JOURNAL OF CATALYSIS 69, 487–494 (1981)

Methanol-Reforming Reaction over Copper-Containing Catalysts—The Effects of Anions and Copper Loading in the Preparation of the Catalysts by Kneading Method

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Received October 15, 1980; revised December 30, 1980

Methanol-reforming reaction $CH_3OH + H_2O = 3H_2 + CO_2$ was carried out over copper-containing catalysts which were prepared from hydroxides of copper or from the hydroxide kneaded with various metal oxides. The specific activity (activity per weight of copper used) either of supported or support-free catalyst was markedly increased when the hydroxide was prepared from alkali solution with addition of copper salt solution at higher pH or when the weight percentage of copper on the support was decreased. However, other kinetic parameters such as activation energy and selectivity of the reaction were unaffected by the preparation of the catalyst unless copper chloride was employed as a starting material of the hydroxide preparation at lower pH. DTA, ir, XPS, AES and other chemical analyses of the catalysts revealed that hydroxide ion in the hydroxide precipitate prepared at lower pH exchanged in part with the anionic group of its starting material during the course of the preparation. The anion or its fragment was found to be strongly held on the surface and inhibited the reaction to a great extent. On the other hand, the anion held was markedly decreased when the catalyst was prepared at higher pH. This catalyst was found to be highly active for the title reaction. The surface area of metallic copper was considerably increased when copper was kneaded with the support. This gave rise to the increase in the specific activity of the catalyst. The effect of the support upon the reaction was examined for the catalyst kneaded with silica, manganese dioxide, ferric oxide, titanium oxide, calcium oxide, and nickel oxide. However, the supports other than nickel oxide exerted no chemical effect upon the reaction. Nickel oxide was suggested to be reduced during the course of the reaction and metallic nickel thus formed catalyzed the methanol decomposition reaction $CH_3OH = CO + 2H_2$.

INTRODUCTION

Methanol decomposed over metal catalysts into hydrogen and carbon monoxide, formaldehyde, or/and methyl formate in the absence of water (*1*). However, this species is transformed into carbon dioxide and hydrogen in the presence of water through methanol-reforming reaction $CH_3OH + H_2O = CO_2 + 3H_2$ (*2–4*) over a proper catalyst. This reaction is thermodynamically very favorable, so that hydrogen atoms in water molecules as well as in methanol are effectively converted into gaseous hydrogen. In the previous work, it was briefly described that this reaction proceeded with high selectivity over copper-containing catalysts and its activity depended upon the preparation of the catalysts (*5*). In the present experiment, the reaction was carried out over copper-containing catalysts which were prepared by kneading copper hydroxide with a variety of metal oxides and the effect of the preparation of the catalyst upon the reaction was investigated as an initial step in designing the catalysts.

MATERIALS AND METHODS

Catalysts. The kneaded catalysts used and their preparative methods are summarized in Table 1. Hydroxide of copper was precipitated by addition of the solution of copper salt (nitrate, formate, or chloride) to that of sodium hydroxide or potassium hydroxide until a given pH of the solution was attained. About 1 to 2 g of the hydroxide was filtered and washed thoroughly with 20

0021-9517/81/060487-08$02.00/0

TABLE 1

Preparation of the Catalysts

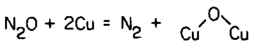
Catalyst	Cu source	Alkali	Final pH	Atomic ratio (Cu : Me)
Cu–SiO_2[2]	$Cu(NO_3)_2$	NaOH	6.5	1 : 2
Cu–SiO_2[8]	$Cu(NO_3)_2$	NaOH	7.74	1 : 2
Cu–SiO_2[12]	$Cu(NO_3)_2$	NaOH	10.53	1 : 2
Cu–SiO_2[13]	$Cu(NO_3)_2$	NaOH	12.16	1 : 2
Cu–SiO_2[14]	$Cu(NO_3)_2$	NaOH	12.16	1 : 5
Cu–SiO_2[15]	$Cu(NO_3)_2$	NaOH	12.16	1 : 19
Cu–SiO_2[16]	$Cu(NO_3)_2$	KOH	12.16	1 : 2
Cu–SiO_2[17]	$Cu(NO_3)_2$	NaOH	12.16	1 : 2
Cu–SiO_2[18]	$Cu(NO_3)_2$	NaOH	12.16	1 : 2
Cu–SiO_2[19]	$CuCl_2$	NaOH	12.16	1 : 2
Cu–SiO_2[20]	$CuCl_2$	NaOH	6.51	1 : 2
Cu–SiO_2[21]	$Cu(HCOO)_2$	NaOH	12.16	1 : 2
Cu–SiO_2[23]	$Cu(HCOO)_2$	NaOH	6.52	1 : 2
Cu–SiO_2[26]	$Cu(NO_3)_2$	NaOH	12.14	1 : 34.7
Cu–Al_2O_3[5]	$Cu(NO_3)_2$	NaOH	12.16	1 : 4
Cu–MnO_2[4]	$Cu(NO_3)_2$	NaOH	9.3	1 : 2
Cu–Fe_2O_3[a]	$Cu(NO_3)_2$	NH_3	9.6	1 : 2
Cu–NiO–SiO_2	$Cu(NO_3)_2$	NaOH	6.7	1 : 2 : 4[b]
Cu–TiO_2	$Cu(NO_3)_2$	NaOH	6.7	1 : 2
Cu–CaO	$Cu(NO_3)_2$	NaOH	6.6	1 : 2
Cu[3]	$Cu(NO_3)_2$	NaOH	12.16	Support free

[a] Calcined at 400°C.
[b] Cu : Ni : Si = 1 : 2 : 4.

liters of distilled water at room temperature. The precipitate was kneaded[1] in mortar with a variety of metal oxides in 1 : 2 Cu/metal atomic ratio. The ratio Cu/Si in silica-supported copper catalyst was varied from 1 : 0 to 1 : 36. The catalyst thus prepared was dried at 120°C overnight and calcined in air at 520°C for 3 hr. In a similar manner, the support-free catalyst was prepared. Silica (Japan-Chromato Industry Company), alumina (Nishio Ind. Company, Ltd., type KHA-46), manganese dioxide (Wako Pure Chemicals Ind. Ltd.), and titanium dioxide (Wako Pure Chemicals Inc. Ltd.) employed as supports were used without any treatment prior to kneading with hydroxide of copper. Ferric oxide and calcium oxide were prepared from their corresponding hydroxides. Ferric hydroxide was prepared from its nitrate, whereas calcium hydroxide was commerically available.

Reaction. The methanol-reforming reaction was carried out at atmospheric pressure in a flow system. An equimolar mixture of methanol and water was fed with a micropump and rapidly vaporized in a nitrogen stream before entering the catalyst bed. The total inflow rate was always kept at 96 cm^3 STP/min. The partial pressure of either methanol or water was kept at 0.24 atm at the inlet of the catalyst bed. The reactants and the products other than formaldehyde were determined by gas chromatography. Formaldehyde was analyzed by coloration at 580 nm (reddish purple) with sodium salt of chromotropic acid and sulfuric acid (*6*).

Metallic copper surface area. The metallic copper surface area of supported or support-free catalyst was determined by titration with nitrous oxide



$$N_2O + 2Cu = N_2 + Cu{-}O{-}Cu$$

according to the method proposed by Scholten and Konvalinka (*7*). The catalyst was brought into contact with nitrous oxide at 90°C and the nitrogen formed was volumetrically determined after nitrous oxide was frozen in a trap immersed in liquid nitrogen. The amount of oxygen held on metallic copper was, therefore, estimated from that of nitrogen formed and the stoichiometry of the above reaction. The surface area of metallic copper was thus estimated from the amount of oxygen on the assumptions (*7*) that (i) one oxygen adatom occupied two surface copper atoms and (ii) 1.7×10^{15} copper atoms were exposed on 1 cm^2 copper surface on the basis of the Sunquist's results (*8*).

Other analytical methods. Differential thermal analyses of hydroxide of copper were carried out with the aid of DTA equipment (Rigaku Denki Company Ltd.). Infrared spectra of hydroxide, and ultraviolet and visible spectra of the solution were

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[1] Copper hydroxide was ball milled together with silica overnight in a preliminary experiment. This catalyst exhibited practically the same activity as that kneaded in mortar.

recorded with infrared (Hitachi-215) and UV-VIS (Hitachi–Perkin–Elmer 139) spectrophotometers, respectively. XPS and Auger spectra were obtained by an ESCA 3 (vacuum generator). The pH of the solution was recorded with a pH meter (Toa Electronics Ltd., model HM-15).

RESULTS AND DISCUSSION

The Effect of Anion in the Starting Material upon the Reaction

Typical results obtained over catalyst Cu–SiO_2[15] are illustrated in Fig. 1 in which the partial pressures of the products at the outlet of the catalyst bed are plotted against the temperature. Carbon dioxide and hydrogen were mainly formed. Carbon monoxide and methyl formate were formed as minor products. The partial pressure of formaldehyde at the outlet was found to be far less than 10^{-4} atm and was negligible compared to those of other products. When a methanol–water mixture was admitted over fresh catalyst, the reaction initially proceeded at a fairly slow rate around 150°C but the rate was gradually increased as hydrogen was evolved. Once the catalyst was reduced, the steady state was rapidly attained. The rates of hydrogen and carbon dioxide formation are plotted in Fig. 2 against the pH at which hydroxides of copper were finally precipitated from sodium hydroxide solution with addition of copper nitrate solution. It is seen that the rates of hydrogen and carbon dioxide formation allotted for 1 g of copper (specific activity) increase with the pH. As Fig. 3 shows, the activation energies are practically kept around 18 kcal/mole irrespective of the pH. The ratios H_2/CO_2 and $CO_2/(CO$

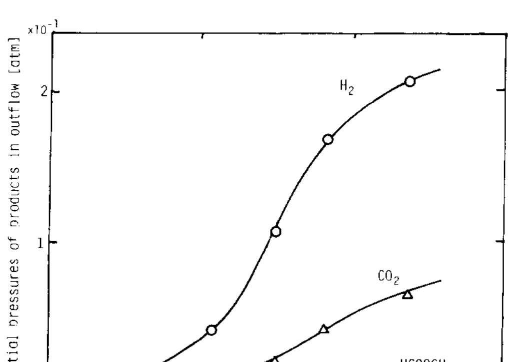

FIG. 1. Partial pressures of products in outflow against temperature.

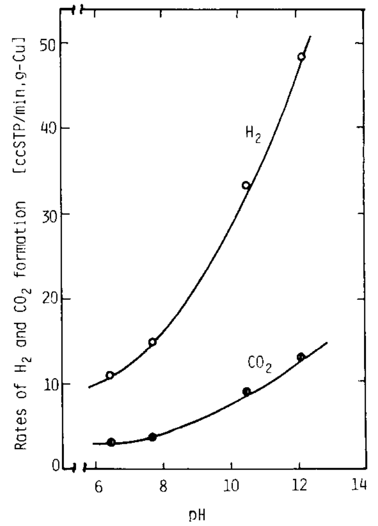

FIG. 2. Effect of pH of the precipitation of copper hydroxide upon the rates of H_2 and CO_2 formation. Reaction temperature, 220°C; atomic ratio Cu/Si = 1/2.

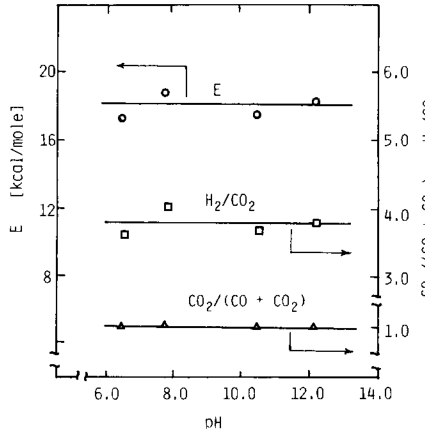

FIG. 3. Activation energy, the ratios of the products H_2/CO_2 and $CO_2/(CO + CO_2)$ in outflow vs pH of hydroxide preparation. Reaction temperature, 220°C; atomic ratio Cu/Si = 1/2.

+ CO_2) obtained at the outlet of the catalyst bed are parameters indicative of the selectivity of the reforming reaction and are also unaffected by the pH.

Figure 4 illustrates DTA curves of copper hydroxides which were prepared at various pH values. An endothermic peak is seen around 195°C for hydroxide prepared at higher pH. The result was much the same as that obtained for copper hydroxide, $Cu(OH)_2$. On the other hand, another endothermic peak was observed around 240°C for hydroxide prepared at lower pH together with the peak that was assigned to copper hydroxide. Figure 5 shows the infrared spectra of hydroxide of copper which was prepared at various pH values. The absorptions occurred around 1420, 1350, and 1048 cm^{-1} for hydroxide prepared at lower pH, whereas no absorptions were observed for that prepared at higher pH in this spectral region. On the basis of the spectra obtained, it was, therefore, concluded that an unidentate type of nitrate (*9, 10*) was present in hydroxide. When the catalyst was heated around 240°C, the absorptions started to decrease and nitrogen oxides were evolved. The endothermic peak observed around 240°C was, therefore, attributed to the decomposition of the

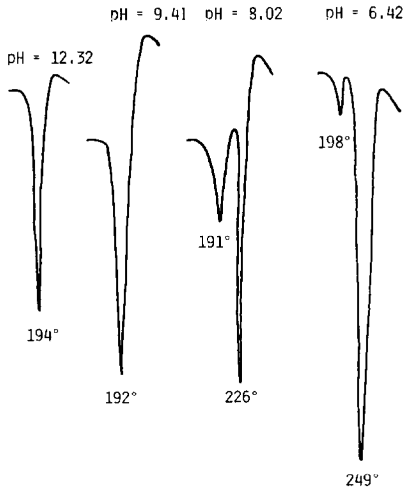

FIG. 4. DTA curves for hydroxides of copper precipitated at various pH values.

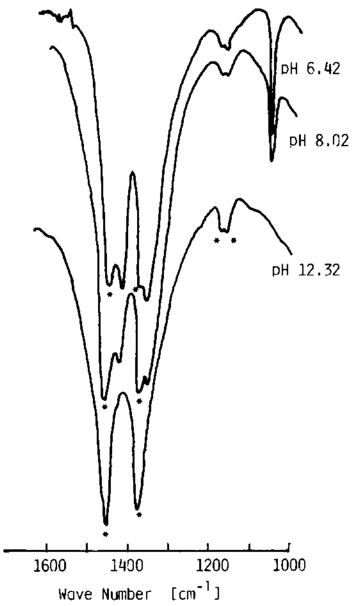

FIG. 5. Infrared spectra of hydroxides of copper precipitated at various pH values; * marks represent the absorptions ascribed to nujol.

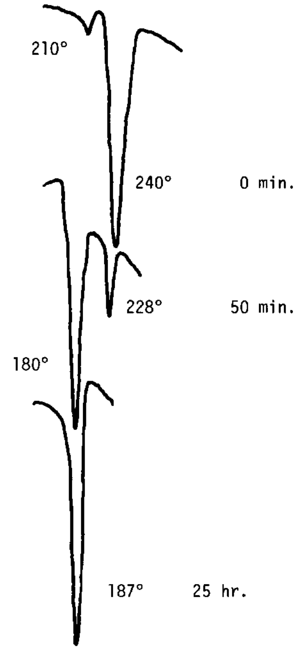

FIG. 6. Change in DTA curve of hydroxide of copper precipitated at pH = 6.42 with time when the precipitate was soaked in 0.1 *N* NaOH solution.

unidentate. These results were also obtained for copper supported on silica.

When hydroxide of copper which was prepared at lower pH was soaked in sodium hydroxide solutions, nitrate ion was eluted and the pH of the solution was lowered. The amount of nitrate ion eluted was estimated to be 1.1 times that of the decrease in hydroxide ion. Figure 6 illustrates DTA curves obtained for hydroxide of copper during the course of this procedure. The peak around 190°C decreases, resulting in the relative increase in the peak at 240°C. In accordance with these observations, nitrate ion was held in the hydroxide and the pH of the solution was raised when copper hydroxide, $Cu(OH)_2$, was soaked in copper nitrate solution. In these respects, we concluded that ion exchange $Cu(OH)_2 + NO_3^- = Cu(OH)NO_3 + OH^-$ reversibly occurred between nitrate ion and hydroxide ion during the course of the precipitation.[2] Nitrate-free copper hydroxide was, therefore, preferentially formed at higher pH, whereas nitrate ion was held in the hydroxide at lower pH.

Hydroxides of copper were also prepared from copper formate or chloride and were kneaded with silica. As Table 2 shows, the activities of the catalysts markedly depend upon copper salts employed as starting materials when the hydroxide was prepared at lower pH. On the other hand, those values obtained over the catalyst prepared at higher pH are much less affected by the starting materials employed.

The XPS spectra of catalysts Cu–SiO_2[2] and [13] were obtained after the reforming reaction was carried out. Figure 7 evidently demonstrates that the broad peak which is attributed to nitrogen-containing species appeared around 397 eV for catalyst [2]. On the other hand, the peak for Cu–SiO_2[13] was extremely small compared to that for Cu–SiO_2[2]. The anion held at lower pH was strongly held even after the reaction was carried out. When nitrogen oxides were admitted on the catalyst during the course of the reaction, the oxides strongly inhibited the reaction. From these results, it was concluded that the anionic group of the starting material or its fragment was firmly held in the catalysts and inhibited the reaction. The reaction was, therefore, markedly influenced by the pH at which copper hydroxide was prepared. The amount of anion held was successfully controlled by the pH of the preparation and the starting material employed.

TABLE 2

Effect of the Starting Material upon the Reaction

Copper salts	pH where hydroxides of copper are precipitated			
	6.5		12.16	
	r_{H_2}[a]	r_{CO_2}[a]	r_{H_2}	r_{CO_2}
$Cu(NO_3)_2 \cdot 3H_2O$	10.85	3.01	48.29	12.96
$CuCl_2 \cdot 2H_2O$	0.88	0.06	24.75	6.94
$Cu(HCOO)_2 \cdot 4H_2O$	22.08	6.94	55.24	17.51

[a] r_{H_2} and r_{CO_2} represent the rates (cm^3 STP/min) of hydrogen and carbon dioxide formations at 220°C, respectively.

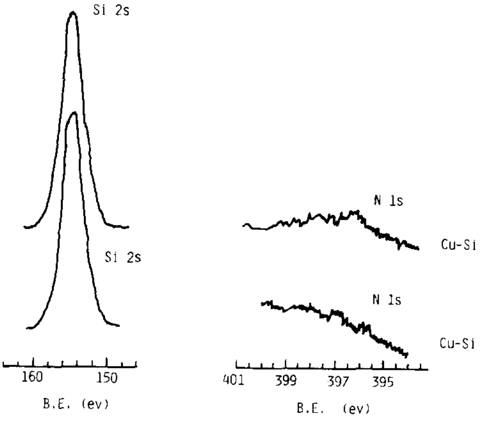

FIG. 7. X-Ray photoelectron spectra of copper–silica catalysts.

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[2] Hydroxide of copper prepared at pH = 6.42 was found to contain about 25 wt% of nitrate ion by a chemical analysis. Copper hydroxide, $Cu(OH)_2$, formed would be transformed into copper hydroxynitrate, $Cu_2(OH)_3NO_3$, via ion exchange in the course of the hydroxide preparation.

The Effect of Cation in the Precipitant upon the Reaction

Potassium hydroxide was employed as a precipitant in place of sodium hydroxide but exerted no influence upon the reaction. In fact, it was found from Auger electron spectroscopy, that no alkali cation was held on the surface.

The Effect of the Amount of Copper Loading upon the Reforming Reaction

Copper hydroxide prepared at higher pH was kneaded with silica at various ratios. As evidenced from Fig. 8, the specific activity of the catalyst markedly increased when copper hydroxide was kneaded with silica. However, the activation energy of the reaction and the parameters H_2/CO_2 and $CO_2/(CO + CO_2)$ were found to be practically unaffected by the amount of copper loading. The surface area of metallic copper was determined by titration with nitrous oxide. As Table 3 shows, this value was appreciably increased when copper was supported on silica. The crystal size of copper fell to 149 Å for catalyst Cu–SiO_2[26]. The turnover frequency of the reaction was estimated from the surface area of metallic copper and the rate of hydrogen formation obtained. This value obtained over silica-supported catalyst was practically the same as that obtained over support-free copper and was unaffected by the particle size of copper under the present experimental conditions. Similar results were also obtained for catalysts prepared at various pH values except for catalysts prepared from copper chloride at lower pH. This evidently demonstrates that most of anion held on the surface only covers the active site and inhibits the reaction. The anion exerted no chemical effect upon the reaction.

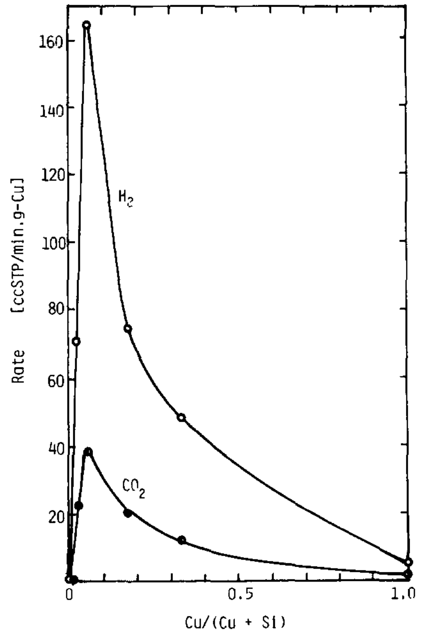

FIG. 8. Rates of H_2 and CO_2 formation vs kneading ratio. Reaction temperature, 220°C; copper hydroxide was prepared at pH = 12.16.

Reaction over Copper Supported on other Metal Oxides

The catalysts were prepared by kneading copper hydroxide with a variety of metal oxides such as MnO_2, Al_2O_3, Fe_2O_3, TiO_2, NiO, and CaO. In Figs. 9 and 10, the

TABLE 3

Specific Surface Area of Metallic Copper, Particle Size, and Turnover Number

Catalyst	S_{Cu} (m^2/g-Cu)	Particle size (Å)	Dispersion (%)	r_{H_2} (cm^3 STP/min · m^2-Cu)	Turnover number (sec^{-1})
Cu–Si[13]	28.04	240	5.03	1.72	0.045
Cu–Si[14]	33.92	198	6.09	2.20	0.058
Cu–Si[15]	27.44	245	4.96	5.98	0.158
Cu–Si[26]	45.08	149	8.08	1.59	0.042
Cu[3]	2.11	3194	0.38	2.49	0.065

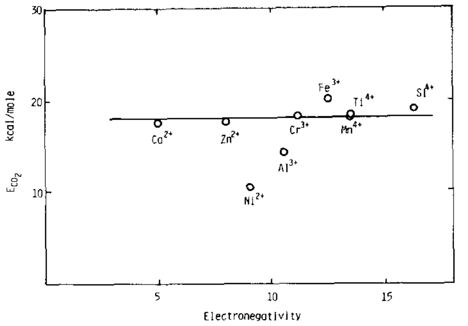

FIG. 9. Activation energy of CO_2 formation vs electronegativity of metal ion of support used.

activation energies and the selectivities of the reaction obtained were plotted against the electronegativities of metal ions of support oxides. They show that these kinetic parameters obtained were practically the same as those for the Cu–SiO_2 catalyst. The only exception is the results obtained for the Cu–NiO catalyst. The turnover frequencies were estimated for the Cu–MnO_2 and Cu–Al_2O_3 catalysts and it was found that these values were practically the same as that obtained for Cu–SiO_2. In these respects, it is concluded that the chemical effect of a support is practically negligible for these catalysts. On the other hand, for the Cu–NiO catalyst, nickel oxide would be reduced during the course of the reaction. Since nickel catalyst was highly active for methanol decomposition (*1*) $CH_3OH \rightarrow CO + 2H_2$, Cu–NiO catalyst would be much less selective for the reforming action.

SUMMARY

The methanol-reforming reaction $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$ was carried out over a variety of copper-containing catalysts which were prepared from copper hydroxide or by kneading them with various metal oxides such as SiO_2, MnO_2, Fe_2O_3, TiO_2, CaO, and NiO. The effect of the preparation of the catalyst upon the reaction was studied in detail with the help of various methods such as differential thermal analysis, infrared, X-ray photoelectron, and Auger electron spectroscopies, the surface area measurement of metallic copper exposed on the catalyst surface, and other chemical analyses. It was found that the specific activity of the catalyst (activity allotted for the weight of copper used) was markedly increased when copper hydroxide was precipitated at higher pH or kneaded with metal oxides. When the hydroxide was prepared at lower pH from various copper compounds having various anionic groups, the activity of the catalyst varied by the starting material employed. Hydroxide ion in the hydroxide precipitate was found to be rapidly exchanged with anion in its starting material at lower pH during the course of the preparation. The X-ray photoelectron spectra and the poisoning experiment revealed that the anion thus incorporated in the catalyst was strongly held on the catalyst even after the calcination or the performance of the reaction and retarded the reforming reaction to a considerable extent. However, this ion exchange was thermodynamically unfavorable at higher pH since hydroxide ion should be eluted in the solution by the exchange. The anion held was, therefore, found to be decreased as the pH of the solution was increased and its effect upon the reaction became practically negligible. The catalysts prepared at higher pH were,

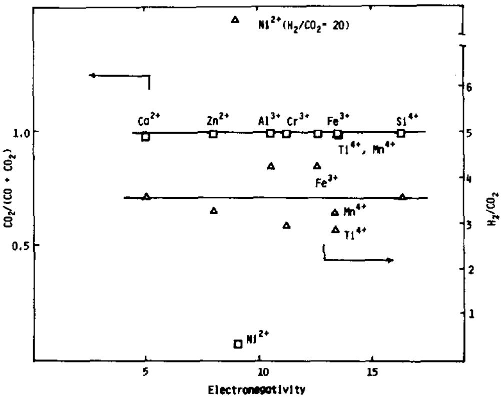

FIG. 10. $CO_2/(CO + CO_2)$, H_2/CO_2 vs electronegativity of metal ion of support used.

therefore, highly active compared with that prepared at lower pH and the activities were practically unaffected by the starting material employed. In contrast to these results, cation in the precipitant such as sodium or potassium hydroxide was not held in the catalyst during the course of the precipitation over the whole pH region, so that the precipitant exerted no influence upon the reaction.

The metallic copper surface area was increased by kneading it with metal oxides. The activity, therefore, increased by kneading. The turnover frequency, selectivity, and the activation energy of the reaction obtained were found to be unaffected by the preparative methods employed. When the reaction was carried out over the catalysts which were kneaded with various metal oxides, these kinetic parameters were found to be held constant irrespective of the supports employed in most cases. The only exception was the case when copper hydroxide was prepared by kneading with nickel oxide for which the formation of carbon monoxide was considerably in excess of that of carbon dioxide. Nickel oxide was suggested to be reduced into metallic nickel which effectively catalyzed the methanol decomposition reaction $CH_3OH \rightarrow CO + 3H_2$.

ACKNOWLEDGMENT

The authors express their sincere thanks to Mr. K. Narita for the metallic copper surface area determination. The present work was supported in part by Asahi Glass Incentive Grant and also in part by a Grant-in-Aid for Research from the Ministry of Education of the Japanese Government which the authors also gratefully acknowledge. Thanks are also extended to Dr. H. Konno for measuring the XPS and Auger spectra of the catalysts.

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