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Hydrogenation of CO_2 on Group VIII Metals

IV. Specific Activities and Selectivities of Silica-Supported Co, Fe, and Ru

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Specific intrinsic rates and product distributions for CO_2 hydrogenation on Co/SiO_2, Fe/SiO_2, and Ru/SiO_2 were determined at 450–650 K, 140–1030 kPa, and a range of space velocities. Specific activities in the form of turnover frequencies for CO_2 hydrogenation decrease in the order Co/SiO_2, Ru/SiO_2, Ni/SiO_2, Fe/SiO_2. The order of decreasing selectivity for methane is Ru/SiO_2, Co/SiO_2, Ni/SiO_2, Fe/SiO_2. High levels of CO are produced in CO_2 hydrogenation on Fe/SiO_2, Co/SiO_2, and Ni/SiO_2 while significant fractions of C_{2+} hydrocarbons (about 1 order of magnitude lower than typical methane fractions) are produced on Fe/SiO_2 and Co/SiO_2 catalysts.

INTRODUCTION

The hydrogenation reactions of CO and CO_2 to methane and higher molecular weight hydrocarbons are important in purification of ammonia feeds, methanation of coal-derived gases, and Fischer–Tropsch synthesis. These reactions are also of interest in the production of process heat from reclaimable waste streams containing dilute carbon oxides or from nuclear reactor steam-reformed CO/H_2 streams as part of a so-called "heat pipeline" (*1*).

Most of the previous research has emphasized the kinetics and mechanisms of CO hydrogenation on Group VIII metals (*2–7*). Previous studies (*2–4, 8–30*) of CO_2 hydrogenation on Group VIII metals have focused mainly on Ni catalysts. Very little work has been reported on other Group VIII metals (*26–30*). Solymosi and Erdöhelyi (*26*) reported turnover frequencies for CO and CO_2 methanation on Ru, Rh, Pt, Ir, and Pd; Ru and Rh were found to be the most active. Gupta and co-workers (*28*) conducted a kinetic study of CO_2 methanation over well-characterized, supported Ru and reported data for both pulse and steady state hydrogenation. They reported activation energies of 30.5 to 57.7 kJ/mol but did not report turnover frequencies for CO_2 conversion or CH_4 production. Lunde and Kester (*29*) found an activation energy of 70.3 kJ/mol for CO_2 hydrogenation on Ru/Al_2O_3 but did not report turnover frequency data. In a study of CO and CO_2 methanation on Fe foils by Dwyer and Somorjai (*30*), turnover frequencies and activation energies were reported for fresh and deactivated surfaces. On the basis of these previous studies (*26–30*) it was not possible (with the exception of the noble metals) to rank order the Group VIII metals according to activity and selectivity in CO_2 hydrogenation.

The objectives of this investigation were to determine (i) the intrinsic specific rates and product selectivities in CO_2 hydrogenation on Group VIII metals (i.e., Co, Fe, Ni, and Ru) under reaction-controlled conditions, and (ii) effects of temperature, pressure, and space velocity on specific rates and product selectivities. In this paper activity and selectivity data for CO_2 hydrogenation on Co/SiO_2, Ru/SiO_2, and Fe/SiO_2

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are presented, discussed, and compared with previously reported data for Ni/SiO_2 (*23, 24*).

EXPERIMENTAL

Analytically pure $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and Ru acetate were used in preparation of the catalysts. Preparation by simple impregnation to incipient wetness of the support (Cab-O-Sil, grade M-5 fumed SiO_2, Cabot Corp.) with an aqueous metal salt solution (ethanol solution was used in preparation of the Ru catalyst) was followed by oven drying at 375 K. The impregnated, dried samples were reduced in flowing hydrogen at a space velocity of 2000 h^{-1} while heating at 2 K/min to 750 K with a 2-h hold at 500 K and a 16- to 36-h hold at 750 K. The samples were then carefully passivated with 1% air in N_2.

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

Previously reduced and passivated samples of each catalyst were rereduced at 723 K overnight (2 h for Ru/SiO_2) and evacuated at 673 K. The metal surface area was then determined by H_2 chemisorption at 298 K using a conventional volumetric vacuum apparatus evacuable to 1.3×10^{-7} kPa (*31*). The total 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 SiO_2 support was also characterized by a full-range argon BET adsorption experiment conducted at 90 K. The desorption isotherm was analyzed using the method of Barrett *et al.* (*32*) to obtain the average pore size.

CO_2 hydrogenation activity was determined using 1- to 2-cm^3 samples of catalyst (approx 0.3–1.0 g) in a 1.25-cm-diam fixed-bed reactor constructed of stainless steel and equipped with a thermocouple in the catalyst bed. Activity tests were conducted at 450–650 K, 140–1030 kPa, and space velocities of 4000–50,000 h^{-1}. Reaction mixtures of 80% H_2 and 20% CO_2 or 95% N_2, 4% H_2, and 1% CO_2 were used for the activity tests. Limited activity tests were also conducted using a 95% N_2, 4% H_2, and 1% CO reaction mixture. Conversion versus temperature tests were conducted using a 4/1 H_2/CO_2 ratio with a 95% N_2 diluent to minimize heat transfer effects and thus more closely approximate isothermal bed conditions at high conversions.

All reactant and product gas concentrations were measured chromatographically using thermal conductivity and flame ionization detectors (HP 5834 and Perkin–Elmer Sigma I chromatographs). Peak areas were determined electronically and related to concentrations by calibrating with a gas mixture containing known amounts of the reactant and product gases. Carbon balances generally accounted for 99% of the input carbon. The largest error in the carbon balance was due to measurement of reactant CO_2 conversion since the conversion of the reactant species was measured by difference (usually small) between reactant and product concentrations. Measurements of CH_4 and C_{2+} hydrocarbon concentrations made directly by FID were significantly more accurate (better than 0.1% of entering carbon). Although a small amount of carbon did deposit on the catalyst surface during reaction, the rate was not great enough to significantly affect the carbon balance.

While carbon deposition did not affect the carbon balance noticeably, it did affect the catalyst activity significantly, particularly at higher reaction temperatures. To avoid this complication the procedure recommended by Sinfelt (*33*) of treating the catalyst at 300°C in H_2 was used to clean the metal surface of carbon deposits between each incremental increase in reaction temperature. Thus, the rates reported here are initial rates, unaffected by carbon deposits.

TABLE 1

Hydrogen Adsorption Uptakes of Silica-Supported Co, Fe, and Ru Catalysts

Catalyst	H_2 Uptake[a] (μmole/g)
3% Co/SiO_2	17
15% Co/SiO_2	52.4
15% Fe/SiO_2	63.9
0.5% Ru/SiO_2	23.0[b]

[a] With the exception of Ru/SiO_2, total H_2 uptake was measured volumetrically at 25°C.

[b] Total H_2 uptake measured volumetrically at 100°C.

RESULTS

Hydrogen chemisorption measurements obtained for each of the catalysts are included in Table 1. From full-range BET measurements the total surface area of the SiO_2 support was found to be 192 m^2/g and the average pore radius to be 6.0 nm, both in good agreement with data supplied by the manufacturer.

Activity/selectivity data obtained for CO_2 and CO hydrogenation on silica-supported cobalt are summarized in Table 2 and Fig. 1. Activity data are reported in the form of turnover frequencies (molecules produced or converted per catalytic site per second), while product selectivities are defined as the fraction of converted CO_2 appearing as a specified product. The results in Table 2 indicate that CO_2 and CO hydrogenation are catalyzed by Co/SiO_2 at approximately the same rates within experimental precision (estimated at ±20%) in the temperature range 500–550 K. Methane turnover frequencies are also about the same at 500 K; however, at higher temperatures methane production via CO hydrogenation proceeds more rapidly on Co/SiO_2. In CO_2 hydrogenation at any given temperature, selectivity for methane increases and that for CO decreases with decreasing space velocity. Thus, Co/SiO_2 exhibits activity/selectivity properties for CO and CO_2 hydrogenation qualitatively similar to those observed for Ni/SiO_2 in previous work (*23*).

Methane turnover frequencies are plotted in Fig. 1 in Arrhenius fashion for CO_2 methanation on Co/SiO_2 at different space velocities. A trend of decreasing activation energy (i.e., departure from the initial linear slope) with increasing temperature is observed. This behavior was attributed to deactivation by carbon, especially at the higher temperatures. Treatment of the catalyst sample in H_2 at high temperature following activity testing resulted in significant levels of methane production for

TABLE 2

Activities and Product Distributions for CO and CO_2 Hydrogenation on 3% Co/SiO_2 (0.36 g of catalyst tested in 1% CO or CO_2, 4% H_2, 95% N_2 at 140 kPa)

Temp (K)	GHSV (h^{-1})	CO_2 methanation					CO methanation				
		N_{CH_4}[a] × 10^3 (s^{-1})	Conversion of CO_2 (%)	% Selectivity[b]			N_{CH_4}[c] × 10^3 (s^{-1})	Conversion of CO (%)	% Selectivity[b]		
				CH_4	CO	C_{2+}[d]			CH_4	CO_2	C_{2+}[d]
500	4340	3.0	9.6	71	25	4.6	3.6	9.8	72	2.9	25
	8480	3.2	6.5	54	35	11	3.4	5.5	62	5.3	33
525	8480	6.5	12.3	59	33	8.2	8.5	11.5	72	9.3	18
	16400	6.8	9.4	42	49	8.9	8.5	6.2	70	19	11
550	16400	10.0	13.7	42	52	5.9	17.7	12.9	70	17	13
	24600	10.4	12.0	32	52	17	17.9	8.4	72	14	14

[a] Turnover frequency for CO_2 hydrogenation to methane in molecules per site per second. The number of sites was determined from H_2 adsorption (Table 1).

[b] The percentage of converted CO_2 or CO which appears as a given product.

[c] Turnover frequency for CO hydrogenation to methane.

[d] These selectivities to C_{2+} hydrocarbons were not measured directly but determined by difference, i.e., % Selectivity of C_{2+} = 100–% CH_4 Select.–% CO (or CO_2) Select.

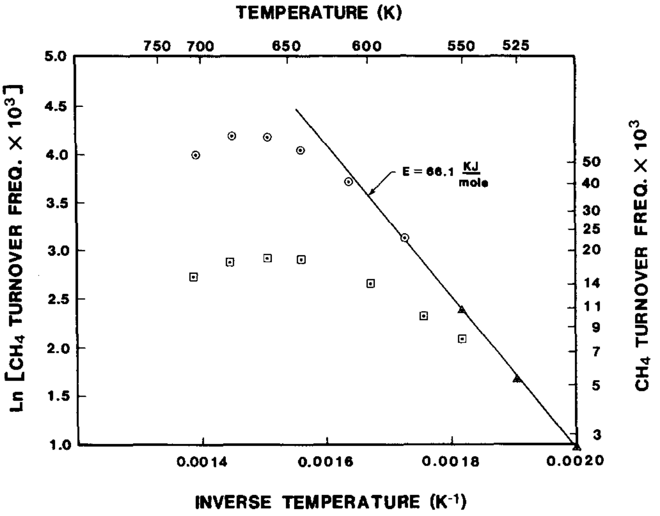

FIG. 1. Arrhenius plot of methane turnover frequencies in CO_2 hydrogenation on 3% Co/SiO_2 at 1 atm and GHSV = 4,340 – 49,400 h^{-1} in 95% N_2, 4% H_2, and 1% CO_2. ○, GHSV = 49,400 h^{-1}; □, GHSV = 4340 h^{-1}; △, average over all GHSV.

several hours and trace levels for up to 12 h. Since by periodic treatment in H_2 it was possible to obtain linear Arrhenius plots, in all subsequent experiments the catalyst surfaces were cleaned in H_2 at 300°C between activity measurements at different temperatures.

Tables 3 and 4 list CO_2 and CH_4 turnover frequencies and product selectivities for CO_2 methanation on SiO_2-supported Co, Fe, Ni, and Ru catalysts at 1 and 11 atm total pressure. Large differences exist in the intrinsic activities and selectivities of these catalysts. For example, the turnover frequencies for CO_2 conversion vary by an order of magnitude while those for methane production vary over two orders of magnitude, the order of decreasing CO_2 conversion activity being Co/SiO_2, Ru/SiO_2, Ni/SiO_2, Fe/SiO_2. In addition, the selectivity to methane varies markedly over these catalysts (Table 4). The decreasing order of methane selectivity is Ru/SiO_2, Ni/SiO_2, Co/SiO_2, Fe/SiO_2. While the production of CO is small or negligible over Ru/SiO_2, very high levels are produced over Fe/SiO_2 and high levels over Co/SiO_2. The decreasing order of CO selectivity is Fe/SiO_2, Co/SiO_2, Ni/SiO_2, Ru/SiO_2. In addition, the Fe/SiO_2 produces significant fractions of C_2–C_5 hydrocarbons, even at relatively high temperatures (525–564 K); Co/SiO_2 and Ru/SiO_2 produce smaller but nevertheless significant quantities of C_2 and C_3 hydrocarbons. The production of C_2 hydrocarbons by Ni/SiO_2 is in comparison negligible.

Figures 2–4 are Arrhenius plots of the low- and high-pressure activity data for CO_2 methanation on SiO_2-supported Co, Fe, and Ru catalysts. As summarized in Table 3, a least squares fit of the data shows the

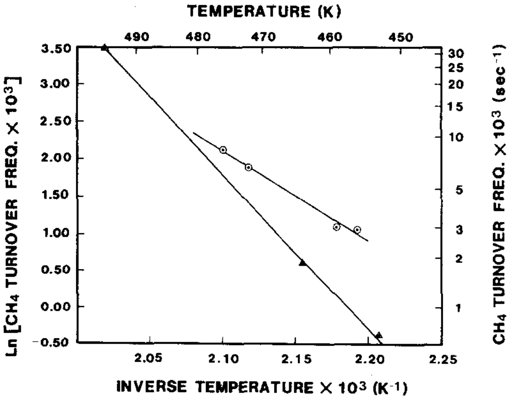

FIG. 2. Arrhenius plots of methane turnover frequencies in CO_2 hydrogenation on 15% Co/SiO_2 at GHSV = 2050 – 9620 h^{-1} in 80% H_2 and 20% CO_2. ○, 1 atm; △, 11 atm.

TABLE 3

Activity Data for CO_2 Hydrogenation on Co/SiO_2, Fe/SiO_2, Ni/SiO_2, and Ru/SiO_2

Catalyst	Operating ranges				Turnover frequency at 500 K × 10^3 (s^{-1})		Activation energies (kJ/mol)	
	Pressure (atm)	Temp (K)	Space velocity (h^{-1})	% CO_2 conversion	N_{CO_2}[a]	N_{CH_4}[b]	E_{CO_2}[c]	E_{CH_4}[d]
Reactant gas: 80% H_2, 20% CO_2								
15% Co/silica	1	456–476	2050–3850	4.7–10.5	30	27	93	99
	11	453–495	450–9620	5.3–11.2	77	69	171	173
15% Fe/silica	1	526–572	1470–6370	6.8– 8.9	0.79	0.083	118	134
	11	564–628	3490–14,730	9.9–12.5	0.84	0.59	83	64
0.5% Ru/silica	1	502–563	1720–5965	5.7–10.3	7.2	7.2	72	72
	11	485–550	720–9920	6.3–10.2	8.5	8.5	103	103
Reactant gas: 95% N_2, 4% H_2, and 1% CO_2								
3% Co/silica	1	500–550	4340–24,600	3.0–10.4	7.6	3.5	79	66
3% Ni/silica[e]	1	500–550	16,350–32,900	3.9–11.2	1.2	0.85	81	80
15% Fe/silica[f]	1	500–550	4340–49,000	f	f	f	—	—
0.5% Ru/silica	1	500–550	5700–49,000	3.5–11.4	6.1	4.2	73	68

[a] Molecules of CO_2 reacted per site per second.

[b] Molecules of CH_4 produced per site per second.

[c] For CO_2 conversion.

[d] For methane production.

[e] Data from Ref. (*23*).

[f] Very low activity under these conditions; only CO was produced.

TABLE 4

Selectivity Data for CO_2 Hydrogenation on Co/SiO_2, Fe/SiO_2, Ni/SiO_2, and Ru/SiO_2

Catalyst	Pressure (atm)	Temp (K)	% CO_2 conversion	CO_2 turnover frequency[a] × 10^3 (s^{-1})	Selectivity (mole %)[b]					
					CH_4	CO	C_2	C_3	C_4	C_5
Reactant gas: 80% H_2, 20% CO_2										
Co/SiO_2	1	476	10.5	9.7	86.9	12.6	0.4	0.3	—	—
	11	478	11.2	19	89.0	10.7	0.3	0.04	—	—
Fe/SiO_2	1	526	7.7	3.3	12.9	83.2	2.2	1.1	0.4	0.2
	11	564	9.9	9.4	39.9	53.0	3.8	2.0	0.7	0.5
Ru/SiO_2	1	502	5.7	7.8	99.8	0	0.2	—	—	—
	11	506	9.0	15	99.7	0	0.3	—	—	—
Reactant gas: 4% H_2, 1% CO_2, 95% N_2										
Co/SiO_2	1	525	9.4	16	42	59	—	—	—	—
Ni/SiO_2[c]	1	525	8.6	2.7	77	15	0.05	—	—	—
Fe/SiO_2	1		Very low	Not measurable	—	~100	—	—	—	—
Ru/SiO_2	1	525	6.0	11	82	9.8	—			

[a] Molecules of CO_2 converted per catalytic site per second.

[b] The percentage of converted CO_2 appearing as a specified product; hydrocarbon selectivities were measured directly.

[c] Data from Ref. (*23*).

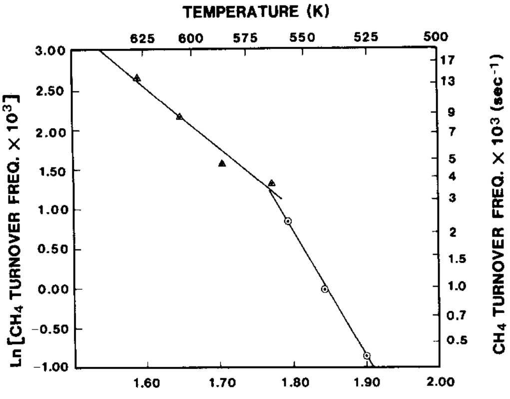

FIG. 3. Arrhenius plots of methane turnover frequencies in CO_2 hydrogenation on 15% Fe/SiO_2 at GHSV = 1470 − 14,700 h^{-1} in 80% H_2 and 20% CO_2. ○, 1 atm; △, 11 atm.

activation energies for CH_4 formation to range from a low of 72 kJ/mol for Ru/SiO_2 to a high of 134 kJ/mol for Fe/SiO_2 at low pressure (1 atm) and from 64 kJ/mol for Fe/SiO_2 to 173 kJ/mol for Co/SiO_2 at high pressure (11 atm).

The Thiele modulus was calculated for CO_2 hydrogenation on each of the silica-supported catalysts. A particle diameter of 0.01 cm, tortuosity of 5, void fraction of 0.5, and the most stringent conditions of temperature, flowrate, and conversion (Table 3) were used in the calculation. In all cases the Thiele modulus was found to be less than 0.017, giving a conservative estimate of the effectiveness factor of 1.00. In other words, pore diffusional resistance did not affect the activity measurements under the conditions used in this study.

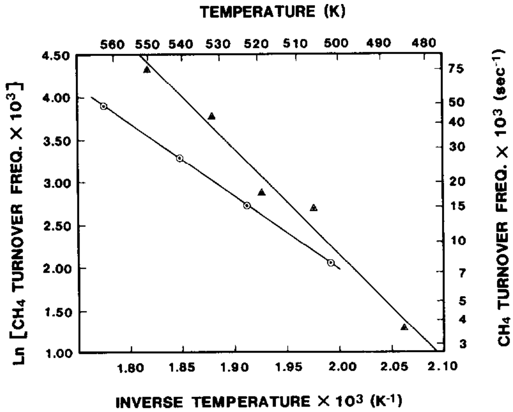

FIG. 4. Arrhenius plots of methane turnover frequencies in CO_2 hydrogenation on 0.5% Ru/SiO_2 at GHSV = 720 − 9920 h^{-1} in 80% H_2 and 20% CO_2. ○, 1 atm; △, 11 atm.

Table 5 lists pressure dependencies of the rates of CO_2 conversion and CH_4 production. The pressure dependence for CO_2 conversion and CH_4 production are 0.026 and 0.82, respectively, over Fe/SiO_2, a catalyst with low selectivity to methane, whereas the corresponding orders over Ru/SiO_2, a catalyst with a very high selectivity to methane, are both 0.069. Co/SiO_2, with an intermediate selectivity to methane, shows moderate pressure dependencies for CO_2 conversion and methane production of 0.39 for each.

Conversion-temperature data for CO_2 methanation over 3% Co/SiO_2 and 0.5% Ru/SiO_2 catalysts are shown in Figs. 5 and 6. The conversion-temperature behavior for Ru/SiO_2 is characterized by extremely high, almost complete, selectivity to methane as seen in Fig. 6. Co/SiO_2, on the other hand (Fig. 5), produces roughly equal amounts of CO and CH_4 over the entire range of temperature under these conditions of pressure and space velocity (1 atm, 49,000 h^{-1}); nevertheless, its selectivity for methane increases with decreasing space velocity (see Table 2) and increasing pressure (see Table 4). In conversion-temperature experiments over Fe/SiO_2 using the dilute reaction mixture, no significant methane production was

TABLE 5

Pressure Dependence of CO_2 Hydrogenation On Co, Fe, Ru

Catalyst	Order in power-law fit	
	CO_2 conversion	CH_4 production
15% Co/SiO_2	0.39	0.39
15% Fe/SiO_2	0.026	0.82
0.5% Ru/SiO_2	0.069	0.069

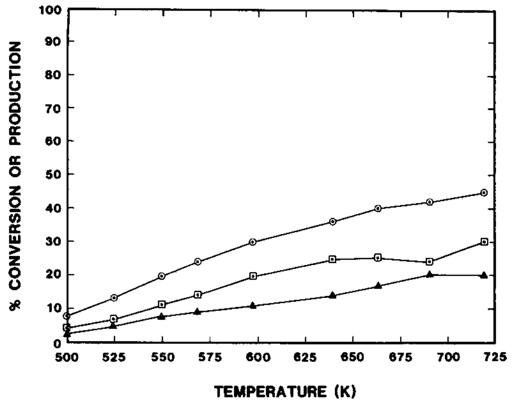

FIG. 5. Conversion vs temperature plots for CO_2 hydrogenation on 15% Co/SiO_2 at GHSV = 49,400 h^{-1} and 1 atm in 95% N_2, 4% H_2, and 1% CO_2. ○, CO_2 conversion; □, CH_4 production; △, CO production.

observed although conversion to CO reached approx 30% at 700 K.

DISCUSSION

Specific Activities of Cobalt, Iron, Nickel, and Ruthenium in CO_2 Hydrogenation

The specific activity data obtained in this study (Tables 2 and 3) for silica-supported cobalt, iron, and ruthenium were obtained in the absence of heat or mass transport disguises. The specific activity data for CO_2 hydrogenation on Co/SiO_2, Fe/SiO_2, and Ru/SiO_2 are to our knowledge the first to be reported for these catalyst systems. Solymosi and Erdöhelyi (*26*) reported a turnover frequency of 194 × 10^{-3} s^{-1} and an activation energy of 67.4 kJ/mol for CH_4 production at 548 K, 1 atm, H_2/CO_2 = 4 on a poorly dispersed 5% Ru/Al_2O_3 catalyst. The activation energy of 72 kJ/mol obtained in this study is in good agreement with their results; however, the methane turnover frequency for Ru/SiO_2 obtained under identical conditions, i.e., 1 atm, 548 K, and H_2/CO_2 = 4 of 33 × 10^{-3} (see Fig. 4) is a factor of 6 smaller. A lower turnover frequency is expected for Ru/SiO_2 in light of previously reported data by Solymosi *et al.* (*26b*) which shows that alumina-supported Rh is significantly more active than silica-supported Rh and by Vance and Bartholomew (*34*) which shows that alumina-supported Ni is more active than silica-supported Ni.

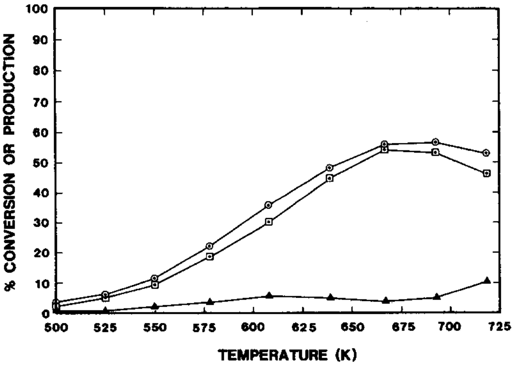

FIG. 6. Conversion vs temperature plots for CO_2 hydrogenation on 0.5% Ru/SiO_2 at GHSV = 16,000 h^{-1} and 1 atm in 95% N_2, 4% H_2, and 1% CO_2. ○, CO_2 conversion; □, CH_4 production; △, CO production.

The methane turnover frequency for Fe/SiO_2 at 11 atm and 573 K of 4.9 × 10^{-3} s^{-1} obtained from extrapolation of the data from this work is in poor agreement with that of 10.9 s^{-1} obtained for an Fe foil by Dwyer and Somorjai (*30*) at 573 K and 6 atm, although the corresponding activation energies for methane production of 64 kJ/mol and 71 kJ/mol for Fe/SiO_2 (this work) and Fe foil (*30*) are in good agreement.

The extremely low activity observed on Fe/SiO_2 can be explained in large part by the observations of Dwyer and Somorjai (*30*) in which initially clean or preoxidized iron foils were rapidly deactivated and then covered with a carbonaceous deposit. The resulting order of magnitude lower activity was found to be comparable with the rate of surface carbon hydrogenation. Given the instability and rapid deactivation of the iron foils it is reasonable to expect the small iron crystallites to be covered with and deactivated by carbon deposits. However, this does not explain the high selectivity to CO or the low production of higher weight hydrocarbons. Further work is needed to establish the nature of the active surface in steady state CO_2 hydrogenation on supported and unsupported iron in order to explain the large differences between the rates on clean, single crystal iron and on supported iron catalysts.

The order of decreasing specific activity of silica-supported Co, Ru, Ni, Fe in CO_2 hydrogenation observed in this study is with the exception of Fe and Ni similar to that observed in CO hydrogenation on alumina and silica-supported Group VIII metals (*35, 36*), namely, Co, Ru, Fe, Ni, and in the water–gas-shift reaction on Group VIII metals (*37*), namely, Co, Ru, Ni, Fe. In recent TPD/TPR studies Falconer and Zagli (*22, 27*) demonstrated that adsorbed CO_2 and CO are hydrogenated on Ni and Ru catalysts at the same temperature, a behavior indicating that both reactions follow similar paths. Results from recent kinetic studies conducted by Dalmon and Martin (*21*), Weatherbee and Bartholomew (*24*), and Peebles *et al.* (*25*) suggest strongly that CO_2 hydrogenation proceeds via CO hydrogenation. It is, therefore, reasonable to expect the orders of catalyst activity to be similar for CO and CO_2 hydrogenation.

The results of this study (Table 3) show that different activation energies are observed for the same catalyst under different conditions of temperature and pressure. These changes in activation energy for CO_2 conversion and CH_4 production can be explained in part by changes in the rate-determining step. A previous kinetic study in this laboratory (*38*) demonstrated that the rate-determining step and hence the activation energy in CO hydrogenation change with temperature. In a recent study Peebles *et al.* (*25*) showed that the rate-determining step for CO_2 hydrogenation changes from CO dissociation at low pressure to carbon hydrogenation at high pressure. For example, a change in rate-determining step to C hydrogenation could easily explain the decrease in activation energy with increasing pressure and temperature for the Fe/SiO_2 catalyst (see Fig. 3). The activation energy of 66 kJ/mol (Table 3) is close to the value of 50 kJ/mol reported by Dwyer and Somorjai (*30*) for carbon-deactivated Fe foils in which the rate was shown to correspond to the rate of carbon hydrogenation. The increases in activation energy for CO_2 hydrogenation on Co/SiO_2 and Ru/SiO_2 (see Table 3) cannot be explained in terms of a shift in the rate-determining step from CO dissociation to C hydrogenation as proposed above for Fe/SiO_2. This does not, however, exclude a change in rate-determining step as the cause of the change in activation energy. Given the complex nature of the CO_2 hydrogenation reaction it is possible that increased pressure results in significant changes in surface species concentrations which lead to changes in the rate-determining step. At present, our limited knowledge of CO_2 hydrogenation kinetics on Co and Ru prohibits any further explanation of this effect.

The relatively small pressure dependencies observed for CO_2 hydrogenation on Co, Fe, and Ru catalysts in this study are consistent with those observed in previously reported kinetic studies of CO_2 hydrogenation on Ni (*23–25*) and Rh (*26*). These results suggest that the H_2 and CO_2 reactants are moderately strongly adsorbed on the metal surface. Again, the present lack of kinetic and adsorption data for CO_2 hydrogenation on Co, Fe, and Ru precludes further discussion of the pressure dependence.

Product Distributions in CO_2 Hydrogenation on Silica-Supported Cobalt, Iron, Nickel, and Ruthenium

Near unity selectivities to methane have been reported in most of the previous literature for CO_2 hydrogenation on Group VIII metals (*8–30*). However, most of these previous studies were conducted at high pressure, low space velocities, and/or high H_2 concentrations, conditions which favor high methane selectivities (*23*). The results in Tables 2 and 4 also indicate that low space velocities and high pressure favor high selectivities to methane on Co/SiO_2 and other Group VIII metals. The results of this work (Table 4) show that with the exception of Ru, significant fractions of CO are produced at relatively high space velocities on Group VIII metals.

The very high methane selectivities observed over a range of operating conditions for Ru/SiO_2 are consistent with previous studies (*26–29*). For example, Gupta and co-workers (*28*) found a small amount of CO (0.2%) to be produced at temperatures above 525 K and at concentrations greater than 2% CO_2 in H_2 during CO_2 hydrogenation over a Ru/molecular sieve catalyst. A very high methane selectivity and low CO selectivity (3–4% of the CH_4 production) were reported by Solymosi and Erdöhelyi (*26*) over Ru/Al_2O_3 at temperatures below 513 K and conversions between 6 and 10%.

Previously reported selectivity data obtained in a batch recycle reactor for polycrystalline Fe foils (*30*) show little resemblance to the data obtained in this study for Fe/SiO_2 using a flow reaction system. Dwyer and Somorjai (*30*) reported 97% selectivity to methane over Fe foils at 6 atm, 3 : 1 H_2/CO_2, and 573 K. Ethane was the only other product detected, although a significant amount of carbonaceous material built up on the surface causing rapid deactivation. Under similar conditions (11 atm, 4 : 1 H_2/CO_2, and 564 K) the methane selectivity of Fe/SiO_2 (see Table 4) was 40%; significant fractions of CO (53%) and C_2–C_5 hydrocarbons (7%) were also observed. The differences in reactor type (hence space velocity and flow conditions), in crystallite size for the Fe foils and Fe/SiO_2, and in the surface composition (previously discussed) are likely responsible for the differences observed in the selectivity behavior of iron between these two studies.

It was previously reported (*2, 3*) that production of hydrocarbons other than methane does not occur in CO_2 hydrogenation. Of all the previous workers, only Dwyer and Somorjai (*30*) reported a hydrocarbon product other than methane, namely, a small fraction of ethane produced on Fe foil. The results of this study (Table 4), however, show that small amounts of C_2 and C_3 hydrocarbons are produced on Co and Ru while significant fractions of C_2–C_5 hydrocarbons are produced on Fe. Our previous study (*23*) showed that very small quantities of C_2 hydrocarbons are formed on Ni at 500–550 K. Nevertheless, the fraction of C_{2+} hydrocarbons formed on any of these catalysts in CO_2 hydrogenation is significantly less than that produced under the same conditions in CO hydrogenation. Dwyer and Somorjai (*30*) also reported the buildup of significant amounts of carbonaceous material on the surface of their iron foil which deactivated the catalyst. In this study, significant levels of carbonaceous materials were found to deactivate the Co and Ru catalysts during some of the early low-pressure activity tests. However, it was possible to remove the carbonaceous buildup and maintain constant catalyst activity with a periodic cleaning of the catalyst surface with H_2 at high temperature.

Conversion-Temperature Behavior of Co/SiO_2 and Ru/SiO_2 in CO_2 Hydrogenation

The conversion-temperature plots in Figs. 5 and 6 show that CO_2 conversions of Co/SiO_2 and Ru/SiO_2 are less than 50% even at relatively high reaction temperatures. These levels of conversion are significantly lower than observed previously for Ni/SiO_2 (*23*) and lower than the predicted equilibrium conversion levels at these temperatures (*23*). This behavior is unexpected in light of the high specific, initial activities of Co/SiO_2 and Ru/SiO_2 and their comparable activation energies relative to nickel. The results suggest that Co/SiO_2 and Ru/SiO_2 are rapidly deactivated during CO_2 hydrogenation at higher temperatures. Recent studies (*39–41*) have shown that cobalt and ruthenium catalysts suffer rapid deactivation from carbon deposits during CO hydrogenation at temperatures above 573 K.

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 (N_2) 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 (*42*) suggest the operation of our reactor to be semiadiabatic/isothermal with an estimated maximum temperature rise of 25–30 K. Due to the placement of the thermocouple at the outlet of the catalyst bed it is believed 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 nonisothermal 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. The decreasing order of specific activity in CO_2 hydrogenation is Co/SiO_2, Ru/SiO_2, Ni/SiO_2, Fe/SiO_2. Fe/SiO_2 has a very low activity for CO_2 hydrogenation.

2. The selectivity of CO_2 hydrogenation to CH_4 is very high on Ru/SiO_2 and decreases in the order Ru/SiO_2, Ni/SiO_2, Co/SiO_2, Fe/SiO_2. Very significant fractions of CO are produced on Ni/SiO_2 and Co/SiO_2; the primary product on Fe/SiO_2 is CO.

3. Significant levels (although low compared to CH_4) of C_2–C_5 hydrocarbons are produced during CO_2 hydrogenation on Fe/SiO_2 and Co/SiO_2. The order of decreasing C_{2+} hydrocarbon production is Fe/SiO_2, Co/SiO_2, Ru/SiO_2.

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