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Hydrogenation of CO_2 and CO_2/CO Mixtures over Copper-Containing Catalysts

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CO_2 hydrogenation was carried out at 473–573 K and 9–17 atm over Cu/SiO_2, La_2O_3/Cu/SiO_2, Cu/La_2O_3, Cu/MnO_2/La2O_3, and NaO_x/Cu powder. The major products were methanol (MeOH) and methane. Methyl formate (MeF) was also produced at temperatures below 523 K. In terms of oxygenate yield (MeOH + MeF), the catalysts ranked in order: $La_2O_3/Cu/SiO_2 > Cu/SiO_2 \gtrsim Cu/La_2O_3 > Cu/MnO_2/La_2O_3 \gg NaO_x/Cu$. Lanthana promotion of Cu/SiO_2 increased the formation of methanol but not that of the other products. The selectivity patterns of the lanthana-supported catalysts were similar to that of Cu/SiO_2. Addition of Mn to Cu/La_2O_3 decreased the selectivity to methanol. Hydrogenation of CO_2/CO mixtures was studied over NaO_x/Cu, Cu/SiO_2 and Cu/La_2O_3. The NaO_x/Cu powder displayed higher selectivity to methanol in CO/H_2 than in CO_2/H_2. The activity and selectivity to methanol decreased with increasing CO fraction over Cu/SiO_2. Both activity and oxygenate selectivity increased with CO fraction over Cu/La_2O_3. C_{2+} alcohols were produced in CO-rich atmospheres. The observed effects of catalyst composition and feed composition on the activity and selectivity of Cu for methanol synthesis are interpreted in terms of the sites required for CO and CO_2 hydrogenation.

INTRODUCTION

The hydrogenation of CO_2 over Cu-containing catalysts has been investigated much less extensively than the hydrogenation of CO (*1*). Previous studies have shown that while CO_2 hydrogenation produces primarily methanol and methane, CO hydrogenation can produce C_{2+} hydrocarbons and alcohols in addition to methanol and methane (*2–4*). These observations have led to the conclusion that the intermediates involved in CO_2 and CO hydrogenation may be different. On the basis of evidence from infrared spectroscopy (*5–9*) and chemical trapping (*10–12*), it has been suggested that formyl groups (HCO) are the key intermediates in CO hydrogenation, whereas formate groups (HCOO) are the key intermediates in CO_2 hydrogenation.

Kinetic and isotopic tracer studies of methanol synthesis from mixtures of CO and CO_2 have provided further evidence of the differences between CO and CO_2 hydrogenation (*3, 13–17*). These studies have shown that, over Cu/ZnO catalysts, CO_2 is hydrogenated to methanol more rapidly than is CO, and that even in mixtures with low CO_2/CO ratios, CO_2 is the main source of methanol. Since the rate of CO consumption from such CO_2/CO mixtures is more rapid than that from pure CO, it has been suggested (*15–17*) that the H_2O produced as a byproduct of CO_2 hydrogenation reacts via the water–gas-shift reaction to produce additional CO_2. The active component for CO_2 hydrogenation is identified as bulk copper, the surface of which is partially oxidized during reaction by CO_2 dissociation (*1*). An alternative explanation of the effects of CO_2 on CO hydrogenation has been proposed by Klier and co-workers (*2*). These authors suggest that Cu^+ ions stabilized in the ZnO lattice are the critical sites

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for CO hydrogenation and that the presence of CO_2 is instrumental in maintaining the +1 oxidation state.

The changes seen in catalyst activity and selectivity when CO_2 is added to CO/H_2 feedstocks have been found to be sensitive to catalyst composition (*4, 18, 19*). For example, while the activity over Cu/ZnO declines beyond an optimum CO_2 feed concentration, addition of lanthana to the catalyst reverses this trend, such that the activity in CO_2/H_2 is higher than that in CO/H_2 (*4*). By contrast, the activity of Cu–Cr_2O_3 for methanol synthesis declines monotonically with increasing addition of CO_2 to the feed (*20*). Support composition has also been found to affect the distribution of products formed over Cu catalysts. Thus, for example, Cu/ZnO dispersed on SiO_2 produces methane with 99% selectivity from both CO and CO_2, whereas Cu/ZnO dispersed on rare earth oxides produces methanol with 99% selectivity from both oxides of carbon (*4*).

The objectives of the present study were: (i) to determine the effect of feed composition on the activity and selectivity of unpromoted Cu for hydrogenation of CO and CO_2; and (ii) to observe the effect of promotion by basic elements (Na, Mn, La) on the catalyst response to changes in feed composition. Cu/SiO_2 was prepared as the control case and was compared to La_2O_3-promoted Cu/SiO_2, Cu/La_2O_3 and Cu supported on MnO_2/La_2O_3. An unsupported copper catalyst containing traces of Na was also studied. The catalysts were tested with gas mixtures in which the $CO/(CO + CO_2)$ ratio was varied from 0 to 1.0, and analyzed after use by x-ray diffraction and x-ray photoelectron spectroscopy to determine the bulk and surface properties.

EXPERIMENTAL

Catalyst Preparation

The catalysts used in this study were identical to those previously examined for CO hydrogenation and a detailed description of their preparation can be found in Ref. (*21*). Each of the catalysts was characterized by elemental analysis, XRD, and XPS. The BET surface area of each sample was determined by N_2 adsorption. Details of the procedures used for catalyst characterization are also given in Ref. (*21*).

Catalytic Testing

The apparatus used to evaluate catalyst activity is described in detail in Ref. (*21*). All catalysts were contained in a stainless-steel flow microreactor supplied with CO, CO_2, and H_2 through individual flow controllers from a high-pressure gas manifold. The products were analyzed by on-line gas chromatography.

All catalysts were evaluated by use of the same procedures. A catalyst sample, 0.5–2 g, was charged to the reactor and reduced for 4–6 h in 80 ml/min pure H_2 at 523 K. Reduction was considered complete when water was no longer detected in the reactor effluent. The reactants were then introduced in the desired volumetric flow ratio, and the temperature and pressure adjusted as desired. After a break-in time of ~15 h on stream, the first data point was taken. After a change in reaction conditions the system required 3–5 h to achieve a new steady state. Reactant conversions were less than 3%, which is well below the equilibrium conversions estimated for the reactions studied.

RESULTS

Catalyst Characteristics

A summary of the catalyst composition, BET surface area, Cu surface area, and Cu particle size are presented in Table 1a. It is noted that while the BET surface areas span a range of 0.74 to 258.0 m^2/g, the Cu crystallite sizes vary by no more than a factor of 2.

Table 1a shows that the Cu powder contains 0.3 wt% Na, most likely as a result of Na^+ ion retention from the preparation of the catalyst. The surface atomic ratio of

TABLE 1a

Catalyst Characteristics

Catalyst	BET area (m^2/g)	Cu area (m^2 Cu/g)[a]	Crystallite size (Å)[b]
Cu/SiO_2 (9.3 wt% Cu)	258.0	0.08	250
$La_2O_3/Cu/SiO_2$ (2.1 wt% La, 8.6 wt% Cu)	205.0	{0.08}	241
Cu/La_2O_3 (9.8 wt% Cu)	11.9	—	≤150
$Cu/MnO_2/La_2O_3$ (9.6 wt% Cu, 12.3 wt% Mn)	6.3	—	330
NaO_x/Cu (0.3 wt% Na)	0.74	0.13	230

[a] Determined from CO chemisorption.

[b] Determined from FWHM of the Cu(111) XRD line.

Na/Cu estimated from XPS observations was 0.11. XPS measurements showed no evidence of Na in any of the other catalysts.

XPS spectra of the Cu $2p_{3/2}$ region are presented in Fig. 1 and the BEs for Cu $2p_{3/2}$, La $3d_{5/2}$, and Mn $2p_{3/2}$ are given in Table 1b. All spectra were taken after the catalysts had been used for CO_2 hydrogenation. As discussed previously (*20*), identification of the oxidation state of Cu from the measured BE's is complicated by the fact that the BE's for Cu^0 and Cu^+ are essentially the same and differ from that for Cu^{2+} by only 1.5 eV. The presence of Cu^{2+} is indicated, however, by the occurrence of shake-up satellite peaks about 10 eV above the major lines in the Cu $2p$ region of the spectrum (*22*). Reference to Fig. 1 shows that shake-up peaks are clearly seen in the case of NaO_x/Cu powder and to a lesser extent in the case of Cu/SiO_2. The low intensity of the Cu $2p$ spectrum for the remaining samples makes it difficult to discern whether or not Cu^{2+} ions are present.

TABLE 1b

XPS Results[a]

Catalyst	Binding energy (eV)		Surface atomic ratios	
	Cu	Mn	Cu/La	Cu/Mn
Cu/SiO_2	932.6[b]	—	—	—
$La_2O_3/Cu/SiO_2$	932.5[b] 931.4[c]	—	3.2	—
Cu/La_2O_3	931.7[c]	—	0.34	—
$Cu/MnO_2/La_2O_3$	931.1[c]	644.1	0.35	0.019
NaO_x/Cu powder	934.2[d]	—	(Na/Cu ≈ 0.11)	—

[a] All catalysts reduced at 523 K and used for reaction. Error in BE is ~1 eV.

[b] Referenced to Si $2p$ (103.4 eV).

[c] Referenced to La $3d_{5/2}$ (834.9 eV).

[d] Referenced to Na $1s$ (1072.5 eV).

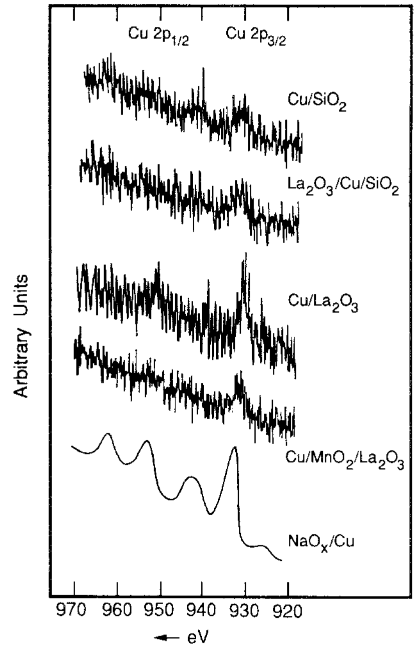

FIG. 1. X-ray photoelectron spectra of spent copper catalysts: Cu $2p$ region. All catalysts reduced at 573 K. Spectra taken after transfer in air.

Hydrogenation of CO_2

CO_2 was converted to methanol, CO, methyl formate, and small amounts of C_1–C_4 hydrocarbons. The conversion of CO_2 to CO by the reverse water–gas-shift reaction (RWGS) was most readily observable at 573 K, at which temperature the rate was roughly equal to that for CO_2 conversion to methanol. At temperatures below 523 K the CO production fell off rapidly and became difficult to detect. In these cases, the RWGS is estimated to account for half (or less) of the total CO_2 conversion. Since CO was not quantifiable at all temperatures, the activity and selectivity data are presented in terms of CO_2 conversion to organic compounds only.[2] The rates of CO_2 conversion on this basis are listed in Table 2 for all catalysts at three values each of temperature and hydrogen partial pressure.

It is evident from Table 2 that promotion of Cu/SiO_2 by lanthana enhances the activity of Cu for CO_2 hydrogenation to organic products. This effect is most pronounced at lower temperatures and reflects the fact that the activation energy for CO_2 hydrogenation over $La_2O_3/Cu/SiO_2$ is lower than that for Cu/SiO_2 (see below). It is interesting to note that while the Cu surface area for NaO_x/Cu powder is comparable to that of Cu/SiO_2, the specific activity of the bulk copper catalyst is significantly lower. It is also evident from Table 2 that inclusion of MnO_2 in the support of Cu/La_2O_3 decreases the CO_2 hydrogenation activity with one exception, namely, the data taken at 573 K, when $H_2/CO_2 = 3$. Under these conditions, the activity of the manganese-containing catalyst was nearly twice that of Cu/La_2O_3. A possible explanation for this observation is that CO_2 hydrogenation over Cu/La_2O_3 is very sensitive to the H_2/CO_2 ratio.

TABLE 2

CO_2 Hydrogenation Activity of Copper Catalysts[a]

Total P (atm)	10.6	13.4	13.4	13.4	17.3
H_2/CO_2[b]	2	3	3	3	4
T(K)	573	573	523	498	573
Catalyst	Rate (μmoles CO_2 converted/min/m^2 Cu)				
NaO_x/Cu	—	1.09	0.31	—	1.46
Cu/SiO_2	12.69	21.66	14.03	3.98	21.07
$La_2O_3/Cu/SiO_2$	28.59	36.31	30.34	18.40	—
Catalyst	Rate (μmoles CO_2 converted/min/m^2 catalyst)				
Cu/La_2O_3	0.15	0.09	0.09	0.02	0.26
$Cu/MnO_2/La_2O_3$	0.08	0.14	0.07	0.02	0.20

[a] Conversion to organic compounds only.

[b] F/WS = 55 cm^3/min/g catalyst for Cu powder; 75 cm^3/min/g catalyst for the rest.

It has been pointed out that the conversion of CO_2 to CO by the RWGS reaction could not be quantified for all conditions. Therefore, the selectivities are quoted exclusive of the product fraction created by the RWGS. Throughout this discussion the products are divided into hydrocarbons (HC), methanol (MeOH), methyl formate (MeF), and dimethyl ether (DME).

Table 3a lists the product distributions for all catalysts at 573 K, H_2/CO_2-3. Hydrocarbons constitute ~17% of the organic products seen over NaO_x/Cu powder, while the hydrocarbon selectivity for the supported catalysts is on the order of 5% or less. For all catalysts dimethyl ether is a small to vanishing fraction. Promotion of Cu/SiO_2 with lanthana increases the selectivity to methanol slightly, but since the overall conversion rate increases by 70%,

TABLE 3a

CO_2 Hydrogenation over Cu Catalysts: Product Distribution at 573 K[a]

Catalyst	% Selectivity[b]		
	HC	MeOH	DME
NaO_x/Cu	16.49	83.50	0.00
Cu/SiO_2	4.78	94.39	0.84
$La_2O_3/Cu/SiO_2$	1.26	98.19	0.54
Cu/La_2O_3	4.37	95.63	0.00
$Cu/MnO_2/La_2O_3$	4.58	94.88	0.54

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[2] We suggest that the observed CO resulted from the reverse water–gas-shift reaction even though the equilibrium for RWGS is small under the conditions of our experiment since the conversion of CO_2 to methanol was less than 3% and the conversion of CO_2 to CO was also less than 3% even at 573 K (the temperature at which the maximum amounts of CO was observed). Thus, under the conditions we employed, $P_{CO} < 0.03\ P_{CO_2}$ and $P_{H_2O} < 0.065\ P_{CO_2}$. Since $P_{H_2} = 3\ P_{CO_2}$, one can estimate that the apparent equilibrium constant, K_{app}, defined by

$$K_{app} = \frac{(P_{CO}P_{H_2O})}{(P_{CO_2}P_{H_2})},$$

is less than 6×10^{-4}, while the actual equilibrium constant under these conditions is 0.025. Therefore, under the conditions used in our studies, the partial pressures of CO and H_2O were far below those set by the RWGS reaction. We note further that there were no other obvious sources of CO.

TABLE 3b

CO_2 Hydrogenation over Cu Catalysts: Product Distribution at 523 K[a]

Catalyst	% Selectivity[b]			
	HC	MeOH	DME	MeF
NaO_x/Cu	6.94	93.06	0.00	0.00
Cu/SiO_2	1.11	90.42	0.56	7.91
La_2O_3/Cu/SiO_2	0.33	95.58	0.54	3.55
Cu/La_2O_3	2.39	88.80	0.65	8.16
Cu/MnO_2/La_2O_3	2.92	87.00	0.00	10.08

[a] $H_2/CO_2 = 3$, $P = 213.4$ atm.

[b] % Carbon atom selectivity among organic products.

the methanol yield actually increases by a factor of 2. The product distribution of Cu/La_2O_3 was not much different from that for Cu/SiO_2. Inclusion of manganese in Cu/La_2O_3 also had no significant effect on the product distribution.

Table 3b describes the product distribution for all catalysts at 523 K, $H_2/CO_2 = 3$. For all catalysts the hydrocarbon selectivity decreased with temperature. With the exception of copper powder, the methanol selectivity also decreased due to the appearance of methyl formate. No methyl formate was seen during CO_2 hydrogenation over copper powder at any other temperature or H_2/CO_2 ratio. The selectivity to methanol of Cu/SiO_2 at 523 K is enhanced by promotion with lanthana. However, considering the change in activity (Table 2), the actual yields of hydrocarbons and methyl formate do not change significantly with lanthana promotion; i.e., lanthana only enhances the yield of methanol. By contrast, use of lanthana as a support increases the selectivities to hydrocarbons and methyl formate, as does inclusion of manganese. It is noted, though, that the rate of CO_2 conversion (Table 2) is such that the yields of methyl formate are roughly the same over both Cu/La_2O_3 and Cu/MnO_2/La_2O_3, but that the yield of methanol is somewhat lower over the latter catalyst. Thus inclusion of manganese in the support appears to inhibit methanol formation but not to any great degree. This effect was also observed for methanol synthesis from CO (*21*).

The variation in selectivity within a wider temperature range is shown for Cu/SiO_2 and Cu/MnO_2/La_2O_3 in Figs. 2a and 2b, respectively. For Cu/SiO_2, the decline in selectivity to methanol with decreasing temperature is accompanied by an increase in the selectivity to methyl formate. For all practical purposes, the selectivity to hydrocarbons falls to zero at 421 K. Similar behavior is seen for Cu/MnO_2/La_2O_3 (Fig. 2b). However, the decline in the ratio S_{MeOH}/S_{MeF} is sharper with temperature, such that at 473 K, the ratio is greater than 1. Since the conversion rate also decreases with temperature, the yield of methyl formate actually declines slightly, while that to

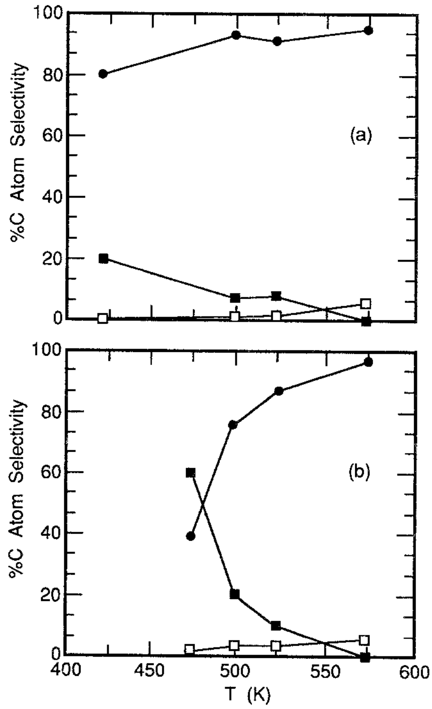

FIG. 2. CO_2 hydrogenation over (a) Cu/SiO_2 and (b) Cu/MnO_2/La_2O_3: effect of temperature on selectivities ($H_2/CO_2 = 3$, $P = 13.4$ atm). (□) HC, (■) MeF, (●) MeOH.

methanol falls off. For the other catalysts (NaO_x/Cu, $La_2O_3/Cu/SiO_2$, Cu/La_2O_3), the production of methyl formate was difficult to detect below 490 K.

The effects of hydrogen partial pressure on the product distribution were investigated at 573 K over all catalysts for $H_2/CO_2 = 2$ to 4. In these experiments the CO_2 partial pressure was kept constant at 4.2 atm, and the hydrogen partial pressure was increased from 6 to 13.7 atm. Very small increases in the selectivities to methane and methanol were seen with increasing hydrogen partial pressure. To observe the effect on methyl formate formation, $Cu/MnO_2/La_2O_3$ was also tested at 499 K with $H_2/CO_2 = 2$ and 3, and the results are presented in Table 4. Increasing the hydrogen partial pressure resulted in a notable decline in the formation of methyl formate and hydrocarbons. While the overall conversion rate decreased only slightly, the selectivities to these products decreased to half their original value.

The effects of space velocity on methyl formate formation were also investigated for $Cu/MnO_2/La_2O_3$ at 499 K, and the data are given in Table 5. The rate of conversion is seen to increase with increasing space velocity. This suggests that at relatively long contact times the rate is inhibited by a higher concentration of products on the surface. The selectivities to methanol and methyl formate change by modest amounts (relative to the change in conversion), suggesting that methyl formate is formed primarily by a reaction that is *concurrent* with methanol formation, rather than *subsequent* to or otherwise dependent upon methanol formation.

Table 6 lists the activation energies determined for methane, methanol, and methyl formate formation for temperatures between 573 and 473 K. For methane, the activation energy is the same for both Cu/SiO_2 and NaO_x/Cu powder. Promotion of Cu/SiO_2 with lanthana lowers the activation energy, as does dispersion of copper on lanthana. The activation energy for methanol formation over Cu/SiO_2 is lowered slightly by promotion with lanthana, whereas dispersion on lanthana increases

TABLE 4

CO_2 Hydrogenation over $Cu/MnO_2/La_2O_3$: Effects of P_{H_2} on Activity and Product Distribution[a]

Total P (atm)	10.6	13.4
H_2/CO_2	2	3
CO_2 conversion (μmol CO_2/min/m^2 catalyst)	0.016	0.018
Selectivities[b]		
Hydrocarbons	4.48	2.64
MeOH	51.06	76.78
MeFormate	44.45	20.57

[a] $T = 499$ K, $P_{CO_2} = 4.2$ atm.

[b] Selectivity among organic products.

TABLE 5

CO_2 Hydrogenation over $Cu/MnO_2/La_2O_3$: Influence of Space Velocity on Activity and Product Distribution[a]

F/W (cm^3/min/g catalyst)	35.7	71.4	142.8
CO_2 conversion (μmol CO_2/min/m^2 catalyst)	0.001	0.016	0.026
Selectivities[b]			
Hydrocarbons	5.35	4.48	2.70
MeOH	58.65	51.06	45.65
MeFormate	36.00	44.45	51.65

[a] $H_2/CO_2 = 2$, $P = 10.6$ atm, $T = 499$ K.

[b] Selectivity among organic products.

TABLE 6

Activation Energies (kcal/mol)

Catalyst	CO_2/H_2		
	CH_4	CH_3OH	MeF
NaO_x/Cu	20.8	14.2	—
Cu/SiO_2	20.8	7.5	14.1
$La_2O_3/Cu/SiO_2$	11.8	5.0	[15.9][a]
Cu/La_2O_3	13.8	28.0	[10.2][a]
$Cu/MnO_2/La_2O_3$	17.8	22.4	[9.8][a]

[a] Estimated from two temperatures below 530 K.

the activation energy by a factor of 4. The presence of NaO_x also increases the activation energy.

The activation energy for methyl formate was difficult to determine with any confidence over the temperature range used, since the rate of methyl formate formation was low over the majority of catalysts. The values given are estimated for temperatures in the range of 490–523 K. Below 490 K, the yield of methyl formate increased for Cu/SiO_2 and $Cu/MnO_2/La_2O_3$, but fell off to zero for the other catalysts.

Hydrogenation of CO_2/CO Mixtures

The activities of NaO_x/Cu powder, Cu/SiO_2, and Cu/La_2O_3 were investigated for hydrogenation of mixtures of CO and CO_2. The results of these experiments are presented in Table 7. Also included in this table are the activities of $La_2O_3/Cu/SiO_2$ and $Cu/MnO_2/La_2O_3$ in pure CO and CO_2. From the table, it is seen that the activities of copper powder and Cu/La_2O_3 increase with increasing CO content, whereas that for Cu/SiO_2 passes through a maximum. In CO/H_2, the activity of Cu/SiO_2 is almost half that in CO_2/H_2, whereas that for $La_2O_3/Cu/SiO_2$ is ~30% higher. The activity of copper powder in CO/H_2 is almost 25 times higher than that in CO_2/H_2, whereas the activity of Cu/La_2O_3 in CO_2/H_2 is higher than that in CO/H_2 by an order of magnitude. By contrast, the activity of $Cu/MnO_2/La_2O_3$ in CO_2/H_2 is higher than that in CO/H_2 by only a factor of 6. The effect of CO/CO_x on the rate of methanol formation is illustrated in Fig. 3. What is particularly striking are the qualitatively different patterns observed for Cu/SiO_2 and for NaO_x/Cu powder and Cu/La_2O_3. For Cu/SiO_2, the methanol activity passes through a maximum at $CO/CO_x = 0.2$ and then rapidly decreases as CO/CO_x increases further. By contrast, both NaO_x/Cu powder and Cu/La_2O_3 exhibit a small increase in methanol activity for CO/CO_x values below 0.8, and then a rapid increase as CO/CO_x approaches 1.0.

TABLE 7

Hydrogenation of CO_2/CO Mixtures over Copper Catalysts: Effect of Feed Composition on Activity[a]

$CO/(CO_2 + CO)$[b]	0.0	0.2	0.8	1.0
Catalyst	Rate (μmole CO_x converted/min/m² Cu)[c]			
NaO_x/Cu	1.21	4.63	7.39	28.20
Cu/SiO_2	21.66	29.98	17.40	11.40
$La_2O_3/Cu/SiO_2$	36.31	—	—	46.24
Catalyst	Rate (μmole CO_x converted/min/m² catalyst)[c]			
Cu/La_2O_3	0.09	0.17	0.20	1.26
$Cu/MnO_x/La_2O_3$	0.13	—	—	0.08

[a] $H_2/CO_x = 3$, $P = 13.4$ atm, $T = 573$ K.

[b] Data for pure CO/H_2 from Ref. (*20*).

[c] Conversion to organic compounds only. BET area for lanthana-supported catalysts, Cu area for the others.

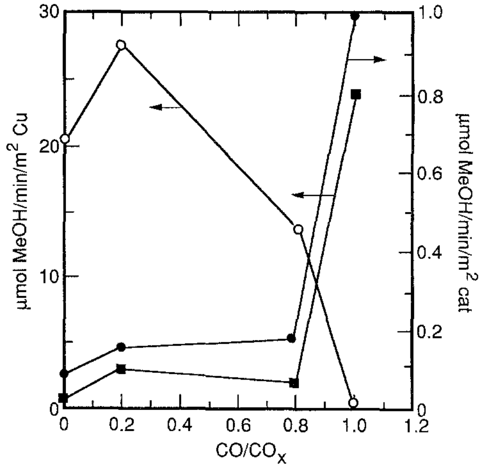

FIG. 3. Hydrogenation of CO_2 and CO over copper catalysts: effect of CO/CO_x ratio on the methanol activity ($H_2/CO_x = 3$, $T = 573$ K, $P = 13.4$ atm). (■) NaO_x/Cu, (○) Cu/SiO_2, (●) Cu/La_2O_3.

The influence of the proportions of CO and CO_2 in the feed gas on the distribution of organic products formed is presented in Tables 8–11. As can be seen from Table 8a, the selectivity of Cu/SiO_2 for methanol decreases and that for hydrocarbons increases as the proportion of CO in the feed

TABLE 8a

Hydrogenation of CO_2/CO Mixtures over Cu/SiO_2: Effect of Feed Composition on Product Distribution[a]

$CO/(CO + CO_2)$[b]	0.0	0.2	0.8	1.0
Selectivities[c]				
Hydrocarbons	4.78	5.93	17.36	79.12
MeOH	94.39	92.28	79.29	4.06
C_{2+} Oxygenates	0.00	1.79	0.00	3.60
Among C_{2+} oxygenates				
EtOH	0.00	0.00	0.00	100.00
MeFormate	0.00	100.00	0.00	0.00

TABLE 9a

Hydrogenation of CO_2/CO Mixtures over Cu/La_2O_3: Effect of Feed Composition on Product Distribution[a]

$CO/(CO_2 + CO)$[b]	0.0	0.2	0.8	1.0
Selectivities[c]				
Hydrocarbons	4.37	10.12	11.77	5.66
MeOH	95.63	89.56	87.89	79.26
C_{2+} Oxygenates	0.00	0.00	0.00	13.13
Among C_{2+} oxygenates				
EtOH	0.00	0.00	0.00	17.46
i-PrOH	0.00	0.00	0.00	1.99
n-PrOH	0.00	0.00	0.00	12.67
i-BuOH	0.00	0.00	0.00	67.24

[a] $H_2/CO_x = 3$, $P = 13.4$ atm, $T = 573$ K.

[b] Data for pure CO/H_2 from Ref. (*20*).

[c] Selectivities among organic compounds.

increases, the largest changes occurring for $CO/CO_x \geq 0.8$. While the selectivity to C_{2+} oxygenates is never large, the nature of the products is strongly dependent on the feed composition. Thus, for $CO/CO_x = 0.2$, the only C_{2+} oxygenate observed is methyl formate, whereas for $CO/CO_x = 1.0$ the only C_{2+} oxygenate is ethanol. The effects of feed composition for $La_2O_3/Cu/SiO_2$ are given in Table 8b. While qualitatively similar to that for Cu/SiO_2, the extent of the changes in methanol and hydrocarbon selectivities are not as large as those observed for Cu/SiO_2.

Tables 9a and 9b list the product distribution for Cu/La_2O_3 and $Cu/MnO_2/La_2O_3$. The effects of feed composition for both catalysts are similar. As CO/CO_x increases, the selectivity to methanol decreases monotonically. The selectivity to hydrocarbons passes through a shallow maximum and is actually somewhat higher in CO/H_2 than in CO_2/H_2. C_{2+} oxygenates are observed over Cu/La_2O_3 only in the case of $CO/CO_x = 1.0$. It is interesting to note that the effect of feed composition is quite sensitive to temperature. Thus, as shown in Table 10, the methanol selectivity of Cu/

TABLE 8b

Hydrogenation of CO_2/CO Mixtures over $La_2O_3/Cu/SiO_2$: Effect of Feed Composition on Product Distribution

	$H_2/CO_2 = 3$	$H_2/CO = 3$[a]
Selectivities[c]		
Hydrocarbons	1.26	34.00
MeOH	98.19	54.50

[a] $H_2/CO_x = 3$, $P = 13.4$ atm, $T = 573$ K.

[b] Data for pure CO/H_2 from Ref. (*20*).

[c] Selectivities among organic compounds; DME makes 100%.

TABLE 9b

Hydrogenation of CO_2/CO Mixtures over $Cu/MnO_2/La_2O_3$: Effect of Feed Composition on Product Distribution[a]

	$H_2/CO_2 = 3$	$H_2/CO = 3$[b]
Selectivities[c]		
Hydrocarbons	4.58	5.93
MeOH	94.88	86.84
C_{2+} Oxygenates	0.00	5.54
Among C_{2+} oxygenates		
EtOH	0.00	30.69
i-PrOH	0.00	6.21
n-PrOH	0.00	21.98
i-BuOH	0.00	41.08

[a] $H_2/CO_x = 3$, $P = 13.4$ atm, $T = 573$ K.

[b] Data for pure CO/H_2 from Ref. (*20*).

[c] Selectivities among organic compounds.

TABLE 10

Hydrogenation of CO_2/CO Mixtures over Cu/MnO_2/La_2O_3: Effect of Feed Composition on Product Distribution[a]

$CO/(CO_2 + CO)$[b]	0.0	0.2	0.8	1.0
CO_x conversion (μmol CO_x/min/m^2 catalyst)				
Selectivities[c]				
Hydrocarbons	4.48	21.82	—	3.17
MeOH	51.06	39.60	—	95.16
C_{2+} Oxygenates	44.45	38.80	—	1.61
Among C_{2+} oxygenates				
MeFormate	100.00	100.00	—	0.00
i-BuOH	0.00	0.00	—	94.60
n-BuOH	0.00	0.00	—	5.40

[a] $H_2/CO_x = 3$, $P = 13.4$ atm, $T = 499$ K.

[b] Data for pure CO/H_2 from Ref. (*20*).

[c] Selectivities among organic compounds.

MnO_2/La_2O_3 at 499 K exhibits a minimum and the C_{2+} oxygenates decrease as CO/CO_x increases. It is also seen that the principal C_{2+} oxygenate switches from methyl formate to isobutanol as CO/CO_x increases.

Table 11 shows that the effects of feed composition on product distribution are more complex for NaO_x/Cu powder than for the other catalysts. As CO/CO_x increases, the selectivity to methanol passes through a minimum at $CO/CO_x = 0.8$, whereas the selectivities to hydrocarbons and C_{2+} oxygenates pass through maxima. As seen in Table 11, the distribution of C_{2+} oxygenates shifts from a roughly equal split between ethanol and methyl formate to a spectrum of higher alcohols.

TABLE 11

Hydrogenation of CO_2/CO Mixtures over NaO_x/Cu powder: Effect of Feed Composition on Product Distribution[a] ($H_2/CO_x = 3$, $P = 13.4$ atm, $T = 573$ K)

$CO/(CO_2 + CO)$[b]	0.0	0.2	0.8	1.0
Selectivities[c]				
Hydrocarbons	26.38	26.70	37.54	9.94
MeOH	73.62	64.39	25.12	85.87
C_{2+} Oxygenates	0.00	8.90	37.34	6.26
Among C_{2+} oxygenates				
EtOH	0.00	47.30	74.60	30.20
MeFormate	0.00	52.70	0.00	0.00
i-PrOH	0.00	0.00	6.46	5.89
n-PrOH	0.00	0.00	7.95	11.24
i-BuOH	0.00	0.00	0.00	13.90
n-BuOH	0.00	0.00	10.99	0.00

[a] $H_2/CO_x = 3$, $P = 13.4$ atm, $T = 499$ K.

[b] Data for pure CO/H_2 from Ref. (*20*).

[c] Selectivities among organic compounds.

DISCUSSION

Nature of the Active Copper Species

The results of this study show that the product distribution for each catalyst differs significantly depending on the composition of the support or promoter. Moreover, the influence of support or composition on catalyst activity and selectivity is strongly dependent on the ratio of CO to CO_2 in the feed. Similar observations have been reported previously by a number of authors (*1–4, 14, 18–20*). Denise *et al.* (*3, 19*) have suggested that the observed effects of feedstock and support composition on methanol synthesis activity reflect the relative importance of two independent pathways of methanol formation: one originating from CO and the other from CO_2. To understand how support or promoter composition influences the activity and selectivity of copper catalysts it is useful to review first what is currently known about the interaction of CO and CO_2 with copper catalysts.

While investigations of the mechanism of CO hydrogenation over metallic Cu have failed to resolve the nature of the active site (or sites) unambiguously (*23–29*), certain insight has been gained. Studies of unpromoted Cu powder (*28*) and Cu/SiO_2 (*21*) indicate that copper metal is relatively inactive for methanol synthesis from CO, but does show activity for hydrocarbon synthesis. When Cu is promoted with or supported on a basic metal oxide, the methanol activity of Cu increases substantially as does the selectivity to methanol (*21, 28*).

NMR and XPS studies of alkali–metal oxide-promoted Cu powder carried out by Sheffer *et al.* (*28, 29*), and Monnier *et al.* (*30, 31*) indicate that the methanol activity increases linearly with increasing surface concentration of Cu^+ ions. These authors suggest that both Cu^0 and Cu^+ sites are required for methanol synthesis: the Cu^0 sites being essential for H_2 adsorption, and the Cu^+ sites being essential for CO adsorption. The Cu^+ sites are believed to be created at junctions between metallic copper and islands of the promoter. Chu *et al.* (*32*) have also suggested that some of the Cu^+ ions may be present within the promoter itself.

In contrast to CO, methanol is formed very readily during CO_2 hydrogenation over unpromoted Cu (*1*). Studies by Chinchen *et al.* (*1*) indicate that the adsorption of CO_2 is enhanced significantly by the presence of adsorbed oxygen on the catalyst surface. The surface coverage by O atoms is governed by the equilibrium

$$CO_{2,g} + S = CO_g + O_s. \qquad (1)$$

In pure CO_2, at low conversions the O coverage can be as high as 0.5 monolayers. When reaction occurs in a mixture of CO and CO_2, CO_2 continues to form methanol much more rapidly than CO (*15–17*). However, when the CO partial pressure becomes sufficiently high, the surface coverage by O_s declines and with it, the adsorption of CO_2.

In view of the preceding discussion, it is now possible to rationalize the effects of catalyst composition on the variation in methanol synthesis activity of a given catalyst with the value of CO/CO_x in the feed. Figure 3 shows that for Cu/SiO_2, the rate of methanol formation decreases significantly as CO/CO_x increases above 0.2. This trend can be attributed to a decrease in the surface concentration of adsorbed CO_2 resulting from a decrease in the surface coverage by O_s due to a shift in the equilibrium of Eq. (1) to the left. The dependence of the rate of methanol formation on the CO/CO_x ratio for NaO_x/Cu powder and Cu/La_2O_3 is just the opposite. The very low activity in feeds containing a substantial fraction of CO_2 may be due to the fact that a significant fraction of the surface of the Cu metal is covered by La_2O_3 or NaO_x. In such instances, the availability of exposed metallic Cu would be limited and hence the types of sites required for CO_2 hydrogenation. By contrast, the number of Cu^+ sites ought to be high. However, such sites might be poisoned for access by CO through a strong interaction with CO_2. It is interesting to note that a similar deleterious effect of CO_2 on methanol synthesis activity has been reported by Denise and Sneeden (*19*) for Cu/MgO, by Monnier *et al.* (*20*) for $Cu–Cr_2O_3$ catalysts, and by Owen *et al.* (*33, 34*) for copper–lanthanide catalysts derived from alloys of copper with various rare earth elements. Particularly relevant to present investigation are the XPS observations of Monnier *et al.* (*20*), which show that the presence of CO_2 has no effect on the concentration of Cu^+ sites, suggesting that the inhibition of methanol synthesis by CO_2 is due to the competitive adsorption of CO_2 on Cu^+ sites needed for CO adsorption.

Methyl Formate Production

An interesting feature of the present study is the observation of large quantities of methyl formate in the products when CO_2 is hydrogenated at low temperatures and hydrogen partial pressures. As may be seen in Table 5, methanol and methyl formate appear to be formed in parallel rather than sequentially, since decreasing the space velocity did not change the methanol selectivity relative to that of methyl formate. This suggests that an intermediate in the route from CO_2 to methanol must also be important in methyl formate synthesis. Amenomiya and Tagawa (*9*) and Ramaroson *et al.* (*4*) have proposed that the rate-determining step in methanol synthesis from CO_2 is the hydrogenation of formate species ($HCOO^-$). While the mechanism of methyl formate formation from CO_2 has not been investigated, it is possible to propose at least two pathways via $HCOO^-$:

$$CH_3OH + HCOO^- = HCOOCH_3 + OH^- \quad (2)$$

$$4H + 2HCOO^- = HCOOCH_3 + 2OH^- \quad (3)$$

Reaction 2 is, in effect, an esterification reaction. Reaction 3 is not an elementary process. While this reaction is not known to occur, a related reaction, namely, the dimerization of formaldehyde (Tischenko reaction) has been reported (*35–37*).

The rate of methyl formate formation is particularly sensitive to the CO/CO_x ratio in the feed. At 573 K, the data in Tables 8a and 11 indicate that over Cu/SiO_2 and NaO_x/Cu the activity and selectivity for methyl formate pass through a sharp maximum at $CO/CO_x = 0.2$. This suggests that in the presence of CO, a new route to methyl formate becomes available that involves the interaction of either CO or surface species derived from CO (e.g., H_2CO) with formate species. Possible candidates are the carbonylation of $HCOO^-$ or a Canizzaro-type condensation involving formate and formaldehyde, instead of two aldehydes (*38*):

$$HCOO^- + CO + 3H = HCOOCH_3 + OH^- \quad (4)$$

$$HCOO^- + H_2CO + 2H = HCOOCH_3 + OH^-. \quad (5)$$

It should be noted, though, that in the absence of CO_2, methyl formate is not formed from CO and H_2 under the conditions used in this study.

The effects of support composition and promoters on the formation of methyl formate cannot be clearly defined. For example, the rate of methyl formate formation over copper appears to be insensitive to the presence of lanthana, since lanthana promotion of Cu/SiO_2 does not affect the production rate (see Tables 2 and 3b). It is also significant to note that the selectivity to methyl formate is virtually the same for Cu/SiO_2, Cu/La_2O_3, and $Cu/MnO_2/La_2O_3$ (see Table 3b). No explanation for the apparent insensitivity of the methyl formate selectivity and activity can be offered at this time.

CONCLUSIONS

The results of this study show that the methanol activity and selectivity of Cu-containing catalysts are highly sensitive to the composition of the support and promoter and to the proportions of CO and CO_2 in the feed gas. Unpromoted Cu/SiO_2 is active for CO_2 hydrogenation to methanol with a selectivity of >90%. The same catalyst is relatively inactive for CO hydrogenation to methanol, exhibiting a selectivity of only 4%. Promotion with La_2O_3 enhances the activity of Cu/SiO_2 for methanol formation from CO_2/H_2 by 70% and increases the methanol selectivity slightly. By contrast, La_2O_3 promotion enhances the activity of Cu/SiO_2 for methanol formation from CO/H_2 by a factor of 50 and the selectivity to methanol by a factor of 20. The distributions of products formed from CO_2/H_2 over Cu/La_2O_3 and $Cu/MnO_2/La_2O_3$ are similar to that observed over Cu/SiO_2, but when reaction occurs in CO/H_2, a much higher selectivity to methanol is observed for the two lanthana-containing catalysts than for Cu/SiO_2. In contrast to $La_2O_3/Cu/SiO_2$, NaO_x/Cu powder has a low activity for methanol formation from CO_2/H_2 and a selectivity of only 74%. The methanol activity of this catalyst in CO/H_2 is 26-fold higher and the selectivity is 15% higher.

The observed differences in catalyst activity and selectivity are interpreted on the basis of the differences in the types of sites required for CO_2 and CO hydrogenation. It is concluded that Cu^0 sites are required to hydrogenate CO_2 to methanol, but that both Cu^0 and Cu^+ sites are required for CO hydrogenation to methanol. It is believed that

Cu^+ sites are created at the junction between metallic Cu particles and the support or the promoter and that basic metal oxides are particularly effective in stabilizing Cu^+ ions. The Cu^+ sites are highly active for CO hydrogenation but appear to be deactivated by CO_2, possibly through excessively strong adsorption.

All catalysts display product distributions in CO_2/H_2 that are different from those in CO/H_2, indicating that CO_2 hydrogenation occurs via a route independent of that for CO hydrogenation. For the majority of catalysts, the formation of methanol from CO_2 is accompanied by the formation of methyl formate, whereas methanol synthesis from CO is accompanied by the synthesis of C_{2+} alcohols. The formation of methyl formate appears to occur in parallel with methanol formation and is competitive at low temperatures and H_2 partial pressures. It is proposed that the formation of methanol and methyl formate from CO_2 proceeds through formate intermediates.

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