Effect of Transition-metal Oxide Additives for Water–Gas-shift Reaction over Supported Copper Catalyst

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The catalytic activities of the low-temperature water–gas-shift (LT-WGS) reaction were investigated for Al_2O_3-supported Cu catalysts containing CrO_x, MnO_x, FeO_x, CoO_x, NiO_x, or ZnO. The catalytic activity of Cu/Al_2O_3 catalyst at 423 K was improved by the small addition of transition-metal oxide. In particular, Cu/Al_2O_3 with CoO_x showed the highest activity among the supported Cu catalysts used in this study.

Removal of carbon monoxide (CO) in the hydrogen fuel produced by reforming hydrocarbon sources is indispensable to attain high and stable performance of polymer electrolyte fuel cells. Cu-based mixed oxide catalysts[1–4] and supported Cu catalysts[5–11] have been reported to exhibit high activity for low-temperature water–gas-shift (LT-WGS) reaction, $CO + H_2O = H_2 + CO_2$. Recently, we reported that Cu/Al_2O_3 catalysts calcined at relatively high temperature (973–1073 K) possess higher Cu dispersion than that calcined at mild temperature ($\approx$773 K) and show high catalytic activity for LT-WGS reaction.[9] Here, we wish to report the influence of transition-metal oxide additives on the catalytic activity of LT-WGS reaction over Cu/Al_2O_3 calcined at high temperature.

Al_2O_3 support was supplied by the Catalysis Society of Japan (JRC-ALO-8). Cu/Al_2O_3 catalysts containing transition-metal oxides (CrO_x, MnO_x, FeO_x, CoO_x, NiO_x, and ZnO) were prepared by a conventional impregnation method using a mixed aqueous solution of copper nitrate (Wako Chem., 99.9%) and transition-metal nitrate (Wako Chem., 98–99.9%). The catalysts were dried at 383 K for 1 h and calcined at 973 K for 8 h in air. The loading of Cu was unified to be 15 wt %. Al_2O_3-supported catalysts are abbreviated as $Cu–M/Al_2O_3$ (1.0) (Cu–transition metal oxide/Al_2O_3 (M/Cu molar ratio)).

The surface area of catalyst was measured by the BET method using N_2 adsorption. XRD analysis was performed to determine the crystalline phase of the catalysts using a Rigaku RINT2200HF diffractometer with Cu Kα radiation. The temperature-programmed reduction with H_2 (H_2-TPR) was carried out by flowing 5 vol % H_2/N_2 (30 cm^3·min^{-1}) in the temperature range 343–1173 K. The DRIFT-IR spectra were recorded with a FT-IR spectrometer (Perkin-Elmer, Spectrum One) equipped with MCT detector.

The LT-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 % H_2/He gas at a flow rate of 30 cm^3·min^{-1} at 523 K for 2 h. The reactant gases contained 9.5 vol % CO, 27.7 vol % H_2O, 56.0 vol % H_2, and 6.8 vol % CO_2. The total flow rate was 96 cm^3·min^{-1}, and the weight of the catalyst bed was 0.5 g (gas hourly space velocity (GHSV) = 7500–14500 h^{-1}). The effluents were analyzed by on-line gas

Table 1. Catalytic activity of $Cu–M/Al_2O_3$ (0.05)[a]

Catalyst	S.A.[b] /m^2 g^{-1}	Conv. of CO/%		
		423 K	473 K	523 K
$Cu–Cr/Al_2O_3$	108	20	61	70
$Cu–Mn/Al_2O_3$	113	20	56	64
$Cu–Fe/Al_2O_3$	114	16	58	70
$Cu–Co/Al_2O_3$	115	25	61	72
$Cu–Ni/Al_2O_3$	112	21	61	75
$Cu–Zn/Al_2O_3$	112	21	63	75
Cu/Al_2O_3	106	15	55	67
$Cu–ZnO–Al_2O_3$[c]	61	25	74	82

[a]GHSV = 7500 h^{-1}.   [b]BET surface area.   [c]GHSV = 14500 h^{-1}.

Table 2. Catalytic activity of $Cu–Co/Al_2O_3$[a]

Catalyst	S.A.[b] /m^2 g^{-1}	Conv. of CO/%		
		423 K	473 K	523 K
$Cu–Co/Al_2O_3$ (1.0)	83	13	38	25
$Cu–Co/Al_2O_3$ (0.5)	100	16	51	67
$Cu–Co/Al_2O_3$ (0.2)	108	17	55	66
$Cu–Co/Al_2O_3$ (0.05)	115	25	61	72
$Cu–Co/Al_2O_3$ (0.01)	117	19	60	71

[a]GHSV changed from 7500 ($Cu–Co/Al_2O_3$ (0.01)) to 13000 h^{-1} ($Cu–Co/Al_2O_3$ (1.0)) with Co content. [b]BET surface area.

chromatography (Shimadzu, GC-8AIT) using an active carbon column.

Table 1 summarizes the catalytic activities of $Cu–M/Al_2O_3$ (0.05) at 423–523 K as well as those of Cu/Al_2O_3 and commercial catalyst ($Cu–ZnO–Al_2O_3$ = 43/49/8 weight ratio) as references. A positive effect of transition-metal oxide additive on the catalytic activity of Cu/Al_2O_3 was observed at 423 K. In particular, the catalytic activity of $Cu–Co/Al_2O_3$ (0.05) was 1.7 times larger than that of Cu/Al_2O_3, suggesting that the number of Cu effective for LT-WGS and/or TON of Cu active for LT-WGS become large by Co addition. As the Cu content of a commercial catalyst is much larger than that of $Cu–Co/Al_2O_3$ (0.05), the latter catalyst shows higher reaction rate per Cu content than the former catalyst although GHSV is different from each other. When the measurement temperature was raised to 473 and 523 K, the transition-metal oxide additive has no or less influence on the catalytic activity of Cu/Al_2O_3.

The catalytic activities of $Cu–Co/Al_2O_3$ are summarized in Table 2 as a function of Co/Cu molar ratio. The catalytic activity was increased by the small amount of Co added; $Cu–Co/Al_2O_3$
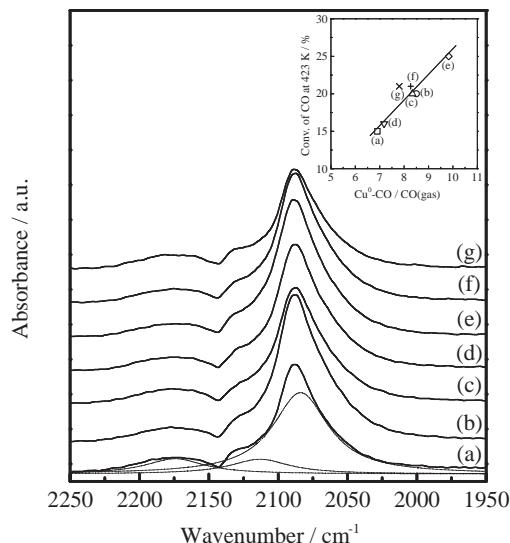
Figure 1. DRIFT-IR spectra of Cu–M/Al$_2$O$_3$ (0.05). M = (a) none, (b) Cr, (c) Mn, (d) Fe, (e) Co, (f) Ni, and (g) Zn.

(0.05) catalyst was the most active for the LT-WGS reaction at 423 K among the Cu–M/Al$_2$O$_3$ catalysts tested in the present study. The catalytic activity was decreased by the further addition of CoO$_x$ to Cu/Al$_2$O$_3$.

The XRD pattern of Cu–Co/Al$_2$O$_3$ (0.05) catalyst was essentially the same as that of Cu/Al$_2$O$_3$ catalyst. H$_2$-TPR profile of Cu–Co/Al$_2$O$_3$ (0.05) provided a large peak in the range 420–520 K, assigned to the reduction of CuO to Cu^0.[9] The profile was also essentially the same as that of Cu/Al$_2$O$_3$ catalyst; however, the reduction peak of Cu–Co/Al$_2$O$_3$ (0.05) catalyst before H$_2$ reduction was slightly shifted to a lower temperature. From the H$_2$-TPR results, it is suggested that the dispersion of CuO was enhanced by the CoO$_x$ additive.

In order to elucidate the adsorption state of CO on Cu–M/Al$_2$O$_3$ (0.05) catalysts, DRIFT-IR measurements were conducted at 423 K. The spectra of Cu–M/Al$_2$O$_3$ (0.05) and Cu/Al$_2$O$_3$ are depicted in Figure 1. When the Cu/Al$_2$O$_3$ and Cu–M/Al$_2$O$_3$ (0.05) samples were exposed to CO (5%) at 423 K, an intense IR peak assigned to Cu^0–CO[12] observed at 2088 cm^{-1}. As Cu^0–CO peak was overlapped with the doublet peaks of gaseous CO (2170 and 2117 cm^{-1}), the experimental IR spectra were deconvoluted as dotted lines. The intensity ratios of Cu^0–CO peak to gaseous CO peaks were plotted against the catalytic activities measured at 423 K, as shown in an insert of Figure 1. It is demonstrated that intensity ratios were linearly correlated with the catalytic activities. This means that the adsorption ability of CO was improved by adding a small amount of transition-metal oxide to Cu/Al$_2$O$_3$, probably resulting in the enhancement of catalytic activity at 423 K. The reason the adsorption ability of CO on Cu/Al$_2$O$_3$ was improved by the addition of transition-metal oxide remains unclear. We are considering the following possibilities although further study is needed. One explanation is that the increase of Cu^0 dispersion by adding small amount of transition-metal oxide resulted in the increase of the peak intensity of Cu^0–CO. Another explanation is that the electronic state of Cu^0 was changed by additives.

Table 3 shows the catalytic activities of Cu–M/Al$_2$O$_3$ (1.0) to Cu/Al$_2$O$_3$ catalyst. The effect of transition-metal additives

Table 3. Catalytic activity of Cu–M/Al$_2$O$_3$ (1.0)[a]

Catalyst	S.A.[b] /m^2 g^{-1}	Conv. of CO/%		
		423 K	473 K	523 K
Cu–Cr/Al$_2$O$_3$	71	20	59	69
Cu–Mn/Al$_2$O$_3$	82	7	46	74
Cu–Fe/Al$_2$O$_3$	78	5	48	78
Cu–Co/Al$_2$O$_3$	83	13	38	25
Cu–Ni/Al$_2$O$_3$	91	16	38	48
Cu–Zn/Al$_2$O$_3$	67	13	48	60

[a]GHSV = 13000 h^{-1}. [b]BET surface area.

seems to divide into two groups. The first group consisting of CrO$_x$, CoO$_x$, NiO$_x$, and ZnO additives has no or less influence on the catalytic activity of Cu/Al$_2$O$_3$ in the temperature range 423–523 K. The second group consists of FeO$_x$ and MnO$_x$ additives; their additives gave the lowering of the original activity of Cu/Al$_2$O$_3$ at low temperature, whereas they gave the enhancement of the catalytic activity at high temperature (523 K). We have reported that the improvement of the activity of Cu/Al$_2$O$_3$ by FeO$_x$ addition was ascribed to the synergistic effect of high-temperature WGS reaction over FeO$_x$ coexisting with Cu^0 in addition of LT-WGS reaction over Cu^0.[11] A similar effect may take place for Cu/Al$_2$O$_3$ with MnO$_x$. In fact, the Cu–Mn-based catalyst was reported to be active for high-temperature WGS reaction.[13]

In conclusion, the catalytic activity of Cu/Al$_2$O$_3$ catalyst at 423 K was enhanced by the addition of transition-metal oxide. A linear correlation between the catalytic activity at 423 K and the adsorption ability of CO was observed. Furthermore, it was found that the addition of FeO$_x$ and MnO$_x$ resulted in the enhancement in the catalytic activity at high temperature.

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