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High sustainability of Cu–Al–Ox catalysts against daily start-up and shut-down (DSS)-like operation in the water–gas shift reaction

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ABSTRACT

Coprecipitated-Cu–Al–Ox catalyst calcined at 823 K (CP-823) showed higher activity and sustainability than a commercial $Cu/ZnO/Al_2O_3$ catalyst even after 50 cycles of the daily start-up and shut-down (DSS)-like operation in the water–gas shift reaction. The high, stable activity of CP-823 is caused by the formation of highly dispersed and stable Cu metal. A boehmite phase formed "*in situ*" during the DSS operation has an important role in inhibition of aggregation of Cu metal particles.

1. Introduction

Polymer electrolyte fuel cells (PEMFCs) using H_2 fuel have been attractive because of their high power density, low temperature operation, low emissions of NO_x, greenhouse gas and so on [1,2]. When hydrogen is supplied to PEMFCs by reforming hydrocarbons such as methane, propane, and methanol, it is necessary to remove CO because it poisons the Pt electrode of PEMFCs and decreases their activity for electrochemical reaction. The water–gas shift (WGS) reaction is promising for removing CO from reformer gas [3,4]. Since daily start-up and shut-down (DSS) operations are envisaged for residential applications of PEMFC systems, the catalysts for the WGS reaction are sometimes exposed to water and/or oxygen containing atmosphere at low temperatures, and the catalytic activity decreases as a result of oxidation and/or aggregation of active species. For that reason, in addition to high activity, high sustainability against fluctuation from oxidative to reductive atmospheres is essential for the catalysts for the WGS reaction. Generally, the activity of copper-based catalysts is higher for this reaction [5–11], but is less stable to oxidant gases than precious metal like Pt, Ru and Au. Therefore, it is important to develop highly stable Cu-based catalysts or highly active precious metal catalysts. Various ceria supported metal catalysts have been prepared and used in the WGS reaction. Cu/CeO_2 and Ni/CeO_2 were prepared by the urea coprecipitation-gelation [12], Pd/CeO_2 was prepared by impregnation [13], Au/CeO_2 was prepared by deposition–precipitation [14], and both Au/CeO_2 [15] and $Cu–Pd/CeO_2$ catalysts [16] were prepared by the urea coprecipitation-gelation method. However, Zalc et al. [17] reported that a large amount of H_2 leads to the irreversible reduction of CeO_2 and the catalyst deactivation. Pt/TiO_2 [18] and Pt/Al_2O_3 [19] were promising candidate as the catalysts for low temperature shift reaction. Ru was also active for the shift reaction. Ru/V_2O_3 catalyst was prepared by the reduction of Ru/V_2O_5 at 673 K in H_2 [20] and Ru/hydroxyapatite catalyst was prepared by deposition–precipitation method [21].

The formation of spinel phase such as Cu–Al, Cu–Mn, and Cu–Fe systems [6–8], CeO_2 impregnation [9], and MgO doping [10] have been proposed to improve the stability of Cu-based catalyst. In addition, a variety of preparation methods have been also investigated [6,7,11]. However, further effort to improve the stability of Cu-based catalysts is still necessary. Moreover, it is important to elucidate the mechanism of improvement of sustainability by the additives.

In this study, we demonstrate unique behavior and high sustainability of simple Cu–Al–Ox catalysts, prepared from homogeneous precursors and calcined at low temperature, against the

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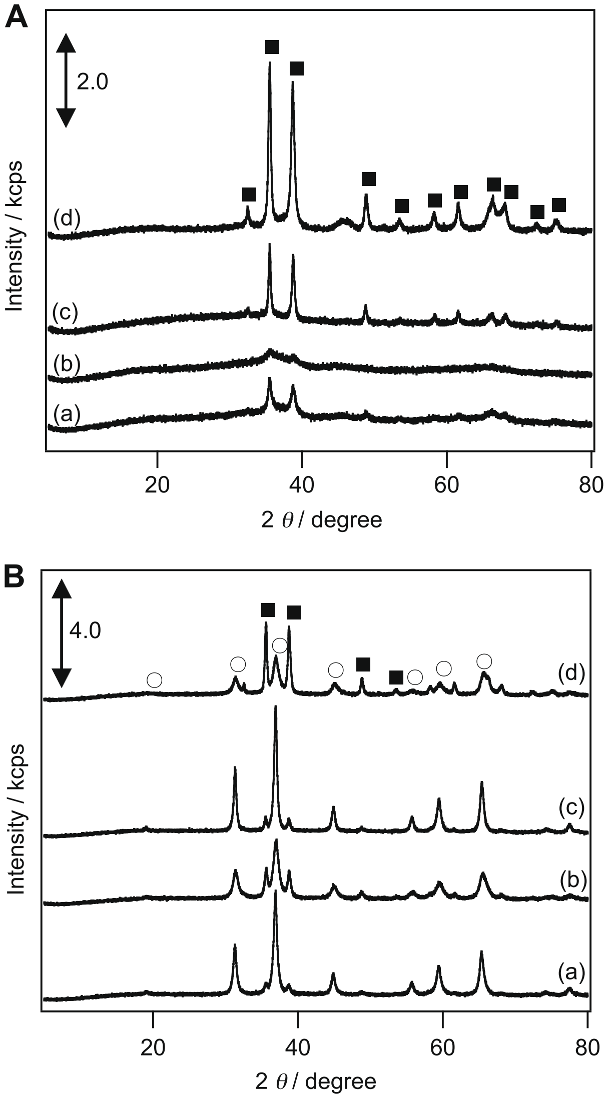

Fig. 1. XRD patterns of Cu–Al–Ox catalysts after calcination at (A) 823 and (B) 1073 K. (a) HP-, (b) CP-, (c) SG- and (d) IMP- catalysts (■) CuO, (○) $CuAl_2O_4$.

DSS-like operation in the WGS reaction. The Cu–Al–Ox catalyst prepared by coprecipitation shows high activity and sustainability even after 50 cycles of DSS-like operation, whereas the commercial $Cu/ZnO/Al_2O_3$ catalyst decreased in activity with repeated DSS-like operation. A mechanism of improvement of sustainability by "*in situ*" formation of boehmite (AlO(OH)) phase is proposed.

2. Experimental

Cu–Al–Ox catalysts (Cu/Al = 1/2) were prepared by homogeneous preparation (HP-), coprecipitation (CP-), sol-gel (SG-) and impregnation (IMP-) methods. The Cu loading in these Cu–Al–Ox catalysts was 5.5 mmol g^{-1}. HP-catalysts were prepared by using urea hydrolysis [21–23] as follows: urea was mixed into a solution of metal nitrates at room temperature, and the urea was hydrolyzed by heating the mixture at 363 K. During the hydrolysis of urea, hydroxide ions are generated in the homogeneous solution (Eq. (1)).

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + HCO_3^- + OH^- \qquad (1)$$

The precipitates were then filtered, washed with distilled water, dried in air at 373 K. CP-catalysts were prepared by coprecipitation, i.e., the aqueous solution of metal nitrates was dropped into aqueous solution of Na_2CO_3 with vigorous stirring and the pH was adjusted at 9 with NaOH. The obtained precipitate was dried at 373 K. SG-catalysts were prepared by the citrate sol-gel method [24,25]. Two kinds of aqueous solutions of copper and aluminum nitrate were treated with an excess amount of citric acid and ethylene glycol, and then each solution was mixed. This mixture was evaporated at 353 K to make a sol of the organometallic complex. IMP-catalysts were prepared by an impregnation method using γ-Al_2O_3 (JRC-ALO-8) and Cu nitrate solution. The catalysts were obtained by calcining the precipitates at 823 or 1073 K in air (abbreviated as CP-*X*, where *X* is the calcination temperature). IMP-Cu/AlO(OH) was prepared by impregnation and calcined at 823 K in air for 3 h. AlO(OH) (Wako) was used as the support and impregnated with Cu nitrate aqueous solution. The Cu loading on IMP-Cu/AlO(OH) is similar to those of Cu–Al–Ox catalysts. The WGS reaction was carried out using a fixed bed reactor at atmospheric pressure with $CO/CO_2/H_2O/H_2$ (7.3/7.3/27.2/58.3) mixed gas at 473 K. Prior to the WGS reaction, the catalysts were reduced with 5 vol.% H_2 diluted with nitrogen at 523 K for 0.5 h. The products were analyzed using two on line gas chromatographs (GC). A GC with packed Molecular Sieve 5A column, Ar carrier gas and TCD were used to analyze H_2. Another GC with packed Porapak-Q column, N_2 carrier gas and FID with methanizer were used to analyze CO and CO_2. The conversion of CO was quantified by a calibration curve method and the following equation (Eq. (2)).

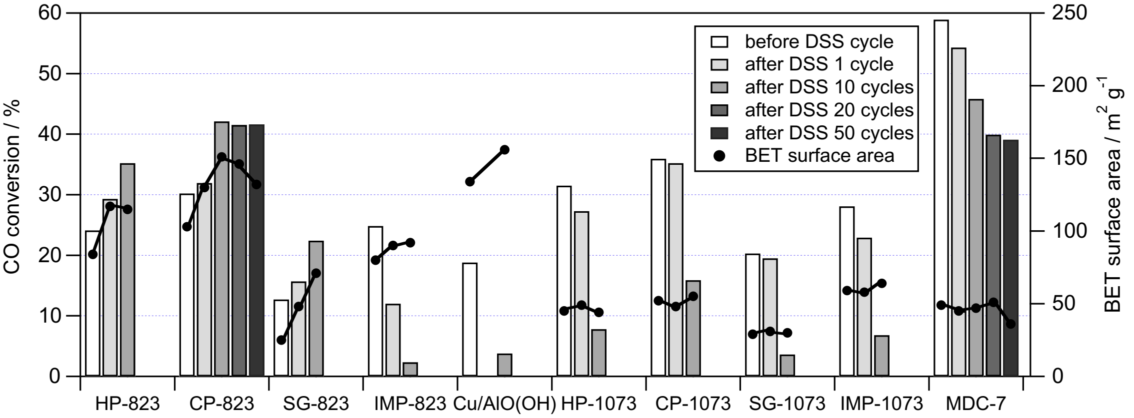

Fig. 2. The change in catalytic activity in the water–gas shift reaction by the DSS-like operation over Cu–Al–Ox, Cu/AlO(OH) and commercial $Cu/ZnO/Al_2O_3$ catalysts. Reaction temperature 473 K, $CO/CO_2/H_2O/H_2$ = 7.3/7.3/27.2/58.3, GHSV = 12.4 L h^{-1} g-cat^{-1}.