



# Durable Cu composite catalyst for hydrogen production by high temperature methanol steam reforming



Yasuyuki Matsumura\*

National Institute of Advanced Industrial Science and Technology (AIST), Kansai Center, Midorigaoka, Ikeda, Osaka 563-8577, Japan

## HIGHLIGHTS

- Activity and durability of Cu/ZnO/ZrO<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub>/In<sub>2</sub>O<sub>3</sub> coprecipitated on ZrO<sub>2</sub> have been tested.
- The composite catalyst containing only 3 wt.% Cu is active and stable at 400 °C.
- The deactivation rate empirically relates to the cube of the activity.
- The lifetime of the 3 wt.% Cu catalyst is as long as  $53 \times 10^2$  h at 400 °C.
- The Cu surface activity increases with a decrease in the Cu particle size.

## ARTICLE INFO

### Article history:

Received 22 May 2014

Received in revised form

2 September 2014

Accepted 5 September 2014

Available online 16 September 2014

### Keywords:

Methanol steam reforming

Coprecipitated Cu catalyst

Zirconia support

Lifetime

Hydrogen production

## ABSTRACT

Durable catalysts are necessitated for the high temperature methanol steam reforming in compact hydrogen processors. The high durability at 400 °C can be obtained with a composite Cu catalyst where a small amount of Cu–ZnO–ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub>–In<sub>2</sub>O<sub>3</sub> is coprecipitated on a zirconia support. The lifetime of the composite catalyst containing 3 wt.% Cu is estimated to be as long as  $53 \times 10^2$  h at 400 °C to produce the full conversion at a contact time of 250 g h m<sup>-3</sup>. The deactivation rate empirically relates to the cube of the activity. The gradual deactivation is caused by the gradual reduction of the Cu surface amount and also by the reduction of the surface activity which is believed to decrease with an increase in the Cu particle size. The interaction between the thin layer of the coprecipitate and the support surface probably suppresses the aggregation of the coprecipitate leading to Cu sintering.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrogen is a fuel of polymer electrolyte fuel cells [1], but its storage is a serious problem for fuel cell vehicles. On-board hydrogen storage vessels, whose working pressure is above 35 MPa, have been developed, but still need to be improved [2]. On-board hydrogen production from methanol was tried by some automobile companies [3–8]; however, it was unsuccessful probably because of the unstable operation conditions of the reactor [9]. That is, the reactor must be rapidly heated up under DSS (daily start and stop) operation mode which damages the catalyst. The reactor should be directly heated with a combustion gas exceeding 300 °C for the thermal efficiency [10]. The operation at around 400 °C is desirable because the short contact time of the reaction leads to a compact hydrogen processor [11]. Although conventional Cu-based

catalysts such as Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> are active and selective for methanol steam reforming ( $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$ ), the sintering of copper at above 300 °C becomes an obstacle in the development of the on-board reformer [7,12]. It should be noted that the Hüttig and Tamman temperatures of Cu metal are as low as 134 and 405 °C, respectively [13].

The addition of zirconia to Cu–ZnO is effective for stabilization of the Cu catalyst at 400 °C, but the activity gradually decreases due to the crystal growth of ZrO<sub>2</sub> accompanying the sintering of Cu and ZnO particles [14,15]. Addition of indium oxide to Cu–ZnO–ZrO<sub>2</sub> significantly improves the durability at the high temperature and suppresses the by-production of carbon monoxide being unfavorable against PEFCs [16]. However, the initial activity is low in comparison with unmodified Cu–ZnO–ZrO<sub>2</sub> whose activity is comparable with Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> at around 250 °C [15,16]. It was found that the low initial activity of Cu–ZnO–ZrO<sub>2</sub>–In<sub>2</sub>O<sub>3</sub> can be increased by the addition of yttrium and coprecipitation of the catalyst on a ZrO<sub>2</sub> support [17]. Although the Cu content of the

\* Tel.: +81 72 751 7821; fax: +81 72 751 9623.

E-mail address: [yasu-matsumura@aist.go.jp](mailto:yasu-matsumura@aist.go.jp).

composite catalyst is 15 wt.% (the content of the support, 50 wt.%), the activity is similar to that of Cu–ZnO–ZrO<sub>2</sub> containing 30 wt.% Cu after a durability test for 25 h mainly at 500 °C. The activity of the composite catalyst is mostly stable in the test while the deactivation of Cu–ZnO–ZrO<sub>2</sub> is rather steep. Thus, the composite catalyst is promising as a catalyst for the hydrogen processor.

In this study, the amount of Cu–ZnO–ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub>–In<sub>2</sub>O<sub>3</sub> coprecipitated on the ZrO<sub>2</sub> support has been reduced significantly. Surprisingly, the initial activity of the composite catalyst containing Cu as small as 3 wt.% is similar to that of the 15 wt.% Cu catalyst in the previous study [17]. Also, the life of the composite catalyst at 400 °C under the DSS condition has been estimated by an acceleration test at 400–550 °C and the lifetime of the 3 wt.% Cu catalyst is as long as  $53 \times 10^2$  h.

## 2. Experimental

A Cu–ZnO–ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub>–In<sub>2</sub>O<sub>3</sub> coprecipitate, whose atomic ratio of Cu/Zn/Zr/Y/In was 1.0/1.0/0.33/0.11/0.076, was deposited on a zirconia support supplied from Catalysis Society of Japan (reference catalyst, JRC-ZRO-2). The catalyst was prepared from a 0.2-M aqueous mixture of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Wako Pure Chemical, S grade), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Wako, S), ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (Wako, 1st), Y(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Wako, 98+%), and In(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Wako, 98+%) with addition of an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (0.5 M) under vigorous stirring at 80 °C as described elsewhere [17]. After filtration and washing with distilled water, the precipitate was dried at 120 °C for 15 h and finally calcined in air at 500 °C for 12 h. The resulting composite catalyst containing 9 wt.% Cu in reduced form (zirconia support content, 70 wt.%) will be denoted as 9Cu. The catalysts containing 6, 3, and 1.5 wt.% Cu (support contents, 80, 90, and 95 wt.%, respectively) were also prepared (6Cu, 3Cu, and 1.5Cu, respectively).

Catalytic tests were performed in a fixed-bed continuous-flow reactor operated under atmospheric pressure as described elsewhere [17]. The catalyst was usually pre-reduced with a reaction mixture of methanol, steam, and argon (1.0/1.2/0.5 in molar ratio) with a flow rate (*F*) of 0.027 m<sup>3</sup> h<sup>-1</sup> at 250 °C for 1 h; then the reactor was heated up to 400 °C in the reaction flow. The weight (*W*) of the catalyst was varied from 0.15 to 0.50 g to change the contact time (*W/F*). Following the reaction for 1 h at 400 °C, the reaction was carried out at 500 °C for 6 h; then, the temperature was decreased to 400 °C for the evaluation of the activity at 400 °C and kept for 1 h. After the reaction, the catalyst was cooled to room temperature under an Ar stream (0.005 m<sup>3</sup> h<sup>-1</sup>). In the next run, the reactor was heated to 400 °C within 0.5 h under the Ar stream; then, the reaction was restarted at 400 °C for 1 h and kept at a desired temperature for 7 h. The final activity was measured at 400 °C for 1 h and the catalyst was again cooled to room temperature under the Ar stream. The procedure was repeated in the following runs. The time interval of the runs was usually 14 h.

No formation of formaldehyde or methyl formate was detected. The selectivities of CO<sub>2</sub>, CO and CH<sub>4</sub> were calculated in molar basis [17].

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded in air at room temperature with an MAC Science MP6XCE diffractometer using nickel-filtered Cu K $\alpha$  radiation.

The structures of the catalysts were evaluated by transmission electron microscopy (TEM) and high-angle annular dark field imaging in scanning transmission electron microscopy (HAADF/STEM) with energy dispersed X-ray spectroscopic (EDS) analysis using an FEI Tecnai G2 F20 Twin with an EDX detecting unit (EDAX Inc.) at the acceleration voltage of 120 kV.

The BET surface areas of the catalysts were determined from the isotherms of nitrogen physisorption.

X-ray photoelectron spectra (XPS) were recorded at room temperature with a JEOL JPS-9010MX spectrometer (Al K $\alpha$ ) and the surface atomic concentrations of Cu, Zn, Zr, Y, In, and O were obtained using the average matrix relative sensitivity factors as described elsewhere [17].

Temperature-programmed reduction (TPR) of the catalyst (10–20 mg) was carried out using a differential scanning calorimeter (Rigaku DSC8230HP). After heated under an Ar stream up to 500 °C, the sample was cooled to room temperature; then, the temperature of the sample bed was linearly increased at a rate of 200 °C h<sup>-1</sup> in a stream of 10-vol.% hydrogen diluted with argon at a flow rate of 6.0 dm<sup>3</sup> h<sup>-1</sup>. As the reference,  $\alpha$ -alumina powder was used. The DSC curve was reproducible with a different amount of the sample. The energy calibration was carried out by measuring the melting of indium.

The profiles of EXAFS (extended X-ray absorption fine structure) for the catalysts containing indium oxide were taken at room temperature in the transmission mode for In K-edge at beam-line BL14B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) as described elsewhere [16].

## 3. Results and discussion

### 3.1. Structure of as-prepared Cu composite catalysts

The XRD peaks for tetragonal ZrO<sub>2</sub> (t-ZrO<sub>2</sub>) were recorded in the patterns of the as-prepared composite catalysts (Fig. 1) [18]. The as-received support is amorphous ZrO<sub>2</sub> (see Fig. 1-a), and the structure is transformed to monoclinic ZrO<sub>2</sub> (m-ZrO<sub>2</sub>) by the calcination at 500 °C for 12 h without the coprecipitate (see Fig. 1-b) [19]. Since no peaks for m-ZrO<sub>2</sub> were recorded in the patterns for 3–9Cu (see Fig. 1-c, d, and e), it is suggested the support surfaces interact with the coprecipitate [17,19–21]. However, the peaks of m-ZrO<sub>2</sub> partly appeared in the pattern for 1.5Cu (see Fig. 1-f), showing that the amount of the coprecipitate (5 wt.%) is insufficient for the complete interaction. The mean crystallite size of t-ZrO<sub>2</sub> was determined from the line broadening of the peak at 30.4° in  $2\theta$  [22] and the values were 14–16 nm regardless of the as-prepared samples. The broad peaks at 28–36° in Fig. 1(c and d) suggest that the presence of the coprecipitate on the support surface disturbs the crystallization of the support from the amorphous phase [17].

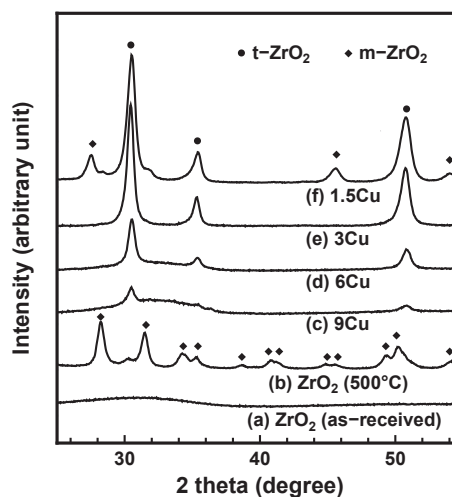


Fig. 1. XRD patterns of as-prepared composite catalysts. (a) as-received ZrO<sub>2</sub> support, (b) ZrO<sub>2</sub> support heated in air at 500 °C for 12 h, (c) 9Cu, (d) 6Cu, (e) 3Cu, and (f) 1.5Cu. The patterns of (a) and (b) are reproduced from Ref. [19].

Download English Version:

<https://daneshyari.com/en/article/1283981>

Download Persian Version:

<https://daneshyari.com/article/1283981>

[Daneshyari.com](https://daneshyari.com)