JOURNAL OF CATALYSIS **169,** 447–454 (1997)
ARTICLE NO. CA971719

Vapor-Phase Dehydrocoupling of Methanol to Methyl Formate over $CuAl_2O_4$

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Received October 30, 1996; revised April 6, 1997; accepted April 7, 1997

$CuO-Al_2O_3$ systems with different Cu/Al ratios were prepared by the amorphous citrate process, and their catalytic activities for the dehydrocoupling of methanol to methyl formate were examined. In the $CuO-Al_2O_3$ systems, $CuAl_2O_4$ samples calcined at temperatures below 1000°C were partially reduced during the reaction at 310°C and decreased the selectivity to methyl formate (MF) with increasing Cu(0) content. Cu(0) species catalyzed the dehydrocoupling reaction without decomposition of methyl formate at temperatures below 210°C, whereas Cu(0) decomposed methyl formate into methanol and CO above 210°C. On the other hand, $CuAl_2O_4$ calcined at 1100°C showed the highest activity of the formation of methyl formate at a reaction temperature of 310°C. Since the $CuAl_2O_4$ sample was not reduced even at 310°C, Cu(II) species in the $CuAl_2O_4$ were found to be effective sites for the dehydrocoupling at temperatures above 250°C. In addition, Cu(I) species in $CuAlO_2$ was also found to be active with keeping high MF selectivity up to 290°C. © 1997 Academic Press

INTRODUCTION

Methyl formate (MF) was produced via the process of the dehydrocoupling of methanol (MeOH) catalyzed by copper-containing catalysts; MF was produced in about 50% yield with MeOH conversions above 60% at 320°C in patent literature (1, 2). MeOH dehydrogenation was performed at a temperature range of 170–350°C, and copper is known to be a catalyst species for selective production of MF (3–16). Transition metals other than Cu, however, decompose MeOH into CO or methane (3). A mechanism of MF formation over supported Cu catalysts has been proposed; formaldehyde or formyl species adsorbed on Cu metal surface is an intermediate of MF formation (13–16). However, no definite conclusions about active copper species for the dehydrocoupling of MeOH have yet been reached. Which kind of copper species, Cu(0) or Cu(II), is effective? Morikawa *et al.* (3–6) found that Cu(II) species in fluoro tetrasilicic mica produces MF with high efficiency, whereas other research groups (7–12) have reported that copper metal of 0 valency plays a significant role among active sites in the formation of MF.

Amorphous citrate process is proposed by Marcilly *et al.* (17) as a preparation method of ceramics powder and is applied to the preparations of various fine ceramics with high crystallinity (18, 19). In the citrate process, a melt containing citric acid and the respective metal salts is decomposed to give homogeneous metal oxides. The citrate process is also applied to prepare solid catalysts such as perovskite-type (10, 20–23) and spinel-type composite oxides (24–26). In addition, Patrick and Gavalas (19) reported that a crystalline $CuAl_2O_4$ was available from the process. Cu(II) species are also reported to be stable in $CuO-Al_2O_3$ mixed oxide systems (27, 28).

In this paper, we will describe the physical and catalytic properties of $CuO-Al_2O_3$ systems, particularly $CuAl_2O_4$, prepared by the amorphous citrate process. In addition, we will discuss whether Cu(0) or Cu(II) is effective for the MeOH dehydrocoupling reaction.

EXPERIMENTAL

$CuO-Al_2O_3$ samples with different copper contents were prepared according to a method which is essentially same as that reported by Patrick and Gavalas (19). After a mixture of copper (II) nitrate trihydrate and aluminum nitrate nonahydrate with a desired ratio together with citric acid monohydrate equimolar to the sum of copper and aluminum ions was dissolved at 70°C in a small amount of water (less than 20 cm^3 of water with respect to 240 mmol of citric acid in a 1000 cm^3 flask), the solution was evacuated under a pressure of 0.7 kPa at 70°C in a rotary evaporator. The solution was gradually solidified, and then a blue foam was formed: the apparent volume of the foam was expanded into about 20-fold of the solution volume during the course of evaporation. The resulting foam was broken up and calcined in air at a prescribed temperature (600–1100°C) for 4 h to give a $CuO-Al_2O_3$ sample.

Another $CuO-Al_2O_3$ sample was prepared by a dry mixing method; powders of CuO and Al_2O_3 with a Cu/Al molar

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0021-9517/97 $25.00

ratio of 1/2 were mixed by using mortar and pestle. After the resulting mixture had been pelletized under a pressure of 200 kg cm^{-2}, it was calcined in air at a prescribed temperature for 4 h.

The dehydrocoupling of MeOH to MF was performed in the usual fixed bed-flow reactor at a prescribed reaction temperature at the MeOH feed rate of 128 mmol h^{-1} with helium flow of 88 mmol h^{-1}. Before each catalytic test, the catalyst sample (0.70 g) was preheated at the same temperature as the catalytic process in helium flow for 2 h. In the case where the catalyst sample was required for reduction treatment, the sample was reduced at 450°C for 2 h with hydrogen flow of 88 mmol h^{-1}, prior to the MeOH feed. The catalytic activity was evaluated in terms of the consumption of MeOH at the steady state after MeOH had been fed for 30 min. MeOH was converted into MF, CO, CO_2, and dimethyl ether (DME) over the $CuO-Al_2O_3$ catalysts.

MeOH consumption rate, R_{MeOH}, is expressed as

$$R_{\mathrm{MeOH}} = 2 * R_{\mathrm{MF}} + R_{\mathrm{CO}} + R_{\mathrm{CO_2}} + 2 * R_{\mathrm{DME}},$$

where R_{MF}, R_{CO}, $R_{\mathrm{CO_2}}$, and R_{DME} are the formation rates of MF, CO, CO_2, and DME, respectively.

Conversion of methanol, X_{MeOH}, is calculated as

$$X_{\mathrm{MeOH}} = R_{\mathrm{MeOH}}/F_{\mathrm{MeOH}},$$

where F_{MeOH} is the flow rate of MeOH.

Selectivities to MF, CO, CO_2, and DME (S_{MF}, S_{CO}, $S_{\mathrm{CO_2}}$, and S_{DME}, respectively) are calculated using the equations

$$S_{\mathrm{MF}} = 2 * R_{\mathrm{MF}}/R_{\mathrm{MeOH}}, \quad S_{\mathrm{CO}} = R_{\mathrm{CO}}/R_{\mathrm{MeOH}},$$
$$S_{\mathrm{CO_2}} = R_{\mathrm{CO_2}}/R_{\mathrm{MeOH}}, \quad \text{and} \quad S_{\mathrm{DME}} = 2 * R_{\mathrm{DME}}/R_{\mathrm{MeOH}}.$$

The decomposition of MF was also tested under the same reaction conditions as the dehydrocoupling of MeOH; MF was fed at a feed rate of 84 mmol h^{-1} over the catalyst of 0.70 g in a helium flow of 88 mmol h^{-1}.

The total surface area of a sample was measured by BET method using nitrogen isotherm at −196°C. Copper metal surface area was measured by pulse-titration method using N_2O decomposition at 90°C (29): N_2O (0.44 cm^3) was injected onto a sample (0.5 g) reduced at a prescribed temperature, and the produced N_2 was recorded by using thermal conductivity detector (TCD) after N_2 had been separated from N_2O in a column of Porapak Q. An XRD spectrum of the sample was recorded by Rigaku Geigerflex at room temperature. A temperature-programmed reduction (TPR) spectrum was recorded by monitoring H_2 consumption using TCD; a catalyst sample (0.01 g) was heated from 100 to 850°C at a rate of 3 K min^{-1} in a H_2/N_2 (1/9) flow of 24 mmol h^{-1}. During the TPR measurement, produced water was removed through a column of dried molecular sieve 13× which was placed between the sample and the TCD.

RESULTS

Catalytic and Physical Properties of $CuO-Al_2O_3$ with Various Cu/Al Ratios

The catalytic activities of $CuO-Al_2O_3$ calcined at 1100°C for the dehydrocoupling of MeOH varied with both copper content and reaction temperature (Table 1). At a reaction temperature of 270°C, every catalyst sample converted MeOH to MF with high selectivities. At 310°C, MeOH was converted to MF with high conversions and relatively high selectivities over the $CuO-Al_2O_3$ samples at the Cu/Al ratios of 1/2 and 1/3. Although a sample at the Cu/Al ratio of 1/1 had low MeOH conversion, the selectivity to MF was over 98% even at 310°C. The sample, however, lost its catalytic activity above 330°C: only 0.6% of MeOH was converted into MF with 100% selectivity at 330°C. At the Cu/Al ratio of 1/10, the sample showed low conversions of MeOH with moderate selectivities to MF at 310°C.

The total surface areas of the samples calcined at 1100°C were smaller than 5 m^2 g^{-1}; the surface areas were 1.8, 3.9, 4.9, and 2.8 m^2 g^{-1} at the Cu/Al ratios of 1/1, 1/2, 1/3, and 1/10, respectively. Specific catalytic activities based on the total surface areas of these samples for the MF formation are also shown in Table 1. At reaction temperatures of 270 and 310°C, the sample with the Cu/Al ratio of 1/2 was most active for MF formation. In addition, the Cu metal surface areas of all the samples were practically zero from the experimental results in the pulse-titration method using N_2O decomposition, even after they had been contacted with H_2 at 310°C for 2 h.

Figure 1 illustrates XRD patterns of the $CuO-Al_2O_3$ samples calcined at 1100°C. A sample at the Cu/Al ratio of 1/1 consisted essentially of $CuAlO_2$ (Fig. 1d). In a

TABLE 1

Catalytic Properties of $CuO-Al_2O_3$ with Different Cu/Al Ratios

Cu/Al	Reaction temperature (°C)	Conversion[a] of methanol (%)	Selectivity[b] (mol%)				Formation[c] rate of MF (mmol h^{-1} m^{-2})
			MF	CO	CO_2	DME	
1/1	270	10.5	100	0	0	0	5.3
1/2	270	26.2	95.4	4.6	0	0	5.9
1/3	270	22.8	94.8	2.0	1.0	2.2	4.0
1/10	270	3.8	100	0	0	0	1.3
1/1	310	7.7	98.9	1.1	0	0	3.8
1/2	310	63.6	57.0	15.9	6.8	20.3	8.5
1/3	310	55.5	67.6	14.0	5.1	13.3	7.0
1/10	310	18.9	78.9	8.6	3.8	8.7	3.0

[a] Conversion of methanol at the prescribed temperature at the MeOH feed rate of 128 mmol h^{-1} over the catalyst of 0.7 g.

[b] Selectivities to the respective products: MF, methyl formate; DME, dimethyl ether.

[c] Formation rate of methyl formate. The samples used for the catalytic tests were calcined at 1100°C for 3 h.

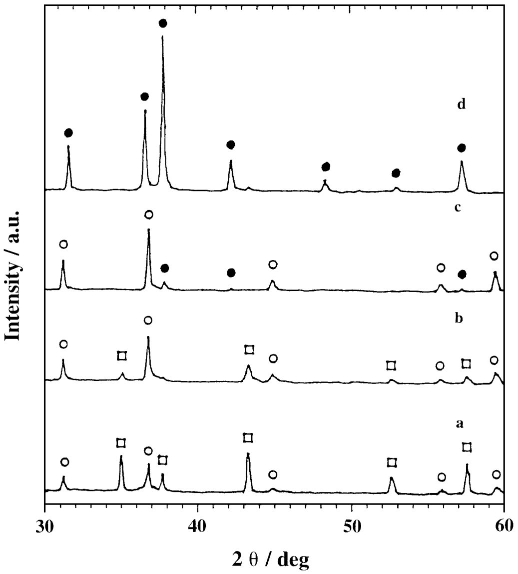

FIG. 1. XRD patterns of $CuO-Al_2O_3$ calcined at 1100°C. a, Cu/Al = 1/10; b, 1/3; c, 1/2; d, 1/1. ○, $CuAl_2O_4$; ●, $CuAlO_2$; △, CuO; ▲, Cu; ■, γ-Al_2O_3; □, α-Al_2O_3.

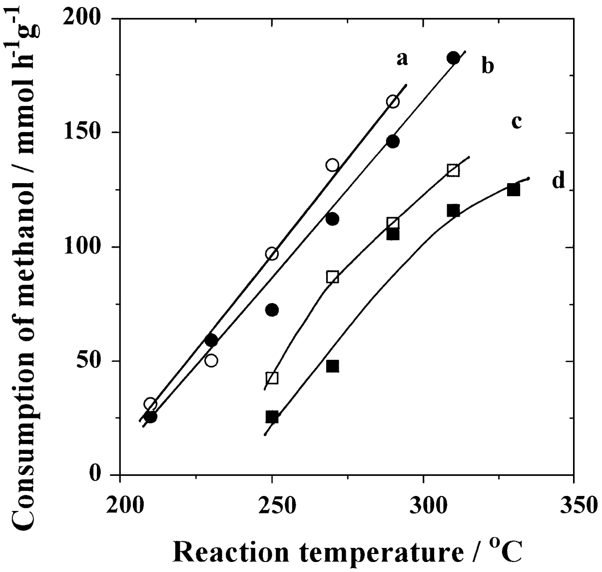

FIG. 3. Variations in consumption rate of methanol with reaction temperature over $CuAl_2O_4$ calcined at different temperatures. a, Calcined at 600°C; b, 900°C; c, 1000°C; d, 1100°C.

sample at the Cu/Al ratio of 1/2, $CuAl_2O_4$ was dominant with a small peak of $CuAlO_2$ (Fig. 1c). Samples at the Cu/Al ratios of 1/3 and 1/10 consisted of a mixture of $CuAl_2O_4$ and α-Al_2O_3 (Figs. 1b and 1a). In addition, XRD patterns of the catalysts calcined at 1100°C were entirely unchanged even after they had been used for the dehydrocoupling reaction of MeOH at 310°C.

Figure 2 shows TPR spectra of the $CuO-Al_2O_3$ samples calcined at 1100°C. $CuAlO_2$ (Cu/Al = 1/1) started to reduce at 650°C, and a sharp reduction peak was observed at 720°C (Fig. 2d). $CuAl_2O_4$ (Cu/Al = 1/2) was reduced at above 400°C and had two reduction peaks at around 450 and 700°C (Fig. 2c). In addition to these samples, the other samples were not reduced at temperatures below 400°C (Figs. 2a and 2b).

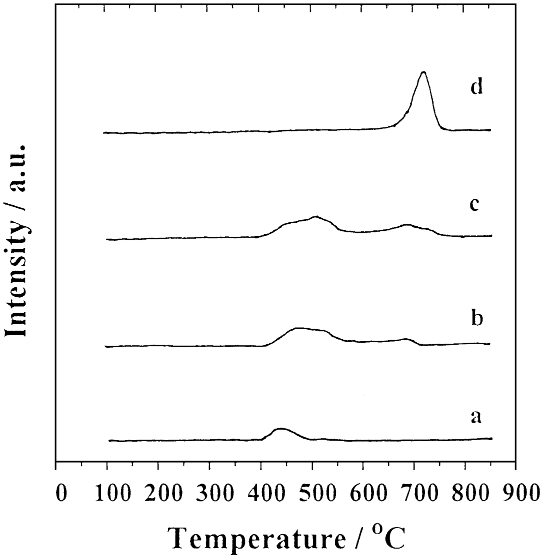

FIG. 2. TPR spectra of $CuO-Al_2O_3$ calcined at 1100°C. a–d, Same as in Fig. 1.

Catalytic Properties of $CuAl_2O_4$

Since the $CuAl_2O_4$ (Cu/Al = 1/2) sample has the highest MF formation activity in the $CuO-Al_2O_3$ systems, the effect of calcination temperatures on the catalytic activities of the sample was examined. Figures 3 and 4 exhibit variations in MeOH consumption rate and in MF formation rate with reaction temperature, respectively. The MeOH consumption rate increased monotonically with an elevation in the reaction temperature, and the curves were shifted to the high temperature side when the calcination temperature of the sample rose (Fig. 3). The variations in MF formation rate showed maxima at different reaction temperatures (Fig. 4). With increasing calcination temperature of the sample, the maximum MF formation rate was increased, and the reaction temperature at which the maximum rate appeared rose. For an example of the sample calcined at 900°C, the maximum MF formation rate was attained at 250°C; the selectivity to CO increased from 21 to 31% upon elevating the reaction temperature from 250 to 310°C; at the same time selectivity to dimethyl ether also increased from 0 to 50% (Table 2). On the other hand, for $CuAl_2O_4$ calcined at 1100°C, the MF formation rate was maximized at 310°C; CO selectivity decreased from 16 to 11% upon elevating the reaction temperature from 310 to 330°C, while DME selectivity increased from 20 to 59%. Figure 5 illustrates

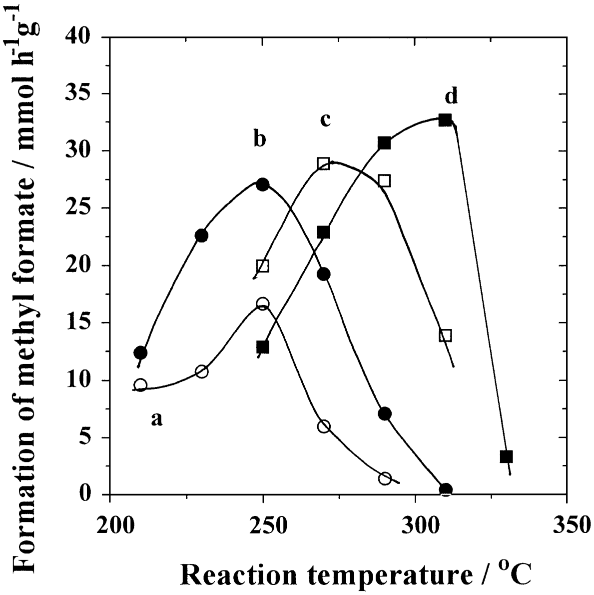

FIG. 4. Variations in formation rate of methyl formate with reaction temperature over $CuAl_2O_4$ calcined at different temperatures. a–d, Same as in Fig. 3.

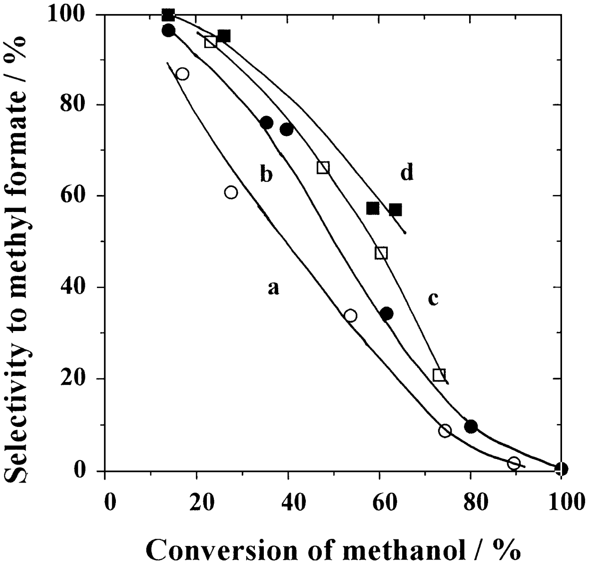

FIG. 5. Relation between MeOH conversion and MF selectivity over $CuAl_2O_4$ calcined at different temperatures. a–d, Same as in Fig. 3.

the qualitative relationship between MeOH conversion and MF selectivity for the data measured at temperatures lower than 330°C. The conversion–selectivity correlation, which was represented with a downward curve, was shifted to the high selectivity side when the calcination temperature of the sample rose.

The product distributions at 250 and 310°C are summarized in Table 2. For the samples calcined at temperatures other than 600°C, MeOH was converted into MF with high selectivities at 250°C (Table 2, second, third, and fourth rows). Even at a high temperature of 310°C, a major product was MF over the $CuAl_2O_4$ sample calcined at 1100°C, and maximum MF formation rate with MeOH conversion of 64% and MF selectivity of 57% was attained at 310°C (eighth row of Table 2). In contrast, for the sample calcined at 600°C, DME was a major product even at a low temperature of 250°C (Table 2, first row). For the sample calcined at 900°C, CO selectivity was more than 20% at 250°C (Table 2, second row), and MeOH was completely converted into CO, CO_2, and DME at 310°C (Table 2, sixth row). As the calcination temperature of the sample had been lowered, the selectivities to by-products such as CO, CO_2, and DME became progressively higher at reaction temperatures of both 250 and 310°C.

Table 3 summarizes the physical properties of $CuAl_2O_4$ calcined at different temperatures. Both the total surface

TABLE 2

Catalytic Properties of $CuAl_2O_4$ Calcined at Different Temperatures

Calcination (°C)	Reaction temperature (°C)	Conversion[a] of methanol (%)	Selectivity[b] (mol%)				Formation[c] rate of MF (mmol h^{-1} g^{-1})
			MF	CO	CO_2	DME	
600	250	53.7	33.8	13.5	14.0	38.8	16.6
900	250	39.8	74.6	20.8	4.6	0	27.1
1000	250	23.3	94.1	5.9	0	0	20.1
1100	250	14.0	100	0	0	0	12.8
600	310	100	0	15.2	21.4	63.3	0
900	310	100	0.4	31.2	18.0	50.4	0.4
1000	310	73.1	20.8	31.4	8.1	39.7	13.9
1100	310	63.6	57.0	15.9	6.8	20.3	33.1

[a] Conversion of methanol at the prescribed temperature at the MeOH feed rate of 128 mmol h^{-1} over the catalyst of 0.7 g.

[b] Selectivities to the respective products: MF, methyl formate; DME, dimethyl ether.

[c] Formation rate of methyl formate.

TABLE 3

Physical Properties of $CuAl_2O_4$ Calcined at Different Temperatures

Calcination temperature (°C)	Total SA[a] (m^2 g-cat.$^{-1}$)	Cu SA[b] (m^2 g-cat.$^{-1}$)	MF decomposition[c] (%)
600	80	4.6	100
900	6.2	4.3	—
1000	5.6	3.5	60.6
1100	3.9	0	6.7

[a] Total surface area of the unreduced sample was measured by BET method.

[b] Cu metal surface area of the sample reduced at 310°C for 2 h was calculated from the amount of N_2 produced during N_2O titration at 90°C.

[c] Conversion of methyl formate in another catalytic test in which the decomposition reaction of methyl formate was carried out at 310°C at a methyl formate feed rate of 84 mmol h^{-1} over the catalyst of 0.70 g.

area of the samples and the Cu surface areas of the samples reduced at 310°C decreased when the calcination temperature rose. Although the sample calcined at 1100°C had no Cu metallic surface, the other samples calcined at temperatures lower than 1100°C had metallic surfaces. Table 3 also shows the results of catalytic tests on the decomposition of MF at 310°C. For the sample catalyst calcined at 600°C, MF was completely decomposed into CO, CO_2, and DME, with compositions of 28, 19, and 53%, respectively. The MF decomposition activity decreased when the calcination temperature of the sample rose; only 6.7% of MF was decomposed over the $CuAl_2O_4$ sample calcined at 1100°C. Additionally, we observed the following facts: even at a low temperature of 230°C for the sample calcined at 600°C, 20.3% of MF was decomposed into MeOH, CO, CO_2, and DME, with compositions of 21, 29, 36, and 14%, respectively, while only 0.9% of MF was decomposed over $CuAl_2O_4$ calcined at 1100°C.

Moreover, we surveyed the reduction effect of catalyst samples with H_2 upon their catalytic activities. As an example of the results, Fig. 6 shows the case of the sample calcined at 1000°C. The sample reduced with H_2 at 450°C for 2 h exhibited the catalytic activities for the dehydrocoupling at temperatures lower than those of the nonreduced sample. The reduced catalyst showed a maximum MF formation rate at 210°C (Fig. 6b); 26.5% of MeOH was converted into MF, CO, CO_2, and DME, with selectivities of 29, 0, 20, and 50%, respectively. At 250°C, MF selectivity was only 1% at MeOH conversion of 70.4%. In contrast, the nonreduced sample showed a maximum MF formation rate at 270°C (Fig. 6d); 47.8% of MeOH was converted into MF, CO, CO_2, and DME, with selectivities of 66, 17, 4, and 13%, respectively. After reduction with H_2 at 450°C, the sample had a Cu metal surface area of 2.0 $m^2 g^{-1}$.

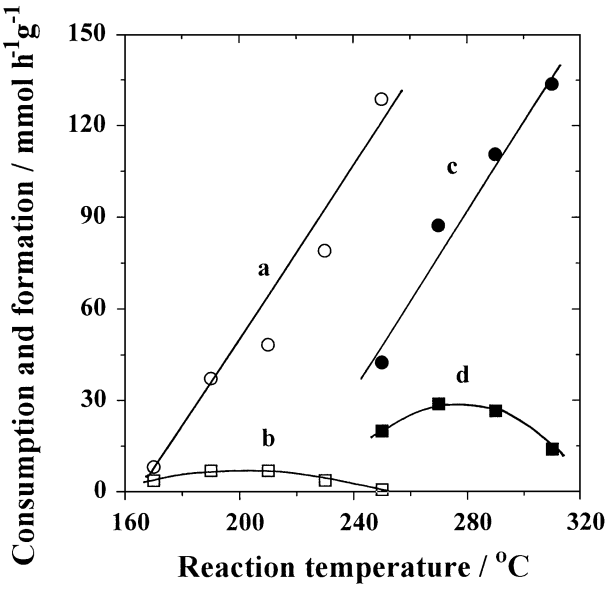

FIG. 6. Effect of the reduction of the sample upon its catalytic activities. Catalyst, $CuAl_2O_4$ calcined at 1000°C. a and b, Sample was reduced at 450°C for 2 h prior to the reaction; c and d, without reduction; a and c, consumption of methanol; b and d, formation of methyl formate.

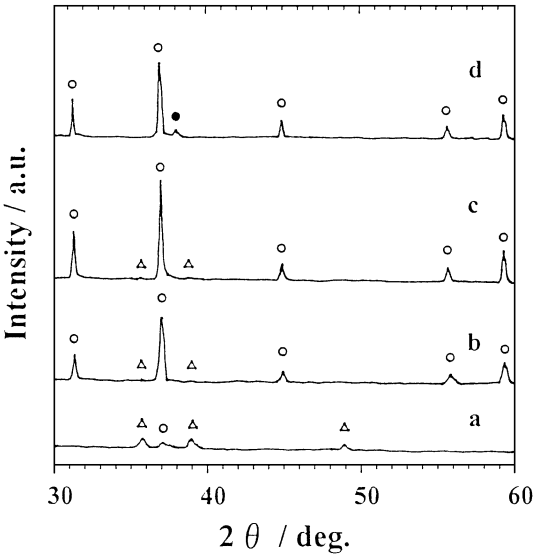

FIG. 7. XRD patterns of $CuAl_2O_4$ calcined at different temperatures. a, Calcined at 600°C; b, 900°C; c, 1000°C; d, 1100°C. Symbols same as in Fig. 1.

Characterization of $CuAl_2O_4$ Catalyst

Figure 7 illustrates XRD patterns of $CuAl_2O_4$ calcined at different temperatures. The sample calcined at 600°C consisted of CuO and $CuAl_2O_4$ (Fig. 7a). By elevating the calcination temperature of the sample, intensities of the diffraction peaks of $CuAl_2O_4$ increased and those of CuO peaks decreased (Figs. 7b and 7c). At the calcination temperature of 1100°C, CuO peaks disappeared and $CuAlO_2$ peaks appeared in addition to the predominant $CuAl_2O_4$ peaks (Fig. 7d). Figure 8 illustrates XRD patterns of $CuAl_2O_4$ after it has been used for the dehydrocoupling reaction at 310°C. The sample calcined at 1100°C did not change in XRD patterns after it had been used for the reaction (Fig. 8d), whereas the samples calcined at 600 and 900°C had Cu peaks (Figs. 8a and 8b). Although small Cu peaks were observed even at the calcination temperature of 1000°C, the sample had strong Cu peaks together with γ-alumina after being reduced by H_2 at 450°C for 2 h (Fig. 8c).

Figure 9 shows TPR spectra of the samples calcined at different temperatures. Reduction peaks shifted to the higher temperature side when the calcination temperature rose. The sample calcined at 600°C started to reduce at 170°C and was completely reduced below 400°C (Fig. 9a). The sample calcined at 900°C was partially reduced at 170°C, and a major part of reduction was subsequently observed at 400°C (Fig. 9b). Even when the sample was calcined at 1000°C, a sharp reduction peak was observed at 400°C (Fig. 9c). In

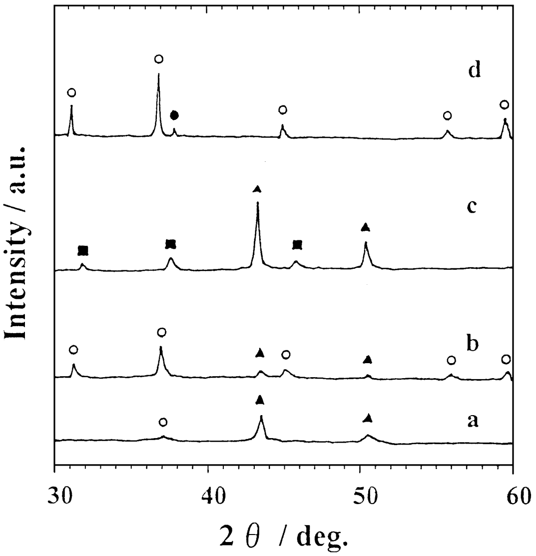

FIG. 8. XRD patterns of $CuAl_2O_4$ after used for the reaction at 310°C. a, Calcined at 600°C; b, 900°C; d, 1100°C; c, a sample calcined at 1000°C was reduced at 450°C prior to the reaction. Symbols same as in Fig. 1.

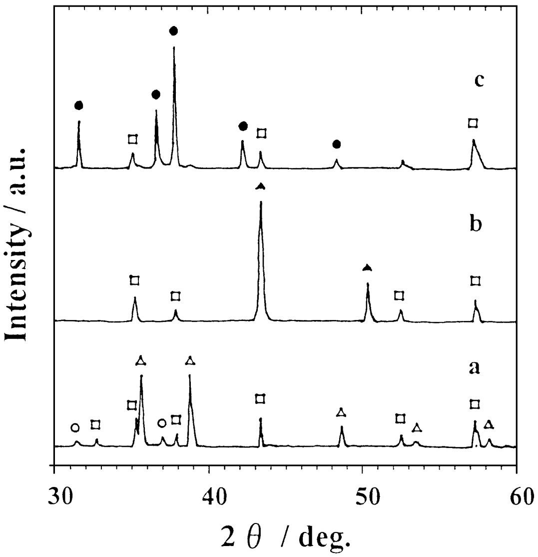

FIG. 10. XRD patterns of $CuAl_2O_4$ prepared by dry method. a, Calcined at 1000°C; b, after sample a had been used for the reaction at 310°C; c, a sample calcined at 1100°C. Symbols same as in Fig. 1.

contrast, the sample calcined at 1100°C was gradually reduced above 400°C and had two reduction peaks at around 450 and 700°C (Fig. 9d).

Comparison with a Reference $CuO-Al_2O_3$ Sample

For comparison with the sample prepared by the citrate process, a $CuO-Al_2O_3$ sample at Cu/Al ratio of 1/2 was prepared by the dry mixing method. Figure 10 shows XRD patterns of $CuO-Al_2O_3$ prepared by the dry mixing method. The sample calcined at 1000°C (Fig. 10a) showed strong CuO peaks, and the oxide was readily reduced during the course of catalytic reaction with MeOH at 310°C (Fig. 10b). In the catalytic test at 310°C, the sample showed low activity with MeOH conversion of 9.1% and MF selectivity of 87.0%. Although the dry-method sample calcined at 1100°C was dominated by $CuAlO_2$ together with α-Al_2O_3 (Fig. 10c), it showed a low activity at 310°C: MeOH conversion, 0.2%; MF selectivity, 100%.

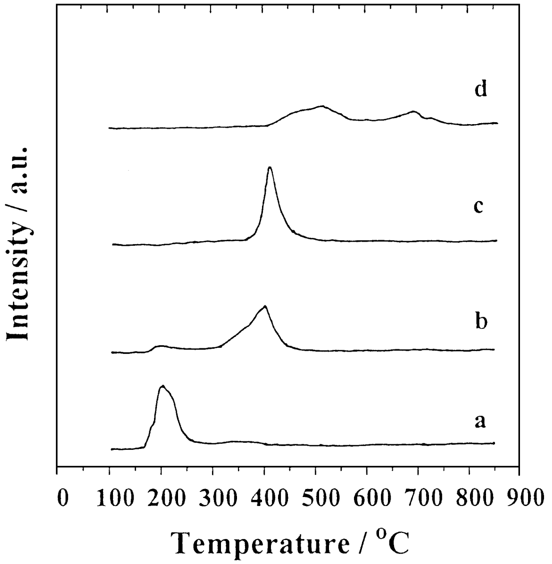

FIG. 9. TPR spectra of $CuAl_2O_4$ calcined at 1100°C. a–d, Same as in Fig. 3.

Comparison among Different Valences of Cu Species in $CuO-Al_2O_3$

Table 4 summarizes specific catalytic activities of the $CuO-Al_2O_3$ samples with different valence of Cu species. In the $CuO-Al_2O_3$ systems, $CuO-Al_2O_3$ (Cu/Al = 1/2) calcined at 900°C, $CuAlO_2$ calcined at 1100°C, and $CuAl_2O_4$ calcined at 1100°C are shown as the representatives of Cu(0), Cu(I), and Cu(II), respectively. Cu(0) species was active even at a low temperature of 210°C for the dehydrocoupling of MeOH to MF and showed a maximum at 250°C. Cu(I) and Cu(II) were effective for the MF formation at temperatures higher than 250°C.

DISCUSSION

$CuO-Al_2O_3$ with Various Cu/Al Ratios

The XRD results of the samples calcined at 1100°C (Figs. 1d and 1c) clarify that the $CuO-Al_2O_3$ at Cu/Al ratios of 1/1 and 1/2 consist of $CuAlO_2$ and $CuAl_2O_4$, respectively. As is shown in Table 1, the catalytic activities of the samples for the dehydrocoupling of MeOH varied

TABLE 4

Comparison among Different Valences of Cu Species in $CuO-Al_2O_3$ Samples

Valence of Cu ($SA^a/m^2\ g^{-1}$)	MF formation^b/mmol h^{-1} m^{-2} (selectivity^c/%)					
	210°C	230°C	250°C	270°C	290°C	310°C
0^d (6.2)	2.0(96.6)	3.6(76.1)	3.8(74.6)	3.1(34.3)	1.1(9.7)	0.1(0.4)
I^e (1.8)	—	3.1(100)	4.9(100)	5.3(100)	5.6(100)	3.8(98.9)
II^f (3.9)	—	—	3.3(100)	5.9(95.4)	7.9(57.3)	8.5(57.0)

[a] Total surface area of the unreduced sample was measured by BET method.

[b] Formation rate of methyl formate at the prescribed temperature at the MeOH feed rate of 128 mmol h^{-1} over the catalyst of 0.7 g.

[c] Selectivity to methyl formate.

[d] $CuAl_2O_4$ calcined at 900°C.

[e] $CuAlO_2$ calcined at 1100°C.

[f] $CuAl_2O_4$ calcined at 1100°C.

with copper content. In the $CuO-Al_2O_3$, the $CuAlO_2$ was active for the selective MF formation. Although its activity increased when the reaction temperature rose to 290°C (Table 4, second row), $CuAlO_2$ was inactive above 330°C: most of the fed MeOH was recovered at 330°C. In contrast, the $CuAl_2O_4$ catalyst decomposed MeOH above 330°C. We have no explanation for the decrease in MeOH conversion over $CuAlO_2$ at higher temperatures. On the other hand, at high alumina contents, MF formation activity was decreased with decreasing with copper content, while the intensities of α-alumina phase in the XRD spectra were increased (Fig. 1).

The results of TPR (Fig. 2) of the $CuO-Al_2O_3$ samples calcined at 1100°C elucidate that $CuAlO_2$ and $CuAl_2O_4$ were hardly reduced at reaction temperatures lower than 310°C. This is consistent with the findings that both the $CuAlO_2$ and $CuAl_2O_4$ samples calcined at 1100°C had Cu metal surface area of 0 $m^2\ g^{-1}$. In addition, the catalytic activities were unchanged during the course of reaction at 310°C. Thus, it can be said that both Cu(I) species of $CuAlO_2$ and Cu(II) of $CuAl_2O_4$ are active sites for the reaction.

Characterization of $CuAl_2O_4$ Catalyst

In the $CuO-Al_2O_3$ samples calcined at 1100°C, it is obvious that the $CuAl_2O_4$ sample was most active for MF formation (the last column of Table 1). The XRD patterns of $CuO-Al_2O_3$ (Cu/Al = 1/2) calcined at different temperatures (Fig. 7) clearly show that the formation of $CuAl_2O_4$ is completed at 1100°C. The other catalysts calcined at temperatures lower than 1000°C have an impurity of CuO (Fig. 7); the CuO phase was readily reduced by H_2 at 310°C (Fig. 8). Patrick and Gavalas (19) previously obtained $CuAl_2O_4$ phase together with small diffraction peaks of CuO after the sample had been calcined at 900°C. They also examined the reducibility of the sample; the bulk CuO was reduced to Cu at low temperatures below 300°C. Although they had examined the sample calcined at 900°C, their data were intrinsically consistent with our results which were obtained by the samples calcined below 1000°C. The TPR results (Fig. 9) are in good agreement with the facts that the sample calcined at 1100°C had no Cu metal surface area and that all of the other samples calcined at lower temperatures had more or less Cu metal surface after they had been contacted with H_2 at 310°C. In comparison with the reference sample prepared by a dry-mixing method (Fig. 10), the samples prepared by the amorphous citrate process had pure $CuAl_2O_4$ or $CuAlO_2$. We have obtained $CuAl_2O_4$ containing no CuO phase by the citrate process at the calcination temperature of 1100°C.

Although the MeOH consumption rate of the $CuAl_2O_4$ sample calcined at 1100°C was lower than those of the other samples calcined at lower temperatures (Fig. 3), the $CuAl_2O_4$ sample has higher catalytic activities for MF formation at higher temperatures (Fig. 4). It is shown that MF selectivity of $CuAl_2O_4$ is higher than those of the samples calcined at lower temperatures at the same conversion level (Fig. 5). The sample prepared by a dry-mixing method showed low catalytic activities because it had some phases other than $CuAl_2O_4$ (Fig. 10). It can be said that the $CuAl_2O_4$ prepared by the amorphous citrate process was found to be significantly active for the dehydrocoupling reaction.

On the other hand, a deep reduction leads to the decrease both in MF formation activity (Fig. 6) and in the Cu metal surface area from 3.5 $m^2\ g^{-1}$ (reduced at 310°C, Table 3) to 2.0 $m^2\ g^{-1}$ (450°C). The deep reduction, however, generates γ-alumina phase (Fig. 8c). The deeply reduced sample produced dominantly DME without producing CO; acid sites on γ-alumina probably catalyzed the intermolecular dehydration of MeOH to DME. For $CuAl_2O_4$ calcined at 1100°C, CO selectivity decreased from 16 to 11% upon elevating the reaction temperature from 310 to 330°C in spite of the increase of MeOH conversion (Fig. 3), while DME selectivity increased from 20 to 59%. The activity of the DME formation indicates that the $CuAl_2O_4$ has acidic sites weaker than γ-alumina whose acid sites are active for DME formation at a low temperature of 250°C. For the $CuO-Al_2O_3$ samples prepared by the citrate process, the decrease in the MF selectivity can be influenced by the DME formation catalyzed by acid sites at high temperature of 310°C (Table 2). On the other hand, no DME formation observed at 250°C indicates that the MeOH conversion is not influenced by the acidic character of the $CuO-Al_2O_3$ samples at 250°C (Table 2, second, third, and fourth row).

Comparison among Different Valences of Cu Species in $CuO-Al_2O_3$

Sodesawa (9) reported that MeOH was converted into MF at 200°C over Cu(0) supported on silica, while MeOH was completely dehydrogenated into CO at 300°C. On the other hand, Morikawa *et al.* reported that nonacidic Cu(II) ion-exchanged fluoro tetrasilicic mica catalyzed the formation of MF with 45% MeOH conversion and 100% MF selectivity at 240°C (3, 5, 6, 30), at which the Cu(0) supported on silica produced CO (9), and that the produced MF was decomposed into CO and H_2 when the reaction temperature rose, even on the Cu(II) species (4). They also found that Cu(I) ion-exchanged fluoro tetrasilicic mica was selective for the MF formation (6).

Cu-containing catalyst also catalyzes the reverse reaction of MF formation. Kim *et al.* found that Cu(0) interacted with cuprous chromate spinel ($CuCrO_2$) in copper chromite catalyst was effective for the decomposition of MF to MeOH and CO in hydrogen flow (26). Our results on the decomposition of MF at 310°C (the last column of Table 3) indicate that $CuAl_2O_4$ calcined at 1100°C is nonmetallic and that the samples calcined at lower temperatures are metallic. In the dehydrocoupling reactions, it can be assumed that CO production is possibly caused by the catalytic action of copper metal at low temperatures.

The summary of the typical catalytic features of $CuO-Al_2O_3$ at different valence of Cu species (Table 4) clearly shows that Cu(0) species is active even at low temperatures for the dehydrocoupling of MeOH to MF as well as for the decomposition of MF (Table 3) and that Cu(II) exhibits the catalytic activities at temperatures higher than those at which Cu(0) is effective. Table 4 also elucidates that Cu(I) is effective for the selective MF formation. However, it is less active than Cu(II) species at higher temperatures. The summary is in agreement with the above-mentioned reports of Morikawa *et al.* (3, 5, 6) and Sodesawa (9).

CONCLUSIONS

$CuO-Al_2O_3$ systems, especially $CuAl_2O_4$, prepared by the amorphous citrate process exhibit an effective catalytic activity for the dehydrocoupling of MeOH to MF. $CuO-Al_2O_3$ samples calcined at temperatures below 1000°C are partially reduced during the catalytic reaction, and the selectivity to MF decreases with increasing Cu(0) content. Although Cu(0) is active and selective at temperatures below 210°C, Cu(0) decomposes MF to CO above 210°C. On the basis of the fact that the $CuO-Al_2O_3$ samples calcined at 1100°C are not reduced at 310°C, it has been summarized that Cu(II) species in the $CuAl_2O_4$ plays an important role as active sites in the dehydrocoupling at temperatures above 250°C, and that Cu(I) species in the $CuAlO_2$ catalyst is also active with maintaining high MF selectivity up to 290°C.

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