

## Catalysts for Low-Temperature Methanol Synthesis

### II. Catalytic Behavior of Cu/Zn/Al Mixed Oxides

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The aim of this work was to study the catalytic behavior of Cu/Zn/Al mixed oxides active in low-pressure methanol synthesis. The maximum activity was obtained for different Cu/Zn ratios as a function of the gas mixture composition. At values higher than 10.0%, the aluminum showed an inhibitor effect with both the mixtures. The determination of the copper surface area by N<sub>2</sub>O decomposition showed that during the reaction the catalysts were in a partially oxidized state. Furthermore, three different copper-containing species were identified in the spent catalysts: metallic copper, CuO, and copper not detectable by XRD analysis, the latter being probably the copper inside or related to the ZnO. While no correlation existed between the catalytic activity and only one of these species, a good fit was observed both with the sum and the product of the amount of CuO and undetected copper. Therefore, both a form of easily reoxidizable copper and the copper related to the ZnO have been suggested as active species, even though it was not possible to determine if they have similar activities or must be present contemporaneously. © 1985 Academic Press, Inc.

#### INTRODUCTION

Cu/Zn/Al mixed oxides are well-known catalysts for the synthesis of methanol at low temperature and pressure (1-4). By examining the scientific and patent literature it is possible to obtain a great deal of data regarding the catalyst compositions and methods of preparation as well as the compositions of the reaction mixtures employed (5-10). It is very difficult, however, to have an idea of the optimum composition of the catalysts and of the role of each element in the catalytic reaction. Regarding the nature of the active species three main hypotheses have been put forward in the literature: (i) metallic copper supported on alumina or ZnAl<sub>2</sub>O<sub>4</sub> or in an alloy (11-15), (ii) Cu(I) inside the ZnO lattice (16-18), and (iii) a more reactive fraction of copper (19-21).

In previous notes the preparation and the characterization of Cu/Zn/Al mixed oxides

with different Cu/Zn and Cu + Zn/Al ratios have been reported and it has been shown that by varying the ratio of the three elements it is possible to obtain precursors with all the elements in the same hydroxal-cite-like phase pure or together with either malachite- or hydrozincite-like side phases (22, 23). These precursors form after calcination oxides and after reduction copper with small crystal sizes.

The aim of this paper is to investigate the catalytic behavior of these oxides using two different H<sub>2</sub>/CO ratios: the stoichiometric ratio and a higher one employed industrially in the recycling loop. The catalytic activity is correlated with the nature of the species identified in the catalysts after reaction and the results are interpreted according to previously reported hypotheses on the nature of the active species.

#### EXPERIMENTAL

The Cu/Zn/Al catalysts were prepared by putting a solution of the nitrates of the elements into a solution of NaHCO<sub>3</sub> at 333 K.

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The precipitates were washed until the sodium content was less than 0.02% (as Na<sub>2</sub>O), then dried at 363 K and calcined at 623 K for 24 h (24). XRD powder patterns were made with Ni-filtered CuK $\alpha$  radiation ( $\lambda = 0.15418$  nm) using a Philips goniometer equipped with a stepping motor and automated by means of a General Automation 16/240 computer. All the XRD powder patterns were made in air and, for the samples after reduction and/or reaction, after titration with N<sub>2</sub>O. Since most of the XRD patterns showed broad and strongly overlapped diffraction lines both phase composition and crystal size were determined by a profile-fitting method comparing the observed profiles with those computed according to Allegra and Ronca (25). The accuracy of this method is better than that of the Debye-Scherrer one, especially when many species are present, however, the precision is similar to that of the Debye-Scherrer method. Quantitative determinations of crystalline Cu and CuO were carried out according to the internal standard method of Chung (26), using SiO<sub>2</sub> quartz and TiO<sub>2</sub> anatase as internal standards.

The calcined precursors were reduced in the reactor by hydrogen diluted in nitrogen, increasing the hydrogen concentration pro-

gressively ( $0.01 < P_{H_2} < 0.15$  MPa) with the temperature in the range 373–573 K. The catalytic tests were performed operating at 1.2 MPa and 473–573 K, using 0.2–0.4 g of catalyst and a space velocity of 15,500–16,500 h<sup>-1</sup>. Two different gas mixtures were used: H<sub>2</sub>/CO/CO<sub>2</sub> = 65:32:3 (v/v) and H<sub>2</sub>/CO/CO<sub>2</sub> = 86:8:6 (v/v). The reaction products were analyzed in-line without condensation by gas chromatography using a Perkin-Elmer F30 gas chromatograph equipped with FID and two columns ( $\frac{1}{8}$ -in. diam.  $\times$  1.5-m long) and fitted with Poropack QS. After cooling at 273 K, the gases were analyzed by a Carlo Erba GT gas chromatograph equipped with TCD and two columns ( $\frac{1}{4}$ -in. diam.  $\times$  2-m long) and fitted with Carbosieve 80-120. The chromatographic data were collected and processed by a Perkin-Elmer Sigma 15 Data Station.

The surface area of the copper was determined *in situ* after reduction and reaction by the N<sub>2</sub>O pulse technique as reported in the literature (27–29); before measuring the surface area the samples were cooled at room temperature under a flow of oxygen-free helium. Tests on Al<sub>2</sub>O<sub>3</sub> and Zn/Al samples did not reveal decomposition or adsorption of N<sub>2</sub>O. The surface areas of the catalysts were determined by N<sub>2</sub> adsorption

TABLE I  
Crystal Sizes of ZnO and CuO (Before Reduction) and of Metallic Copper  
(after Reduction and Reaction)

Sample	Cu/Zn/Al (atomic ratio)	Crystal size (nm)					
		ZnO		CuO		Cu (after reaction)	
				Cu (after reduction)		Cu (after reaction)	
				XRD analysis	N <sub>2</sub> O pulse technique	XRD analysis	N <sub>2</sub> O pulse technique
Cat 1	25.3/50.7/24.0	6.0	4.0	4.5	3.8	4.5	11.8
Cat 2	38.0/38.0/24.0	4.6	3.0	3.5	12.5	4.0	22.0
Cat 3	50.7/25.3/24.0	2.5	6.0	10.0	12.4	10.0	18.4
Cat 4	60.8/15.2/24.0	2.6	7.5	12.5	12.7	13.0	17.8
Cat 5	30.0/60.0/10.0	7.0	3.6	5.0	7.2	5.5	9.8
Cat 6	45.0/45.0/10.0	7.0	6.0	5.0	7.0	4.5	11.3
Cat 7	60.0/30.0/10.0	6.0	6.0	10.0	10.6	10.0	17.1
Cat 8	34.5/34.5/31.0	1.5	1.5	2.5	11.2	3.5	27.0

TABLE 2  
Surface Area of the Catalysts and of the Copper,  
after Reduction and Reaction

Sample	Catalyst surface area <sup>a</sup> (m <sup>2</sup> g <sub>Cat</sub> <sup>-1</sup> )	Copper surface area <sup>b</sup> (m <sup>2</sup> g <sub>Cu</sub> <sup>-1</sup> )		B/A (%)
		(A) After reduction	(B) After reaction	
Cat 1	112	89	53	60
Cat 2	65	27	15	56
Cat 3	61	27	18	67
Cat 4	57	27	19	70
Cat 5	58	47	34	72
Cat 6	72	48	30	63
Cat 7	46	32	20	63
Cat 8	103	30	14	47

<sup>a</sup> Determined by N<sub>2</sub> adsorption (BET method).

<sup>b</sup> Determined by N<sub>2</sub>O pulse technique.

using a Carlo Erba Model 1800 Sorptomatic.

## RESULTS

### Characterization of the Catalysts after the Reduction and the Reaction Stages

The crystal sizes of the CuO before reduction and of the Cu after reduction and after the catalytic tests, calculated by XRD analysis are reported in Table 1. The table also shows the values of the crystallite dimensions of Cu calculated from the N<sub>2</sub>O decomposition using a spherical particles hypothesis. The ZnO crystallites were not modified after either the reduction or the reaction stage. The surface areas of the catalysts measured by N<sub>2</sub> adsorption and of metallic copper after reduction and after reaction measured by N<sub>2</sub>O decomposition are reported in Table 2. The values both of the surface area and of the crystal size after reaction with the two different gas mixtures were practically the same. It may be noted that the ratio between the two values of copper surface area is very similar for all the samples except the one with 31.0% aluminum.

Reported in Fig. 1 are the XRD powder patterns of the catalysts with 24.0% alumi-

num, discharged in air after reaction with the H<sub>2</sub>/CO/CO<sub>2</sub> = 86 : 8 : 6 (v/v) gas mixture and titration with N<sub>2</sub>O. The percentages of copper, referred to the nominal value, determined by XRD analysis as metallic copper and CuO, together with the undetected amounts are reported in Table 3. In the last column of this table the percentage solubility of copper in ZnO, calculated assuming that all the undetected copper was inside the ZnO, also is reported.

### Catalytic Tests

Table 4 reports the rate of methanol formation measured at 523 K for all the catalysts investigated and the two gas mixtures tested: the data have been expressed in different units in order to allow a comparison with the data reported in the literature. The table also shows the selectivity in methanol; in all the cases methane was the main by-product observed. The activity data expressed as kilograms of methanol per hour and liter of catalyst (the most interesting for industrial applications) are reported in Figs.

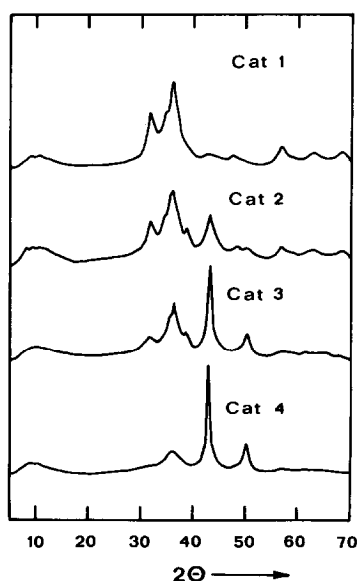


FIG. 1. XRD powder patterns of the catalysts with 24.0% aluminum, discharged in air after reaction with the H<sub>2</sub>/CO/CO<sub>2</sub> = 86 : 8 : 6 (v/v) gas mixture and titration with N<sub>2</sub>O.

TABLE 3

Percentages of Copper Detected in Different Forms by XRD (Undetected Copper Calculated by Difference) and Solubility of Copper Inside the ZnO (Calculated on the Basis of Undetected Copper Amount)

Sample	Percentage of copper as			Calculated solubility of copper in ZnO (%)
	Metallic	CuO	Not revealed	
Cat 1	53 <sup>a</sup>	—	47	19
	48 <sup>b</sup>	—	52	21
Cat 2	46	38	16	13
	51	33	16	13
Cat 3	56	35	9	15
	70	22	8	13
Cat 4	90	—	10	32
	90	—	10	32
Cat 5	20	25	55	22
	25	22	53	21
Cat 6	53	27	20	16
	35	46	19	15
Cat 7	50	35	15	24
	57	29	14	22
Cat 8	90	—	10	8
	87	—	13	10

<sup>a</sup> After reaction with H<sub>2</sub>/CO/CO<sub>2</sub> = 65 : 32 : 3 (v/v).

<sup>b</sup> After reaction with H<sub>2</sub>/CO/CO<sub>2</sub> = 86 : 8 : 6 (v/v).

2–4 as a function of the Cu/Zn ratio and of the aluminum content, for both the gas mixtures investigated.

DISCUSSION

Many features of the catalysts investigated are similar to those of the industrial

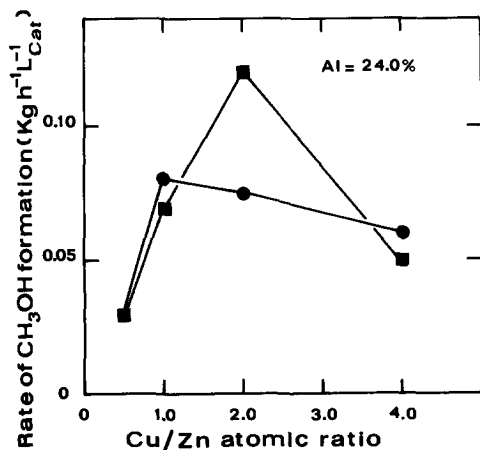


FIG. 2. Rate of methanol formation as a function of the Cu/Zn atomic ratio (Al 24.0%). (●) H<sub>2</sub>/CO/CO<sub>2</sub> = 86 : 8 : 6 (v/v); (■) H<sub>2</sub>/CO/CO<sub>2</sub> = 65 : 32 : 3 (v/v).

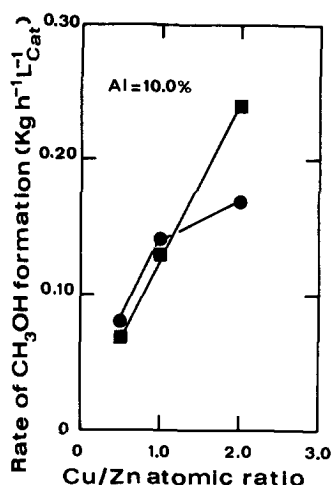


FIG. 3. Rate of methanol formation as a function of the Cu/Zn atomic ratio (Al 10.0%). (●) H<sub>2</sub>/CO/CO<sub>2</sub> = 86 : 8 : 6 (v/v); (■) H<sub>2</sub>/CO/CO<sub>2</sub> = 65 : 32 : 3 (v/v).

catalysts. The activity data extrapolated to 5.0 MPa (this extrapolation is possible as a first approximation since a first-order dependence of the reaction rate on the pressure was found) are comparable with the data reported in the literature (2, 3). Also the crystal sizes of Cu and ZnO are near to the values reported by Andrew as typical and stable catalysts (12).

From Table 4 it is possible to observe

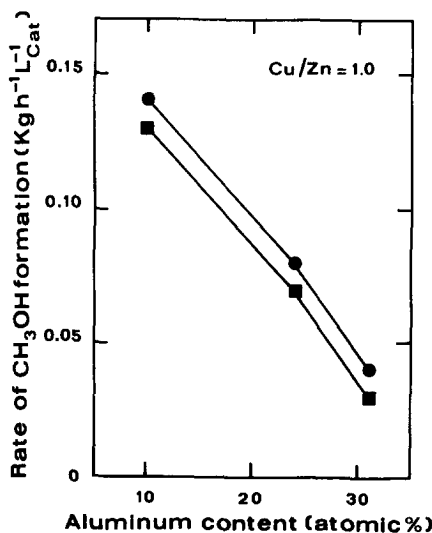


FIG. 4. Rate of methanol formation as a function of aluminum content (Cu/Zn = 1.0). (●) H<sub>2</sub>/CO/CO<sub>2</sub> = 86 : 8 : 6 (v/v); (■) H<sub>2</sub>/CO/CO<sub>2</sub> = 65 : 32 : 3 (v/v).

TABLE 4

Rate of Methanol Formation and Selectivity for the Two Different Tested Gas Mixtures

Sample	$H_2/CO/CO_2 = 86:8:6$ (v/v)					$H_2/CO/CO_2 = 65:32:3$ (v/v)				
	Selectivity (%)	Rate of methanol formation				Selectivity (%)	Rate of methanol formation			
		$kg\ h^{-1}\ kg_{Cat}^{-1}$	$kg\ h^{-1}\ kg_{Cu}^{-1}$	$kg\ h^{-1}\ m_{Cu}^{-2}$			$kg\ h^{-1}\ kg_{Cat}^{-1}$	$kg\ h^{-1}\ kg_{Cu}^{-1}$	$kg\ h^{-1}\ m_{Cu}^{-2}$	
Cat 1	>99.9	0.06	0.20	0.02 <sup>a</sup>	0.04 <sup>b</sup>	98.6	0.06	0.20	0.02 <sup>a</sup>	0.04 <sup>b</sup>
Cat 2	>99.9	0.18	0.42	0.16	0.28	98.8	0.16	0.37	0.14	0.25
Cat 3	99.8	0.14	0.24	0.09	0.13	99.4	0.22	0.39	0.14	0.21
Cat 4	99.8	0.11	0.16	0.06	0.08	99.1	0.10	0.14	0.05	0.07
Cat 5	99.7	0.19	0.61	0.13	0.17	99.5	0.18	0.57	0.12	0.17
Cat 6	99.5	0.35	0.75	0.16	0.25	99.7	0.34	0.72	0.15	0.24
Cat 7	99.0	0.36	0.57	0.18	0.28	99.8	0.49	0.78	0.25	0.40
Cat 8	99.7	0.11	0.26	0.09	0.19	99.7	0.09	0.21	0.07	0.15

<sup>a</sup> Referred to the copper surface area after reduction.<sup>b</sup> Referred to the copper surface area after reaction.

that the selectivity in methanol is higher than 98.0% for all the catalysts investigated, however, higher values were obtained with the catalysts with 24.0% aluminum and the  $H_2/CO/CO_2 = 86:8:6$  (v/v) mixture, while a lower selectivity was obtained with the same catalysts using the  $H_2/CO/CO_2 = 65:32:3$  (v/v) mixture.

From Figs. 2 and 3 it can be seen that the scale of activity for the different catalysts depends mainly on the gas mixture, the differences being more evident for the  $H_2/CO/CO_2 = 65:32:3$  (v/v) composition, similar to that used in many scientific papers. For both gas mixtures, the activity strongly decreases with increasing aluminum content (Fig. 4). The same behavior was observed for the other Cu/Zn ratios when the aluminum content was raised from 10.0 to 24.0%. This inhibitive effect is similar to that reported by Shimomura *et al.* (11), while other authors observed either no effect (2) or a promoting effect (30). These results show that the catalysts obtained from pure hydrotalcite-like precursors are less active than those obtained from mixed precursors.

In order to give some insights on the role of the different parameters on the catalytic behavior of the copper, the activity per kilogram and square meter of copper will be discussed in the following sections.

### The Role of Aluminum

The data in Table 4 illustrate the inhibitive effect of aluminum on the copper. In fact, for all the Cu/Zn ratios studied, the activity per kilogram of copper decreases with increasing aluminum content. On the basis of the activity per square meter of copper, this inhibitive property of aluminum may be attributed both to a decrease in copper reactivity (compare Cat 1 and 5, 3 and 7, 2 and 8) or to a decrease in surface area (compare Cat 2 and 6).

The lower activity of the copper in the catalysts obtained from hydrotalcite-like precursors can be related to the presence of all the elements in the same structure, which after calcination gives rise to a strong interaction, changing their activity. This interaction also is responsible for the destruction of the alumina acidity. In fact, also for the catalyst with 31.0% aluminum, the dimethyl ether was practically absent as a by-product.

### The role of the Cu/Zn Ratio

The effect of this parameter is more complex and its influence on the copper activity depends both on the gas composition and on the aluminum content. For the catalysts with 24.0% aluminum, a maximum of activ-

ity both per kilogram and square meter of copper was observed for the Cu/Zn ratio = 1.0 with the hydrogen-rich mixture, while with the other gas composition the maximum occurred in the Cu/Zn = 1.0–2.0 range.

A similar trend was observed for the catalysts with 10.0% aluminum on the basis of the activity per kilogram of copper, while for both the gas mixtures, the activity per square meter increased with the Cu/Zn ratio.

The low activity of Cat 1 that occurs in spite of the small crystal size and highest values of surface area should be noted.

From Table 1 it is possible to single out a stabilizing effect of zinc during the reduction. In fact, the catalysts with Cu/Zn = 1.0 have a copper crystal size (measured by XRD) similar to that of the starting CuO.

Further information on the nature of the active species may be obtained from the characterization of the spent catalysts.

#### *Nature of the Spent Catalysts*

The measurements of surface area show that after the catalytic tests only a part of the copper reacts with N<sub>2</sub>O, the percentage of copper surface area after reaction relative to that after reduction varies from 47 to 72% (Table 2). It is worth noting that the crystal sizes determined by XRD are practically the same for all the samples after both the treatments and similar values were obtained for the reduced catalysts both by XRD and N<sub>2</sub>O decomposition (Table 1). Furthermore, when the spent catalysts were reduced again, the starting values of copper surface area were obtained.

Therefore, this decrease may be attributed to the fact that during the reaction the catalysts are in a partially oxidized state. Evidence has been reported in the literature that the CO<sub>2</sub> can oxidize the copper to Cu(I) and then become strongly adsorbed on it, thus preventing further oxidation (16, 24, 31–33).

Three different copper-containing species were found in the spent catalysts by

XRD analysis: metallic copper, CuO, and undetected copper (the relative percentages are reported in Table 3). The metallic copper is the copper that after passivation by N<sub>2</sub>O during the surface area measurements is not reoxidized when kept in air. The fact that the crystal sizes of the copper determined by XRD are practically the same both after reduction and reaction indicates that this species is not influenced by the reaction mixture.

When the catalysts were kept in air, CuO was detected after the different steps (reduction, reaction, and titration with N<sub>2</sub>O). On the other hand, measurements in a thermobalance with a 2% hydrogen in nitrogen mixture, showed complete reduction to metallic copper for all the catalysts (34). Therefore, the CuO observed is formed only by oxidation in air and its amount must be considered a measure of a more oxidizable form of copper not stabilized by the reaction with N<sub>2</sub>O. The presence of species more easily reoxidizable also has been observed by other authors on the same type of catalysts by ESCA analysis (19–21).

The undetected copper is calculated as the difference between the theoretical value of copper and the sum of the metallic copper and CuO determined by XRD analysis. The amounts are different for the different catalysts, but the percentages referred to the ZnO present are near to the value of 15% claimed by Klier as the amount of copper dissolved inside the ZnO lattice (2, 16). The lower percentage for Cat 8 can be due to the higher amount of aluminum present that can decrease the available ZnO, very likely through the formation of ZnAl<sub>2</sub>O<sub>4</sub>. Some catalysts have higher values due to the fact that small amounts of CuO cannot be detected by XRD analysis, and therefore were computed as undetected copper.

All attempts to correlate the catalytic activity to only one of these copper species failed. It is easy to check this, observing for instance that the catalysts with large amounts of metallic copper or undetected copper are the less active. Also, no correla-

tion exists between the activity and the copper surface area, however, these results are not in contrast with those reported by Andrew (12); since in his case the correlation with the surface area was referred to catalysts with the same composition.

To interpret the catalytic behavior it is necessary to take into account both the amount of CuO and of undetected copper. Reported in Figs. 5a and b are two correlations of the catalytic activity per kilogram of catalyst, the first referred to the sum of CuO and undetected copper per kilogram of catalyst and the second to the product of CuO and undetected copper. In this last case, for Cat 1 and 4, for which no CuO could be detected by XRD analysis, the amount of CuO was calculated assuming that the excess of undetected copper with respect to the value of 15% reported by

Klier (2, 16) as the amount of copper which is held inside the ZnO lattice was due to CuO. This was not possible for Cat 8, but very probably as discussed above the higher amount of aluminum decreased the available ZnO.

The first correlation means that the two species have similar activities, while in the second they must both be present in order to have active catalysts. In our case, both these correlations are rather good and at this stage of the experiments it is not possible to discriminate between these two different hypotheses. In all cases, a high catalytic activity is correlated to the presence of a reactive form of copper and of copper inside and/or related to the ZnO. Therefore, it is worth noting that these results on the role of different copper containing species are in good agreement with the mechanism recently proposed by Henrici-Olivé and Olivé (35, 36).

#### CONCLUSION

During the synthesis of methanol at low temperature, the catalysts work in a partially oxidized state, probably due to the presence of CO<sub>2</sub> in the gas mixtures.

The choice of a particular Cu/Zn/Al ratio depends mainly on the gas mixture composition, but in all cases, aluminum in concentration higher than 10.0% inhibits the activity. The selectivity in methanol is always high, but the formation of by-products is lower for the catalysts with 24.0% aluminum and lower amounts of copper and the hydrogen rich mixture.

The catalytic activity is related to the amounts of different copper containing species, one easily reoxidizable to CuO and one related to the ZnO, but it was not possible to establish if these species have similar activities or must be present contemporaneously.

No data was obtained on the catalyst life, since the data recorded refer to about 50 h of reaction activity. However, the results show that the catalysts prepared from precursors rich in zinc or aluminum give rise to

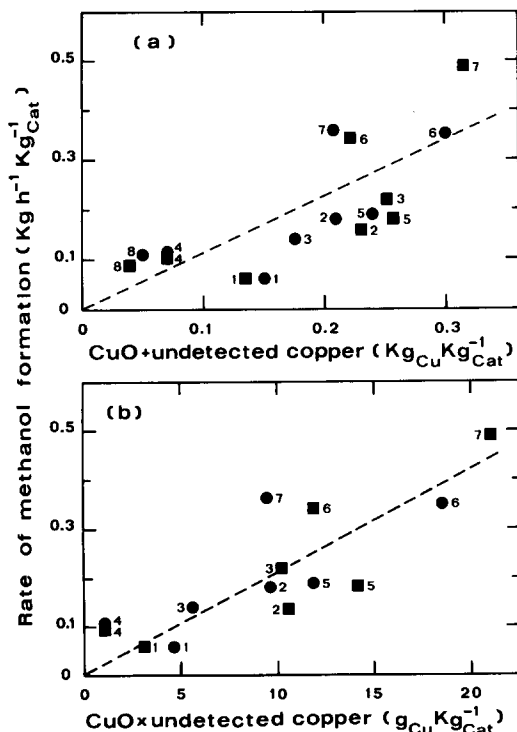


FIG. 5. Rate of methanol formation as a function of (a) the sum of CuO and undetected copper; (b) the product of CuO and undetected copper. (●) H<sub>2</sub>/CO/CO<sub>2</sub> = 86:8:6 (v/v); (■) H<sub>2</sub>/CO/CO<sub>2</sub> = 65:32:3 (v/v); the numbers refer to the catalysts of Table 1.

copper with a very small and stable crystal size.

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