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Catalysis Communications 7 (2006) 228–231
CATALYSIS COMMUNICATIONS
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Effect of calcination temperature on the catalytic activity of copper supported on γ-alumina for the water-gas-shift reaction

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Received 11 September 2005; received in revised form 3 November 2005; accepted 4 November 2005
Available online 27 December 2005

Abstract

The effect of calcination temperature on the catalytic activity for water-gas-shift (WGS) reaction was investigated for copper/alumina catalysts prepared by the impregnation method. The catalyst calcined at 1073 K, followed by the treatment in H_2 at 523 K, showed a high activity for WGS reaction. XRD and H_2-TPR measurements revealed that the catalyst calcined at 1073 K contained both highly dispersed CuO and spinel $CuAl_2O_4$ particles. The former species was reduced by the treatment in H_2 at 523 K to yield the highly dispersed metallic copper which would act as catalytically active sites in WGS reaction.

Keywords: Water-gas-shift reaction; Carbon monoxide; Alumina; Supported catalyst; Metallic copper; Spinel; $CuAl_2O_4$

1. Introduction

Removal of carbon monoxide (CO) in the hydrogen fuel produced by reforming of hydrocarbon sources is indispensable to attain a high and stable performance of polymer electrolyte fuel cells (PEFCs) operated at low temperature because CO is irreversibly adsorbed on the platinum electrode of a PEFC. The water-gas-shift (WGS) reaction, $H_2O + CO = H_2 + CO_2$, has been used in industry to achieve the removal of CO in the relatively high concentration range (ca. 7–10% CO). The most promising catalyst for the WGS reaction is Cu/ZnO-based mixed oxide prepared by the coprecipitation method [1–5]. Supported copper catalysts have been also reported to be active for the WGS reaction [6–9].

It is well-known that the catalytically active site in WGS reaction is metallic copper (Cu^0). Therefore, the formation of highly dispersed Cu^0 particles would result in an enhancement of the catalytic activity. In the present paper, we wish to report that the Cu/Al_2O_3 catalyst calcined at 1073 K, giving highly dispersed Cu^0 particles on alumina supports, showed a high activity in the WGS reaction.

2. Experimental methods

The γ-alumina used as a support material was supplied from Catalysis Society of Japan (JRC-ALO-8). Cu/Al_2O_3 catalysts were prepared by a conventional impregnation method using an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (Wako Chem., 99.9%). The catalysts were dried at 383 K for 24 h and calcined at 773–1173 K for 8 h in air. The loading of Cu was unified to be 12 wt%.

The WGS reaction was carried out in a fixed-bed continuous flow reactor at 473–523 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. The reactant gases contained 5.4 vol% of CO, 21.6 vol% of H_2O, 57.0 vol% of H_2, and 16.0 vol% of CO_2. The total flow rate was 30 $cm^3\ min^{-1}$ and the volume of the catalyst bed was 1.8 cm^3 (gas hourly space velocity = 6000 h^{-1}). The effluents were analyzed by on-line gas chromatography (Shimazu, 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

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doi:10.1016/j.catcom.2005.11.004

Rigaku RINT2200HF diffractometer with CuKα radiation. Temperature-programmed reduction was carried out by flowing 5 vol% H_2/Ar (30 $cm^3 min^{-1}$) in the temperature range 373–773 K (H_2-TPR). The sample temperature increased with a rate of 2 K min^{-1} and the amount of H_2 consumed was measured by a thermal conductivity detector of the gas chromatograph (Shimazu, GC-8AIT). The surface area of catalyst was measured by the BET method using N_2 adsorption. The surface area of the Cu^0 particles formed on the catalysts was measured by a N_2O-pulse titration method ($N_2O + 2Cu \rightarrow Cu_2O + N_2$) at 373 K [10,11]. Catalysts were reduced with 20 vol% H_2/He at 523 K for 1 h prior to the injection of the N_2O pulse. The surface area of Cu^0 particles was calculated by assuming that a reduced Cu^0 surface has a surface density of 1.46×10^{19} copper atoms m^{-2} [10,11].

3. Results and discussion

The catalytic activities of Cu/Al_2O_3 catalysts are shown in Fig. 1 as a function of calcination temperature. The catalysts were reduced by H_2 at 523 K before the WGS reaction. The conversion of CO gradually increased with increasing calcination temperature, reached a maximum value at 1073 K, and then drastically decreased at 1173 K. This temperature-dependence was clearly different from that of a commercially available $Cu/ZnO/Al_2O_3$ mixed oxide catalyst, for which the activity decreased monotonously with increasing calcination temperature [3,12]. The BET surface area and the bulk density of the catalysts calcined at 773–1173 K are summarized in Table 1. The BET surface area of the Cu/Al_2O_3 catalysts gradually decreased with an increase in calcination temperature while the bulk density increased. The significant change in both BET surface area and bulk density of the catalyst calcined at 1173 K was due to the formation of spinel oxide as described later. The catalyst calcined at 1073 K showed a high activity in spite of the lower BET surface area than those for the catalysts calcined at 773 and 973 K.

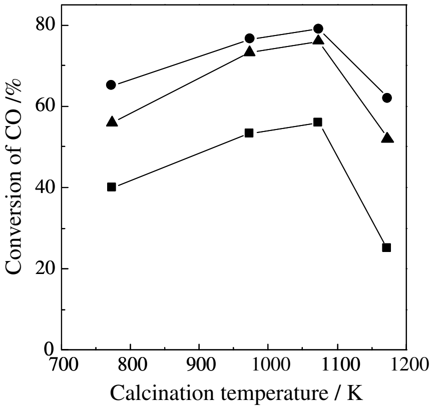

Fig. 1. Conversions of CO at (■) 473, (▲) 498, and (●) 523 K, as a function of calcination temperature. Reaction conditions: 5.4 vol% of CO, 21.6 vol% of H_2O, 57.0 vol% of H_2, and 16.0 vol% of CO_2, total flow rate 30 $cm^3 min^{-1}$, and gas hourly space velocity 6000 h^{-1}.

Table 1
BET surface area and bulk density of catalysts calcined at each temperature

	Calcination temperature/K			
	773	973	1073	1173
Surface area/$m^2 g^{-1}$	163	137	115	18
Bulk density/g cm^{-3}	0.739	0.741	0.749	0.918

The catalytic activity of the catalyst calcined at 1073 K was compared with that of the well-known oxide catalyst, $CuO/ZnO/Al_2O_3$, with the weight ratio 43:49:8. Under the present conditions, the catalytic activities of the oxide catalyst were 66%, 86%, and 88% at 473, 498, and 523 K, respectively. The activity of the catalyst calcined at 1073 K was slightly lower than that of the oxide catalyst; however, considering that the copper content of the latter catalyst was ca. 3 times larger than that of the former catalyst, the activity per copper in the catalyst calcined at 1073 K was higher than that in the oxide catalyst.

XRD patterns of the catalysts calcined at 773–1173 K are illustrated in Fig. 2A. The catalysts calcined below

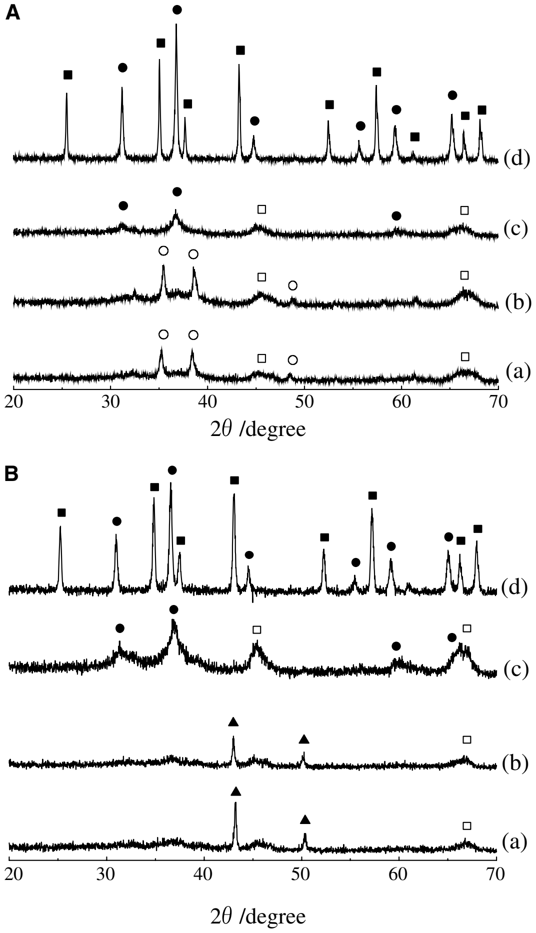

Fig. 2. Powder X-ray diffraction patterns of catalysts calcined at (a) 773, (b) 973, (c) 1073, and (d) 1173 K, (A) before and (B) after the treatment with H_2 at 523 K: (□) γ-Al_2O_3, (■) α-Al_2O_3, (○) CuO, (▲) Cu^0, and (●) $CuAl_2O_4$.