

New Catalytic System for Producing Pure Hydrogen -Water-gas-shift Reaction of Supported Copper Catalysts-

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ABSTRACT

The catalytic activities of the low-temperature water-gas-shift (WGS) reaction were investigated for Al₂O₃-supported Cu catalysts containing CrO_x, MnO_x, FeO_x, CoO_x, or NiO_x. The catalytic activity of Cu/Al₂O₃ catalyst at 423 K was enhanced by the addition of transition metal oxide. FeO_x and MnO_x additives additionally gave the enhancement in the catalytic activity at 523 K. The preparation conditions concerning calcination temperature and MO_x/Cu molar ratio were optimized for Cu-FeO_x/Al₂O₃ and Cu-CoO_x/Al₂O₃ catalysts. The reason why the catalytic activity was enhanced by adding FeO_x and CoO_x to Cu/Al₂O₃ was proposed on the basis of XRD and H₂-TPR results.

Keywords: hydrogen, copper catalyst, wgs reaction, iron oxide.

1 INTRODUCTION

It is well-known that removal of carbon monoxide (CO) in the hydrogen fuel produced by reforming of hydrocarbon sources is indispensable to attain high and stable performances of polymer electrolyte fuel cells (PEFCs). The low-temperature water-gas-shift (WGS) reaction, CO + H₂O = H₂ + CO₂, has been used in industry to achieve the removal of CO in the relatively high concentration range (*ca.* 7-10% CO). Cu-based mixed oxide catalysts [1-4] and supported Cu catalysts [5-10] have been reported to exhibit the high activity for the WGS reaction.

Recently, we have reported that Cu/Al₂O₃ catalysts calcined at relatively high temperature contain both highly dispersed Cu and CuAl₂O₃ spinel and the former species act as active sites for the WGS reaction [9]. Here, we wish to report the influences of transition metal oxide additives on the catalytic activity of Cu/Al₂O₃ for WGS reaction. In particular, the catalytic performances of Cu-FeO_x/Al₂O₃ and Cu-CoO_x/Al₂O₃ catalysts having the highest catalytic activity for WGS reaction at low and high temperature, respectively, were investigated.

2 EXPERIMENTAL

Al₂O₃ support was supplied from the Catalysis Society of Japan (JRC-ALO-8). Cu/Al₂O₃ catalysts containing FeO_x were prepared by a conventional impregnation method

using the mixed aqueous solution of Cu(NO₃)₂·3H₂O (Wako Chem.) and Fe(NO₃)₃·9H₂O (Wako Chem.). Cu/Al₂O₃ catalysts containing other transition metal oxides were prepared by a similar way. The catalysts were dried at 383 K for 1 h and calcined at 873-1073 K for 8 h in air. The loading of Cu was unified to be 15 wt%. The surface area of catalyst was measured by the BET method using N₂ adsorption. Al₂O₃-supported catalysts with and without H₂ reduction at 523 K are abbreviated as Cu-FeO_x/Al₂O₃ [973](1.0) (Cu-transition metal oxide (MO_x)/Al₂O₃ [calcination temperature] (MO_x/Cu molar ratio)) and CuO-FeO_x/Al₂O₃ [973](1.0), respectively.

The WGS reaction was carried out in a fixed-bed continuous flow reactor at 423-523 K. Prior to the activity test, the catalyst was reduced by flowing 20 vol% H₂/He gas at a flow rate of 30 cm³·min⁻¹ at 523 K for 2 h. The reactant gases contained 9.5 vol% of CO, 27.7 vol% of H₂O, 56.0 vol% of H₂, and 6.8 vol% of CO₂. The total flow rate was 96 cm³·min⁻¹ and the weight of the catalyst bed was 0.5 g (gas hourly space velocity = 7500-13000 h⁻¹). The effluents were analyzed by on-line gas chromatography (Shimadzu, GC-8AIT) using an active carbon column.

X-ray powder diffraction (XRD) analysis was performed to determine the crystalline phase of the catalysts using a Rigaku RINT2200HF diffractometer with CuK_α radiation. Hydrogen temperature-programmed reduction (H₂-TPR) was carried out by flowing 5 vol% H₂/N₂ (30 cm³·min⁻¹) in the temperature range 343-1173 K. The sample temperature increased with a rate of 2 K·min⁻¹ and the amount of H₂ consumed was monitored by a thermal conductivity detector of a gas chromatograph (Shimadzu, GC-8AIT). The DRIFT-IR spectra were recorded with FT-IR spectrometer (Perkin Elmer, Spectrum One) equipped with MCT detector.

3 RESULTS AND DISCUSSION

3.1 Supported Cu-MO_x Catalysts

The catalytic activities of Cu-MO_x/Al₂O₃[973](1.0) catalysts are summarized in Table 1. A unique promotive effect of MO_x additives on the catalytic activity of Cu/Al₂O₃ was observed. For Cu/Al₂O₃ catalyst, no catalytic activity was observed at temperature as low as 423 K. However, the catalytic activity of Cu/Al₂O₃ catalyst was enhanced by MO_x additives at 423 K. In addition, FeO_x and MnO_x additives gave the enhancement of the catalytic

activity at high temperature (523 K). As can be seen in Table 1, no relation between catalytic activities of WGS reaction and BET surface area was observed.

Figure 1 shows the XRD patterns of as-calcined CuO-MO_x/Al₂O₃ [973](1.0) catalysts before H₂-reduction at 523 K. CuO/Al₂O₃[973](1.0) catalyst provided the XRD pattern consisting of the intense and the broad peaks assigned to CuO (2θ = 35.3 and 38.5 degree) and γ-Al₂O₃ (2θ = 31.7, 37.2, and 45.4 degree), respectively (Fig. 1(a)). When MO_x were added to CuO/Al₂O₃, the peak intensity of CuO more or less decreased, suggesting that MO_x additives were reacted with CuO and/or made CuO particles highly dispersed state. In the following sections, the catalytic performances of Al₂O₃-supported Cu-FeO_x and Cu-CoO_x catalysts will be presented as instances.

M	Conversion of CO / %			BET surface area / m ² g ⁻¹
	423 K	473 K	523 K	
Cr	20	59	69	71
Mn	7	46	74	82
Fe	4	52	87	78
Co	13	38	25	83
Ni	16	38	48	91
None	0	44	65	105

Experimental condition: 9.5 vol% of CO, 27.7 vol% of H₂O, 56.0 vol% of H₂, and 6.8 vol% of CO₂; the total flow rate = 96 cm³ · min⁻¹; the weight of the catalyst bed = 0.5 g (gas hourly space velocity = 7500-13000 h⁻¹).

Table 1: Catalytic activities and BET surface areas of Cu-MO_x/Al₂O₃ [973](1.0) catalysts.

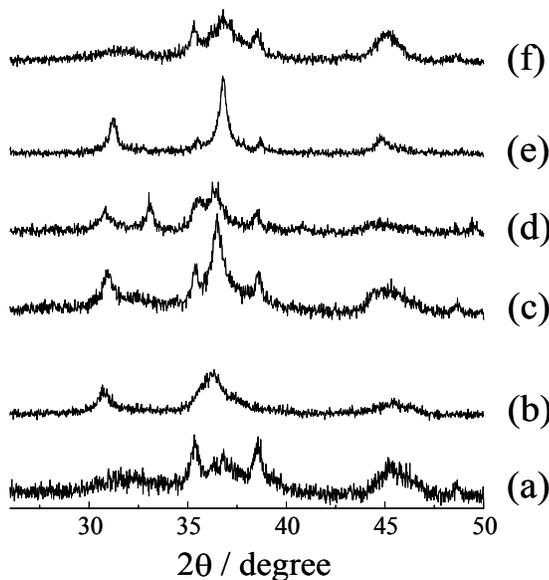


Figure 1: XRD patterns of CuO-MO_x/Al₂O₃ [973](1.0) catalysts. M = (a) none, (b) Cr, (c) Mn, (d) Fe, (e) Co, and (f) Ni.

3.2 Supported Cu-FeO_x Catalysts

The catalytic activities of Cu-FeO_x/Al₂O₃ and Cu/Al₂O₃ are summarized in Table 2, as functions of calcination temperature and FeO_x/Cu molar ratio. The less change in the catalytic activity of Cu/Al₂O₃ was observed at 873-1073 K of calcination temperature. On the other hand, the catalytic activity of Cu-FeO_x/Al₂O₃ increased with calcination temperature, reached a maximal value at 973 K, and then decreased with further increasing calcination temperature. When the catalytic activity of Cu-FeO_x/Al₂O₃[973](1.0) was compared with that of Cu/Al₂O₃[973], it was found that the enhancement of the catalytic activity by FeO_x addition was pronounced for the catalytic reaction performed at higher temperature, 523 K.

The catalytic activities of Cu-FeO_x/Al₂O₃ catalysts calcined at 973 K were dependent on FeO_x/Cu molar ratio, as shown in Table 2. The catalytic activity was increased by the addition of FeO_x to Cu/Al₂O₃. It should be noted that the activity of Cu-FeO_x/Al₂O₃ with FeO_x/Cu > 0.5 exceeded the initial value (Cu/Al₂O₃). FeO_x/Al₂O₃ catalysts calcined at 873-1073 K exhibited no catalytic activity for the WGS reaction at 473 and 523 K; therefore, the increase in the catalytic activity by FeO_x additive may be due to the synergistic effect of co-existence of Cu and FeO_x.

Catalyst	Conversion of CO / %		
	423 K	473 K	523 K
Cu-FeO _x /Al ₂ O ₃ [873](1.0)	0	28	81
Cu-FeO _x /Al ₂ O ₃ [973](1.0)	4	52	87
Cu-FeO _x /Al ₂ O ₃ [1073](1.0)	0	27	72
Cu-FeO _x /Al ₂ O ₃ [973](0.5)	1	50	83
Cu/Al ₂ O ₃ [873]	5	39	61
Cu/Al ₂ O ₃ [973]	0	44	65
Cu/Al ₂ O ₃ [1073]	3	38	68

Experimental conditions were the same as those in Table 1.

Table 2: Catalytic activities of Cu-FeO_x/Al₂O₃ catalysts.

The XRD patterns of Cu-FeO_x/Al₂O₃ catalysts calcined at 973 K in air, followed by the H₂-reduction at 523 K, are shown in Fig. 2. Cu/Al₂O₃ catalyst calcined at 973 K gave the diffraction lines assigned to metallic copper (Cu⁰) species as well as the broad diffraction lines from γ-Al₂O₃. The intensity of Cu⁰ diffraction line decreased by the addition of FeO_x, suggesting the formation of highly dispersed Cu⁰ particles. Interestingly, the diffraction lines assigned to Fe₃O₄ appeared in XRD pattern of Cu-FeO_x/Al₂O₃, although no reduction of Fe₂O₃ to Fe₃O₄ took place in the absence of copper species (probably Cu⁰).

Figure 3 shows H₂-TPR profiles of Cu/Al₂O₃[973], FeO_x/Al₂O₃[973], and Cu-FeO_x/Al₂O₃[973](0.5 and 1.0). A large peak in the range 450-500 K was observed for Cu/Al₂O₃[973] catalyst (Fig. 3(a)), being assigned to the reduction of CuO to Cu⁰ [9]. On the other hand, FeO_x/Al₂O₃[973] exhibited a very broad peak in the

temperature range 493-1050 K (Fig. 3(d)). When the content of Fe additive increased, an additional peak was observed at *ca.* 530 K just after the reduction peak attributable to CuO, as shown in Fig. 3(c). This additional peak was tentatively assigned to the reduction of Fe₂O₃ to Fe₃O₄ strongly interacted with metallic Cu. A similar H₂-TPR profile was reported for Cu-FeO_x/SiO₂ [11] and copper ferrite spinel [12].

From the present XRD and H₂-TPR results, we are considering the two possible interpretations of the enhancement in the catalytic activity by adding FeO_x to Cu/Al₂O₃. One is the formation of highly dispersed Cu⁰ formed by Fe additives. The XRD patterns of Cu-FeO_x/Al₂O₃ catalysts, as shown in Fig. 3, indicates that the addition of FeO_x to Cu/Al₂O₃ catalysts resulted in the decrease in the intensity of diffraction lines of Cu⁰. This may be correspondence to the formation of Cu⁰ fine particles. As the catalytic activity of WGS reaction depended on the surface area of Cu⁰ [9], it is appreciably expected that the formation of fine particles leads to enhance the catalytic activity.

The other explanation is the participation of the reduced FeO_x to WGS reaction in the presence of Cu⁰. FeO_x has reported to be active for high temperature-WGS reaction (*ca.* 623-723 K) [13]. In this case, it is considered that the redox property between Fe₂O₃ and Fe₃O₄ was important for WGS reaction over FeO_x catalysts. The present XRD and H₂-TPR studies proved that the Fe₂O₃ was easily reduced to Fe₃O₄ in the presence of Cu⁰ at lower temperature. Considering the report that the oxygen on Cu⁰ can rapidly diffuse to Fe surface [11], the redox process of FeO_x sufficiently take place in the present condition.

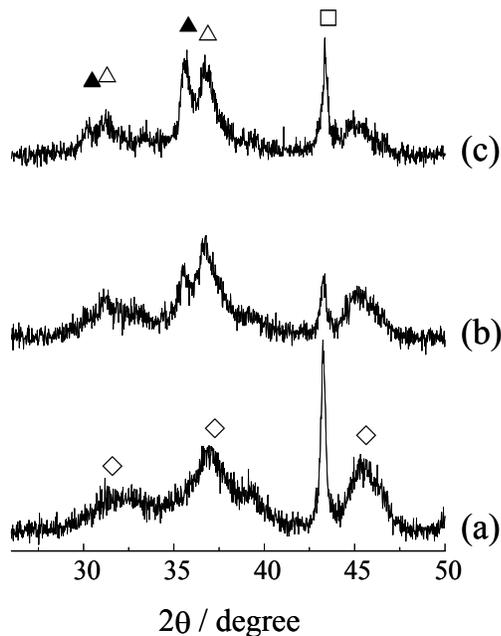


Figure 2: XRD spectra of Cu-FeO_x/Al₂O₃ [973] (x) catalysts. x = (a) 0, (b) 0.5, and (c) 1.0. (□)Cu⁰, (▲) Fe₃O₄, (Δ)FeAl₂O₄, and (◇)γ-Al₂O₃.

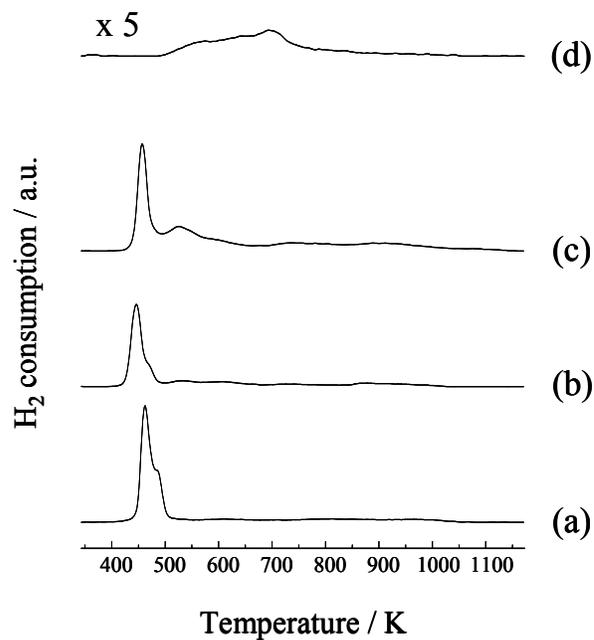


Figure 3: H₂-TPR profiles of (a) CuO/Al₂O₃[973], (b) CuO-FeO_x/Al₂O₃[973](0.5), (c) CuO-FeO_x/Al₂O₃[973](1.0), and (d) FeO_x/Al₂O₃[973].

3.3 Supported Cu-CoO_x Catalysts

The catalytic activities of Cu-CoO_x/Al₂O₃ are summarized in Table 3 as a function of CoO_x/Cu molar ratio. As shown in Table 1, Cu-CoO_x/Al₂O₃ exhibited the higher catalytic activity than Cu/Al₂O₃ at 423 K. The catalytic activity was significantly increased by the small amount of CoO_x added; Cu-CoO_x/Al₂O₃ [973](0.05) catalyst was the most active for WGS reaction at 423 K among the Cu-MO_x/Al₂O₃ catalysts tested in the present study. However, the catalytic activity was slightly decreased by the further addition of CoO_x to Cu/Al₂O₃.

Catalyst	Conversion of CO / %		
	423 K	473 K	523 K
Cu-CoO _x /Al ₂ O ₃ [973](1.0)	13	38	25
Cu-CoO _x /Al ₂ O ₃ [973](0.5)	16	51	67
Cu-CoO _x /Al ₂ O ₃ [973](0.2)	17	55	66
Cu-CoO _x /Al ₂ O ₃ [973](0.05)	25	61	72
Cu-CoO _x /Al ₂ O ₃ [973](0.01)	19	60	71
Cu/Al ₂ O ₃ [973]	0	44	65

Experimental conditions were the same as those in Table 1.

Table 3: Catalytic activities of Cu-CoO_x/Al₂O₃ catalysts

The XRD pattern of Cu-CoO_x/Al₂O₃[973](0.05) catalyst was essentially the same as that of Cu/Al₂O₃[973] catalyst. H₂-TPR profile of Cu-CoO_x/Al₂O₃[973](0.05) provided a

large peak in the range 450-500 K; this profile was also essentially the almost same as that of Cu/Al₂O₃[973] catalyst. These results indicated the dispersion state of Cu⁰ was very similar to that of Cu/Al₂O₃.

In order to elucidate the adsorption state of CO on Cu-CoO_x/Al₂O₃ catalyst, DRIFT-IR measurements were conducted. The spectra of Cu-CoO_x/Al₂O₃[973](0.05) and Cu/Al₂O₃[973] are depicted in Fig. 4. When the Cu/Al₂O₃[973] and Cu-CoO_x/Al₂O₃[973](0.05) samples were exposed to CO at 473 K, an intense IR peak assigned to Cu⁰-CO was observed at 2108 cm⁻¹. It is clear that the intensity of Cu⁰-CO peak was increased by the addition of CoO_x. Assuming that the morphology of Cu⁰ (for example, particle size) was unchanged by the small amount of CoO_x added, CoO_x addition provides the enhancement in the adsorption ability of CO on Cu⁰ supported on Al₂O₃, although further studies are needed.

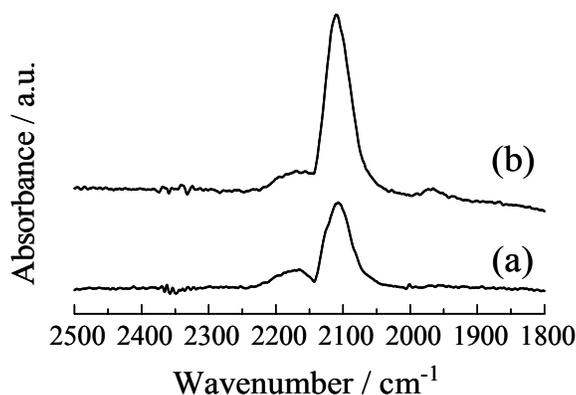


Figure 4: DRIFT-IR spectra of (a) Cu/Al₂O₃[973] and (b) Cu-CoO_x/Al₂O₃[973](0.05) catalysts after the introduction of CO (5.0 vol%, N₂ balance) for 60 min. Measurement temperature was 423 K.

4 CONCLUSION

The catalytic activities of the low-temperature WGS reaction were investigated for Al₂O₃-supported Cu catalysts containing various transition metal oxides. For Cu/Al₂O₃ catalyst, no catalytic activity was observed at temperature as low as 423 K. However, the catalytic activity of Cu/Al₂O₃ catalyst at 423 K was enhanced by the addition of transition metal oxide. Furthermore, the addition of FeO_x and MnO_x resulted in the enhancement in the catalytic activity at high temperature (523 K). The effect of FeO_x additives on the catalytic activity may be explained by two possibilities; one is the formation of highly dispersed Cu⁰ formed and the other is the participation of reduced FeO_x in WGS reaction in the presence of Cu⁰. It was found that CoO_x addition provides the increase in the adsorption ability of CO on Cu⁰ supported on Al₂O₃.

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