Ni/SiO₂

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Received March 14, 1980; revised September 25, 1980

Specific, intrinsic rates and product distributions for CO₂ hydrogenation on Ni/SiO₂ were determined at 500–575 K, 140–2500 kPa, and a range of space velocities. The data show that the turnover number for CO₂ methanation on nickel is the same as for CO methanation at 525 K; apparent activation energies for CH₄ formation are 96 and 80 kJ/mol in CO and CO₂ hydrogenation, respectively. Besides methane, CO and small amounts of C₂ hydrocarbons are produced as products of CO₂ methanation; the product distribution is a function of space velocity from 4000 to 49,000 h⁻¹, the yield of methane being significantly higher at low space velocities. Results of conversion vs temperature tests show that the production of CH₄ is higher from CO than CO₂ hydrogenation over the temperature range 500–725 K.

INTRODUCTION

CO hydrogenation reactions have been extensively investigated since the discovery of methane production over nickel in 1902 by Sabatier and Sendersens (1). In recent years renewed interest in the production of synthetic fuels has stimulated a number of fundamental studies of the kinetics and mechanisms of CO hydrogenation on Group VIII metals (2–8). Kinetic and mechanistic studies of CO₂ hydrogenation have been far less extensive than those of CO hydrogenation. Most of the previous work has been detailed in two previous reviews (2, 3).

Previous kinetic studies of CO₂ hydrogenation on nickel (2, 9–16) were performed under widely varying experimental conditions using poorly characterized catalysts; thus, comparison of the results is difficult or impossible. In addition most of the previous kinetic studies were performed under high conversion conditions using large catalyst particles or pellets, so that the intrinsic kinetics were masked by pore diffusional resistance and heat/mass transport limitations. None of the previously reported rates

were based on nickel metal surface area so as to enable a meaningful comparison of data from catalyst to catalyst.

The purpose of this investigation was to determine (i) the intrinsic, specific rate of CO₂ hydrogenation on Ni/SiO₂ under chemical-reaction-controlled conditions, (ii) the temperature dependency of the reaction rate, and (iii) effects of temperature, pressure, and space velocity on specific rate and conversion. In this paper, data for CO₂ methanation on Ni/SiO₂ are presented, discussed, and also compared with corresponding data for CO methanation on the same catalyst.

EXPERIMENTAL

Analytically pure Ni(NO₃) · H₂O and Cabosil SiO₂ (Cabot Corp.) were used in preparation of a 3% Ni/SiO₂ catalyst. Preparation by simple impregnation to incipient wetness of the support with an aqueous metal salt solution was followed by oven drying at 375 K. The impregnated, dried sample was reduced in flowing hydrogen at a space velocity of 2000 h⁻¹ while heating at 2 K per minute to 750 K with a 2 hr hold at 500 K and a 12 hr hold at 750 K. The sample

was then carefully passivated with 1% air in N₂.

Hydrogen and nitrogen gases (99.99%) were purified by passing both through a palladium Deoxo purifier (Engelhard) and a dehydrated molecular sieve trap. Carbon monoxide (Matheson Purity 99.99%) was purified by passing through a Molecular Sieve Trap. Carbon dioxide (Matheson Purity 99.99%) was used without further purification.

The metal surface area of the catalyst was determined by H₂ chemisorption at 298 K using a conventional volumetric apparatus capable of 1.3×10^{-7} kPa (17). The hydrogen adsorption uptake was determined as a function of pressure and the linear portion of the isotherm extrapolated to zero pressure to obtain the amount chemisorbed. The catalyst was also characterized by a full range argon BET adsorption conducted at 90 K. The desorption isotherm was analyzed using the Barrett, Joyner, and Halenda method (18) to obtain the average pore size.

CO₂ methanation activity was determined using 1 cm³ of catalyst (approx. 0.3 g) in a 1.25-cm-diameter fixed bed reactor constructed of either glass (17) or stainless-steel (19) and equipped with a preheater and a thermocouple in the catalyst bed. Activity measurements were conducted at 500–550 K, 140 kPa, and space velocities of 4000–50,000 h⁻¹ using a reaction mixture consisting of 95% N₂, 4% H₂, and 1% CO₂. Limited measurements were also conducted at 1030 and 2600 kPa. CO methanation tests were conducted under identical conditions using a reactant gas mixture of 95% N₂, 4% H₂, and 1% CO.

All reactant and product gas concentrations were measured chromatographically using thermal conductivity and flame ionization detectors. Peak areas were determined electronically and related to concentrations by calibrating with a gas mixture containing known amounts ($\pm 1\%$) of CO, H₂, CO₂, and CH₄. Carbon balances generally accounted for 99% of the input carbon.

The largest error in the carbon balance (usually about 1%) was due to measurement of reactant CO₂ and CO conversion since the conversion of reactant species was measured by difference (usually small) between reactant and product concentrations. Measurements of methane and C₂₊ hydrocarbon concentrations made directly by FID were significantly more accurate (better than $\pm 0.1\%$ of entering carbon). Carbon deposition was not significant at the low temperatures and CO₂/CO concentrations used in this study, and thus had negligible effect on the carbon balance.

RESULTS

Hydrogen chemisorption measurements showed 3% Ni/SiO₂ to have an uptake of 100 μ mol H₂ per gram of catalyst (both before and following reactor tests). This corresponds to a nickel dispersion (percentage exposed) of 39% assuming complete reduction of nickel to the metal and an average metal crystallite diameter of 2.5 nm, assuming spherical particles and a nickel planar density of 6.77×10^{-2} (nm)²/atom. From full range BET measurements the total surface area of the 3% Ni/SiO₂ catalyst was found to be 192 m²/g and the average pore radius to be 6.0 nm.

Table 1 lists methane turnover numbers (molecules methane produced per site per second) and product yields (fractions of converted CO or CO₂ appearing as specified products) for CO₂ and CO methanation at 140 kPa and 500, 525, and 550 K. The methane turnover number for CO₂ methanation is slightly higher at 500 K, the same at 525 K and slightly lower at 550 K than for CO methanation. In CO₂ methanation a significant fraction of CO is produced, which increases with increasing temperature. Only small amounts of C₂₊ hydrocarbons are formed during CO₂ and CO methanation. The conversion of CO₂ to C₂ hydrocarbons is 3–4 orders of magnitude smaller than the conversion to CH₄ (no higher molecular weight products were detected). Production of C₂ hydrocarbons is

TABLE 1
Specific Activity and Product Distribution of 3% Ni/SiO₂ in CO and CO₂ Hydrogenation^a

Temp. (K)	GHSV (h ⁻¹)	CO ₂ hydrogenation					CO hydrogenation					
		Conv of CO ₂ (%)	N _{CH₄} ^b × 10 ³	Percentage yield ^c			Conv of CO (%)	N _{CH₄} ^b × 10 ³	Percentage yield ^c			
				CH ₄	CO	C ₂			CH ₄	CO ₂	C ₂	C ₃
500	16350	3.9	0.85	70	9	0.07	2.4	0.71	75	0	4.7	1.9
525	16350	8.6	2.1	77	15	0.05	7.4	2.1	76	2	2.2	0.3
550	32900	11.2	5.0	70	25	0.02	9.4	5.9	82	2	1.1	0.0

^a 140 kPa, reaction mixture: 95% N₂, 4% H₂, 1% CO₂, or 1% CO.

^b Methane turnover number: the rate of methane production per nickel site (measured by H₂ adsorption at 298 K) per second.

^c Yield is the fraction of converted CO₂ or CO appearing as a specified product. Since the overall carbon balance was accurate to ±1%, the yields at 5–10% conversion are accurate to ±10–15%.

significantly higher in CO methanation, i.e., 1–2 orders of magnitude smaller than the CH₄ production; very small amounts of C₃ are also formed.

Figure 1 is an Arrhenius plot of the low temperature activity data for CO₂ and CO methanation plotted as the natural log of

the CH₄ turnover number vs inverse temperature. A least-squares fit of the data shows the activation energy for CH₄ formation in CO₂ methanation to be 80 kJ/mol. A similar fit of the CO methanation data gives an activation energy of 96 kJ/mol. The plot reveals that at higher temperatures (<550

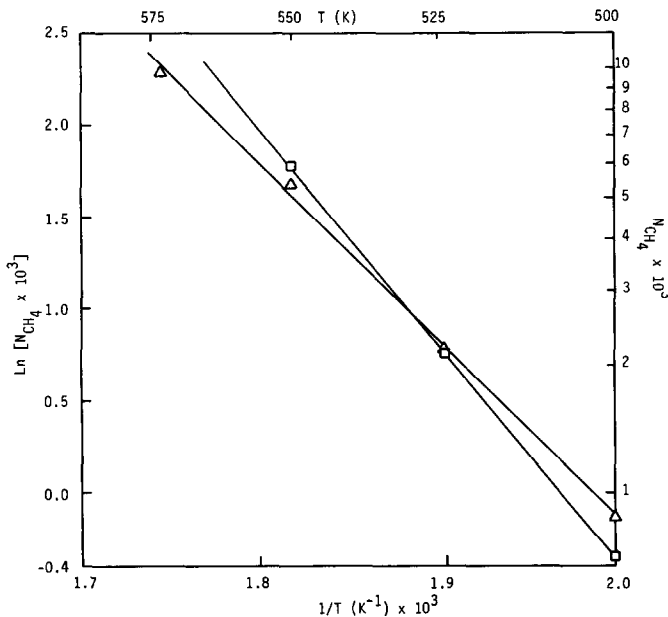


FIG. 1. Arrhenius plot of methane turnover numbers in CO and CO₂ methanation on 3% Ni/SiO₂ at 140 kPa and GHSV = 16,000–50,000 h⁻¹ in 95% N₂, 4% H₂, and 1% CO₂ or CO. Δ CO₂ methanation; \square CO methanation.

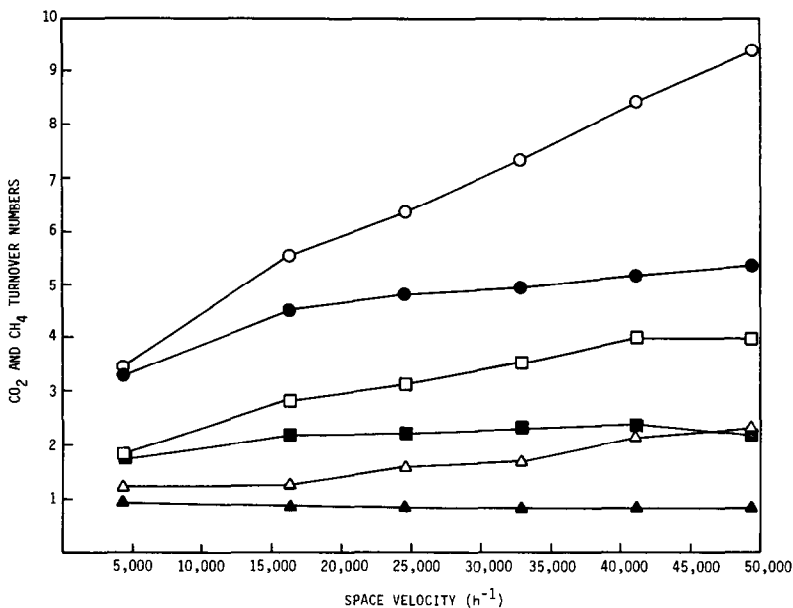


FIG. 2. CH₄ and CO₂ turnover numbers as a function of space velocity for CO₂ methanation at 140 kPa. ○ 550 K, □ 525 K, △ 500 K. CO₂ turnover numbers—open symbols; CH₄ turnover numbers—closed symbols.

K), the specific rate of CO methanation is larger than for CO₂ methanation.

Figures 2 and 3 show the results of CO₂ methanation activity tests as a function of

space velocity. It is evident from Fig. 2 that the CH₄ turnover number is nearly constant at each temperature tested while the CO₂ turnover number varies greatly with space

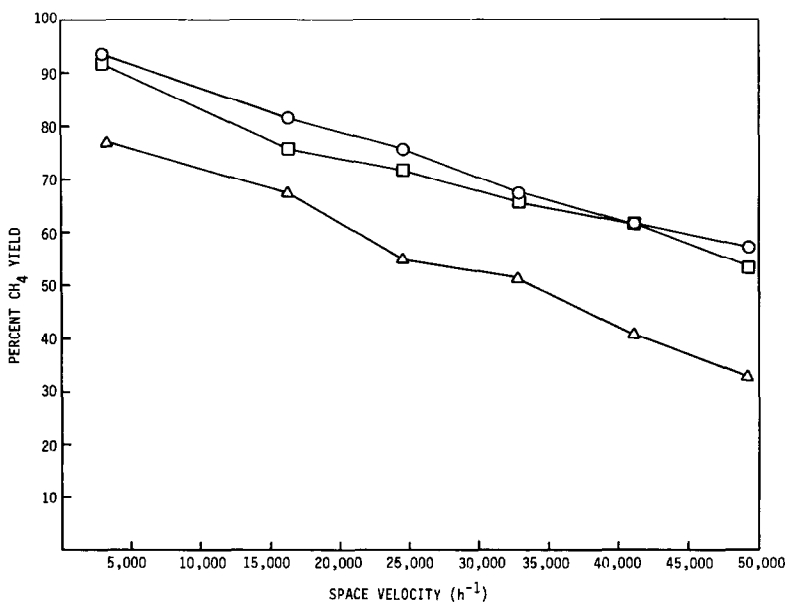


FIG. 3. Methane yield as a function of space velocity at 140 kPa in 95% N₂, 4% H₂, and 1% CO₂. △ 500 K, □ 525 K, ○ 550 K.

velocity, the extent of this variation increasing with increasing temperature. From the data in Fig. 3, it is apparent that the selectivity to methane also decreases greatly with increasing space velocity (and hence decreasing residence time and/or conversion). At the same time, the yield of CO increases with increasing space velocity. In fact, it was found that while the outlet methane concentration decreased with increasing space velocity, outlet CO concentration was constant at any given temperature and pressure over a wide range of space velocities (4000 to 50,000 h⁻¹). For example, at 140 kPa, the steady-state outlet concentrations of CO were 0.0023, 0.010, and 0.026% at 500, 525, and 550 K, respectively.

The Thiele Modulus was calculated for CO₂ methanation over 3% Ni/SiO₂ at 575 K, 140 kPa, and a GHSV of 49,400 h⁻¹. A summary of catalyst properties, reaction conditions, and the results of the calculations are given in Table 2. The calculations show the Thiele Modulus and effectiveness factor to be 0.011 and 1.0, respectively. In other words, pore diffusional resistance did not affect the activity measurements at temperatures of 575 K and below.

Table 3 shows the effects of pressure on CO₂ methanation activity and product distribution. The data show that pressure has little effect on the conversion of CO₂. There is, however, a large increase in the CH₄ turnover number and methane yield (and a concurrent decrease in the rate of produc-

TABLE 2
Thiele Modulus Calculations for 3%
Ni/SiO₂

Average pore radius: 6.0 nm
Average particle diameter: 1.0×10^{-4} m
Pressure: 140 kPa
Temperature: 575 K
GHSV: 49,400 h ⁻¹
Conversion CO ₂ : 0.17
Thiele Modulus: 0.011
Effectiveness factor: 1.0

TABLE 3

Effects of Pressure on Specific Activity and Product Distribution in CO₂ Hydrogenation^a on 3% Ni/SiO₂

Pressure (kPa)	$N_{\text{CO}_2}^b \times 10^3$ (s ⁻¹)	$N_{\text{CH}_4}^b \times 10^3$ (s ⁻¹)	Percentage CH ₄ yield ^c
140	4.0	2.4	59
1030	4.6	4.3	94
2600	4.5	4.5	100

^a At 525 K and a space velocity of 38,000–40,000 h⁻¹. Reactant gas mixture: 95% N₂, 4% H₂, 1% CO₂.

^b Turnover number: molecules of CO₂ converted or methane produced per nickel site (measured by H₂ adsorption at 298 K) per second.

^c CH₄ yield is the fraction of converted CO₂ appearing as methane.

tion and yield of CO) as the pressure is increased. The data at 140 and 1030 kPa show the overall pressure dependence for formation of CH₄ to be 0.3 order, compared to 0.07 order for CO₂ conversion.

Conversion temperature data for CO₂ and CO methanation at both low and high space velocities are shown in Figs. 4 and 5, respectively. At a very high space velocity (49,400 h⁻¹), CO₂ conversion rises slowly to a maximum of about 50% at 725 K and methane production (the fraction of reactant CO₂ converted to methane) reaches a maximum of about 38% at 675 K (see Fig. 4). CO production reaches almost 20% at 725 K. At a low space velocity (4340 h⁻¹) CO₂ conversion reaches a maximum of about 70% at 600 K; essentially all of the CO₂ is converted to methane below 650 K. A similar behavior is observed in CO methanation (Fig. 5) in that CO conversion and methane production are higher, CO₂ production lower at the lower space velocity. However, comparison of Figs. 4 and 5 reveals that at any given temperature and space velocity, CO conversion (in CO methanation) exceeds CO₂ conversion (in CO₂ methanation) and methane production is always higher in CO methanation. In CO methanation complete con-

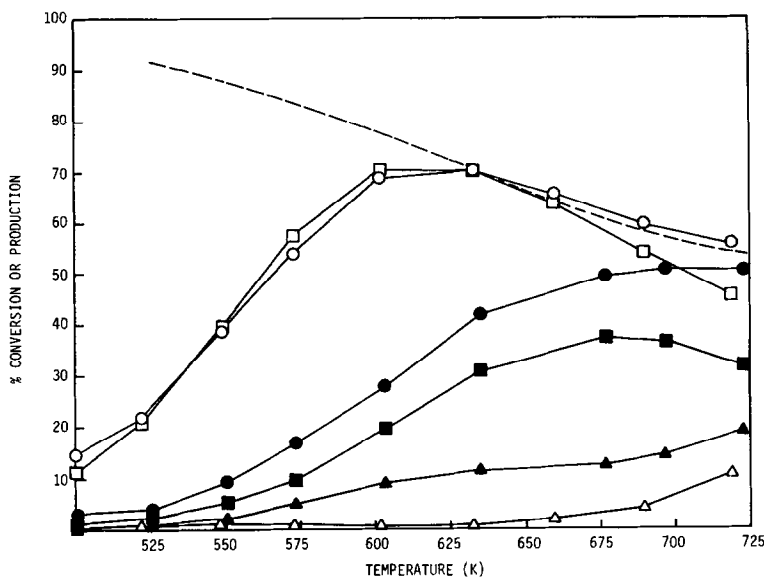


FIG. 4. Conversion vs temperature plots for CO₂ methanation at 140 kPa in 95% N₂, 4% H₂, and 1% CO₂. Closed symbols—49,400 h⁻¹; open symbols—4340 h⁻¹. ○ CO₂ conversion, □ CH₄ production, △ CO production. Dashed line is equilibrium CO₂ conversion.

version of CO is obtained at low space velocity; complete conversion of CO₂ does not occur in CO₂ methanation. On the other hand the methane yield is greater for CO₂ methanation (100% compared to 80% at 625 K) at the low space velocity.

Figure 6 shows conversion temperature data for CO₂ methanation at high pressure (1030 kPa) at both low and high space velocities. At high space velocity the conversion of CO₂ reaches a maximum of 72% at 650 K while the production of CH₄ reaches a maximum of about 58% at the same temperature. The data at low space velocity (4340 h⁻¹) show that CO₂ is almost completely converted to methane with the CO₂ conversion and CH₄ production reaching a maximum of 88% at 610 K. At high pressure the production of CO from CO₂ is small or negligible at both low and high space velocities.

DISCUSSION

Specific Activity of Nickel for CO₂ Methanation

The specific activity data determined in

this study (Table 1) for a well-characterized 3% Ni/SiO₂ under conditions where heat and mass transfer effects clearly did not influence the rate measurements reveal that methane turnover numbers for CO₂ and CO methanation are the same within experimental error at low temperatures (500–550 K). These are, to our knowledge, the first reported specific activity data for CO₂ methanation on nickel. Most previous studies of CO₂ methanation were conducted on commercial catalyst pellets of unspecified metal surface area under high-pressure, high-temperature conditions such that the rates were influenced by heat, mass transport, and pore diffusional resistances.

The data of this study (Table 1 and Fig. 1) show that CO methanation involves a higher activation energy for CH₄ production than does CO₂ methanation. Hence CO methanation occurs at a significantly higher rate than CO₂ methanation on nickel at temperatures of 550 K and above. The activation energy of 96 kJ/mol reported for CO methanation on Ni/SiO₂ is in close agreement with values of 90–110 kJ/mol reported in previous studies of Ni/SiO₂ and

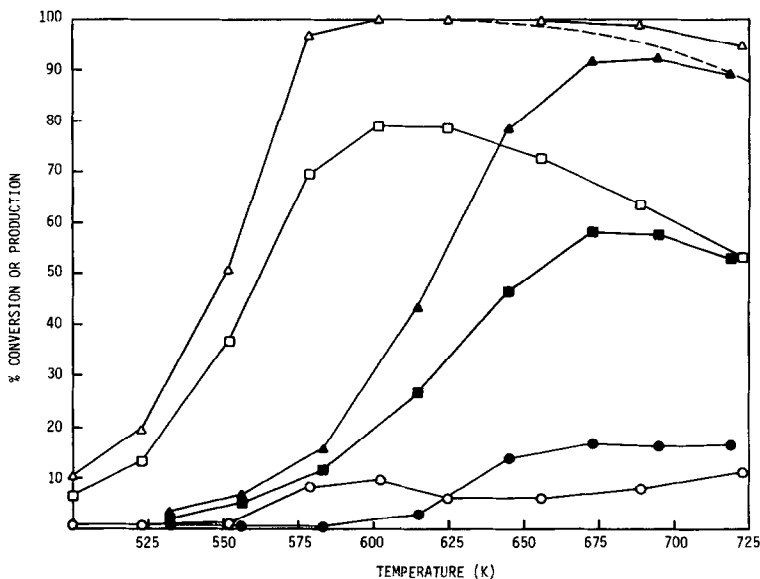


FIG. 5. Conversion vs temperature plots for CO methanation at 140 kPa in 95% N₂, 4% H₂, and 1% CO. Closed symbols—49,400 h⁻¹; open symbols—4340 h⁻¹. Δ CO conversion, \square CH₄ production, \circ CO₂ production. Dashed line is equilibrium CO conversion.

Ni/Al₂O₃ (4, 6, 8, 17, 19). Previously reported activation energies for CO₂ methanation are generally 30 to 50% lower than

those reported here (see Table 4). However, as noted earlier, these studies were conducted on large catalyst particles under

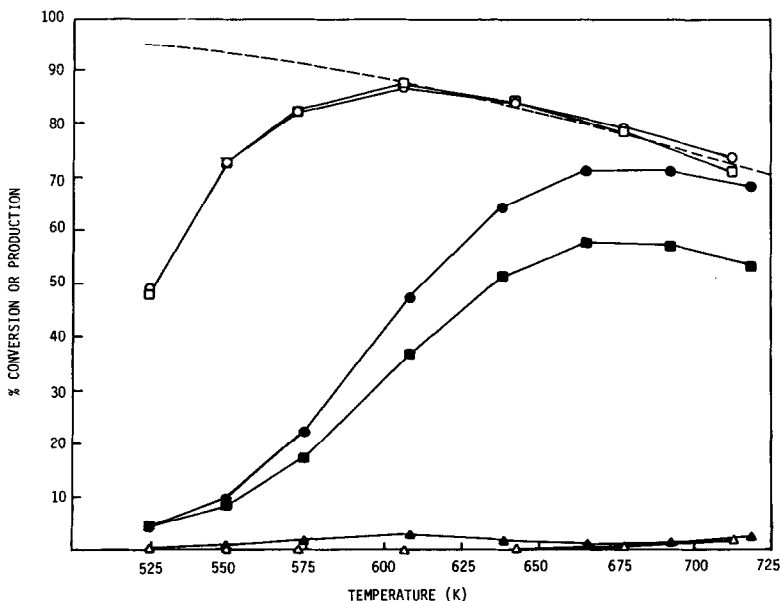


FIG. 6. Conversion vs temperature plots for CO₂ methanation at 1030 kPa in 95% N₂, 4% H₂, and 1% CO₂. Closed symbols—49,400 h⁻¹; open symbols—4340 h⁻¹. \circ CO₂ conversion, \square CH₄ production, Δ CO production. Dashed line is equilibrium CO₂ conversion.

TABLE 4
Activation Energies Reported for
CO₂ Hydrogenation on Nickel

E_{act} (kJ/mole)	Reference
54.8–58.1	11, 12
54.8	13
85.7	14, 15
54.3	4
105.8	16
70, ^a 80 ^b	This study

^a For CO₂ hydrogenation.

^b For methane formation.

industrial conditions where heat and mass transfer effects and especially pore diffusional resistance would tend to result in a lower observed activation energy than if such effects were absent. Herwijnen *et al.* (16) reported an activation energy of 106 kJ/mol for a high loading commercial Ni on γ -Al₂O₃ catalyst at low pressure and low temperature. Their calculations showed that there were negligible film and pore diffusion resistances under the conditions of their study. The value of 80 kJ/mol obtained in this study for Ni/SiO₂ is clearly significantly less than that obtained by Herwijnen for Ni/Al₂O₃ but in good agreement with the value of 86 kJ/mol obtained by Sols (14) and by Solc and Pour (15).

Data from this and previous studies (8, 17) show that CO and CH₄ turnover numbers in CO methanation are generally independent of space velocity at sufficiently low temperatures and conversion. However, the same is not true of CO₂ turnover numbers in CO₂ methanation. Indeed, the data from this study (Figs. 2 and 3) show that the CO₂ and CO turnover numbers increase with increasing space velocity while the CH₄ turnover number remains constant over the same range of space velocity. This observed fact is explained experimentally by the constant outlet concentration of CO (at any given temperature and composition) and the simultaneous decreasing outlet concentration of CH₄ with

increasing space velocity. In other words, the production of CO is apparently determined by an equilibrium phenomenon while the production of methane is kinetically determined. The mechanistic implications of this will be discussed in a later paper dealing with the kinetics (20).

Product Distribution in CO₂ Hydrogenation on Ni

The selectivity of nickel for the production of CH₄ has been reported to be higher in CO₂ hydrogenation than in CO hydrogenation (2, 3). Indeed, this is generally borne out by the conversion-temperature data in this study (Figs. 4–6). However, previous studies were generally conducted at high pressures, low space velocities, and high conversions all of which favor methane formation. Moreover, some of these studies (14–16) were carried out at very high H₂ concentrations, conditions which favor high methane yields at any temperature, pressure, or space velocity. Nearly 100% yields of methane were obtained in this study under high-temperature, low space velocity conditions; however, at high space velocities fairly substantial yields of CO were observed (see Figs. 4 and 6). This observation is somewhat unique, since with the exception of a recent TPD investigation (21) most previous studies (2, 3, 9–16, 22) reported little or no CO as a product of CO₂ methanation.

It was also previously reported (2, 3) that production of higher molecular weight hydrocarbons does not occur in CO₂ hydrogenation. The results of this study, however, show that very small amounts of C₂ hydrocarbons are formed at 500–550 K, although the amount is significantly less than that produced under the same conditions in CO hydrogenation.

Conversion Temperature Behavior in CO and CO₂ Hydrogenation

The conversion temperature plots in Figs. 4 and 5 show that CO hydrogenation on Ni occurs at higher conversion of reac-

tants and higher production of CH₄ than does CO₂ hydrogenation. This could be anticipated in light of the higher activation energy for the production of CH₄ in CO hydrogenation. Equilibrium calculations performed using the Edwards Thermochemical program (23) show that equilibrium limitations occur in CO₂ hydrogenation, especially at high temperatures. In fact, it is impossible to obtain complete conversion with the reaction mixture used in this study above 500 K (see Fig. 4). Equilibrium conversion data for CO hydrogenation (Fig. 5) show conversion of CO is almost complete over the temperature range of interest and that production of CH₄ (assumed to be at equilibrium) is significantly higher than that for CO₂ methanation (Fig. 4). At high pressure (1030 kPa) the equilibrium production of CH₄ from CO hydrogenation exceeds 90% up to 725 K while the equilibrium production of CH₄ from CO₂ hydrogenation is significantly less (Fig. 6). Thus, the experimental conversion-temperature data in Figs. 4–6 approach equilibrium at high temperatures and high space velocities and over a broad temperature range at low space velocities in both CO and CO₂ hydrogenation. These results are in good agreement with the equilibrium data and thermodynamic calculations reported for CO and CO₂ methanation by Anderson *et al.* (24).

It should be pointed out that it is generally not possible to obtain conversion-temperature data for an exothermic reaction such as methanation in a fixed bed reactor under completely isothermal conditions, i.e., there is typically a temperature gradient across the bed at any fixed inlet temperature, especially at high conversions. In this study the use of a diluent helped to minimize this temperature rise through the catalyst bed. In fact, the adiabatic temperature rise calculated for the reaction mixture used in this study would be a maximum of 50 K at complete conversion. Moreover, recent modeling studies conducted in our laboratory (8) suggest the operation of our

reactor to be semi-adiabatic/isothermal with an estimated maximum temperature rise of 25–30 K. Due to the placement of the thermocouple at the outlet of the bed we believe that the measured temperature was approximately indicative of somewhat less than the maximum temperature in the bed. Although the conversion-temperature data in this study were obtained under non-isothermal conditions, they are considerably more reliable than previously reported conversion-temperature data obtained at high conversions in large industrial reactors using undiluted feeds.

CONCLUSIONS

(1) CO₂ hydrogenation on Ni/SiO₂ occurs at the same rate as CO hydrogenation at low reaction temperatures (500–575 K). Above 575 K the rate of CO hydrogenation is significantly higher. This is explained by the significantly different apparent activation energies for methane production of 80 and 96 kJ/mol in CO₂ and CO hydrogenation on nickel.

(2) At high reaction temperatures, the conversion of CO₂ to methane is always less than the corresponding conversion of CO to methane for any fixed set of reaction conditions.

(3) For any fixed temperature, pressure, and composition, the outlet CO concentration is space velocity invariant, suggesting that adsorbed CO from dissociative adsorption of CO₂ is in equilibrium with gas phase CO.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support from the National Science Foundation (Grant No. CPE-7910823) and technical assistance by Wayne L. Sorenson.

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