

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ijhe](http://www.elsevier.com/locate/ijhe)

# Stable and selective hydrogen production through steam reforming of dimethyl ether with an Al<sub>2</sub>O<sub>3</sub> and PdZn composite catalyst

H. Yoshida, N. Iwasa, H. Akamatsu, M. Arai\*

Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

## ARTICLE INFO

### Article history:

Received 10 July 2014

Received in revised form

18 February 2015

Accepted 23 February 2015

Available online 20 March 2015

### Keywords:

Hydrogen

Steam reforming

Dimethyl ether

Palladium–zinc alloy

Alumina

## ABSTRACT

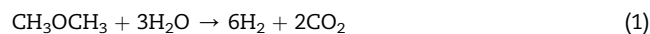
Hydrogen production through steam reforming of dimethyl ether was investigated with a simple composite catalyst prepared by physically mixing two active components of Al<sub>2</sub>O<sub>3</sub> and PdZn alloy. A mixture in a weight ratio of 9/1 (Al<sub>2</sub>O<sub>3</sub>/PdZn) gave an excellent catalytic performance at 400 °C with a 94% H<sub>2</sub> yield at 100% conversion. Hydrolysis of dimethyl ether to methanol occurred on Al<sub>2</sub>O<sub>3</sub>, followed by steam reforming of methanol formed on PdZn alloy. The composite catalyst showed good stability and durability and no catalyst deactivation was observed at such a high temperature.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Hydrogen is an ideal fuel for fuel cells in both mobile and stationary applications [1,2]. One of useful ways of hydrogen production is steam reforming of various organic compounds, among which dimethyl ether (DME) is an efficient source because of its high hydrogen-to-carbon ratio, non-toxic and non-corrosive natures, easy handling and transportation. The physical properties of DME are similar to those of LPG and so the present infrastructure for LPG may be employed. Thus, the steam reforming of DME, Eq. (1), has been attracting practical attention as a potential hydrogen production process [3]. The steam reforming of DME proceeds through two consecutive reactions [3], the hydrolysis of DME to methanol (Eq. (2)) and

the steam reforming of methanol formed (Eq. (3)). The former is catalyzed by acids such as zeolite and Al<sub>2</sub>O<sub>3</sub> and the latter by Cu- and Pd-based catalysts including Cu/ZnO and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> [3,4]. However, the less costly Cu-based catalysts may lose their activity at high temperatures above 300 °C; that is, their durability is still not satisfactory [5,6]. Previously, the authors showed that PdZn alloy catalyst was active and selective to the steam reforming of methanol [5,7,8] and had good stability with no significant deactivation during the reaction even at a high temperature of 350 °C.



\* Corresponding author. Fax: +81 0 11 706 6594.

E-mail address: [marai@eng.hokudai.ac.jp](mailto:marai@eng.hokudai.ac.jp) (M. Arai).

<http://dx.doi.org/10.1016/j.ijhydene.2015.02.111>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.



Hence, it is interesting to use a composite catalyst of  $\text{Al}_2\text{O}_3$  and PdZn alloy, which have good catalytic features for the first (Eq. (2)) and second (Eq. (3)) steps involved in the steam reforming of DME (Eq. (1)), respectively. A simple, physically mixed composite catalyst of  $\text{Al}_2\text{O}_3$  and PdZn alloy has been applied for the steam reforming of DME at 300 °C–400 °C and at atmospheric pressure in the present work. The composition of the composite catalyst has been optimized and the influence of reaction temperature has been examined. The performance of the composition-optimized  $\text{Al}_2\text{O}_3$  and PdZn composite catalyst has been compared with that of another one including  $\text{Al}_2\text{O}_3$  and a Cu based catalyst to examine and confirm the durability of the former. This work shows that a simple, physically mixed  $\text{Al}_2\text{O}_3$  and PdZn alloy composite catalyst can contribute to the stable and selective hydrogen production through the steam reforming of a relatively green and handling-easy hydrogen source of DME.

## Experimental

### Catalyst preparation

PdZn catalyst was prepared by coprecipitation method [9,10]. A mixed solution of  $\text{Pd}(\text{NO}_3)_2$  (Tanaka Kikinzoku Kogyo) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Wako Pure Chemical), in which Pd: Zn = 1:3 in mole, was prepared and placed in water bath at 70–80 °C. Then, drops of another solution of  $\text{Na}_2\text{CO}_3$  (Wako) were added slowly to this solution until pH of the mixture became to 8. The precipitate formed was filtered, washed with distilled water, separated by centrifuge, and dried at 110 °C. The resultant solid materials were calcined at 500 °C for 3 h. The loading of Pd was 30% by weight. Those ZnO-supported Pd samples were reduced in 4%  $\text{H}_2$  (in  $\text{N}_2$ ) at 500 °C for 1 h. Cu/ZnO catalyst was also prepared in a similar way to the case of PdZn catalyst. A solution of  $\text{Na}_2\text{CO}_3$  was placed in water bath at 70–80 °C and drops of a mixed solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in which Cu: Zn = 3: 7 in mole, were added slowly to this solution and kept for 90 min. The precipitate formed was filtered, washed with 80 °C hot water and dried in an oven at 110 °C. The materials obtained were calcined in 20%  $\text{O}_2$  (in  $\text{N}_2$ ) at 350 °C for 4 h. After cooling to room temperature, those samples were reduced in 4%  $\text{H}_2$  (in  $\text{N}_2$ ) at 230 °C for 30 min and further reduced in 100%  $\text{H}_2$  at 250 °C for 30 min. These materials were mechanically mixed with a different

amount of commercially available  $\text{Al}_2\text{O}_3$  powder (Catalysis Society of Japan, JRC-ALO1) and used for the reactions.

### Steam reforming

The steam reforming of DME was carried out in a glass fixed-bed flow reactor at atmospheric pressure. A composite catalyst including  $\text{Al}_2\text{O}_3$  and PdZn (total 0.5 g) sieved in the size of 180–250  $\mu\text{m}$  was placed in the reactor and reduced under the above-mentioned conditions. After cooling to room temperature, the reactor was purged by  $\text{N}_2$  and heated to the reaction temperature of 300 °C, then a mixture of DME and water diluted with  $\text{N}_2$ , of which the partial pressures were 0.05 and 0.15 atm, respectively, was introduced at a total flow rate of 100  $\text{cm}^3 \text{min}^{-1}$ . All the products after the reaction were analyzed by gas chromatographs with TCD and FID. The total conversion of DME was determined from the concentration measured before and after reaction. The selectivity to the carbon containing products was determined on the carbon basis and the selectivity to  $\text{CO}_2$  was used as the selectivity of DME steam reforming reaction. The  $\text{H}_2$  yield was determined from the amount of  $\text{H}_2$  formed divided by the stoichiometric maximum amount of  $\text{H}_2$  in the steam reforming of DME to be obtained under the conditions used.

## Results and discussion

The present work used a commercially available  $\text{Al}_2\text{O}_3$  powder and a laboratory-made PdZn alloy powder sieved in the size of 180–250  $\mu\text{m}$ . These powders were introduced in a glass bottle and the mixture was mechanically mixed by shaking for about 5 min. Fig. 1 displays pictures of those powders, which were used for the steam reforming of DME under different conditions.

### Influence of catalyst composition

The  $\text{Al}_2\text{O}_3$  and PdZn powders were mixed in different weight ratios, where the total weight of the two components was fixed, and used for the DME steam reforming at 300 °C. As shown in Fig. 2, when  $\text{Al}_2\text{O}_3$  was absent, the DME conversion and the  $\text{H}_2$  yield were very small since PdZn was less active for the transformation of DME to methanol. As the relative amount of  $\text{Al}_2\text{O}_3$  was increased, the conversion and the yield increased significantly and both maximized at an  $\text{Al}_2\text{O}_3$  amount of around 90%, at which the conversion and the  $\text{H}_2$  yield were about 50% and 45%, respectively, under the reaction conditions used. At larger  $\text{Al}_2\text{O}_3$  amounts, the DME

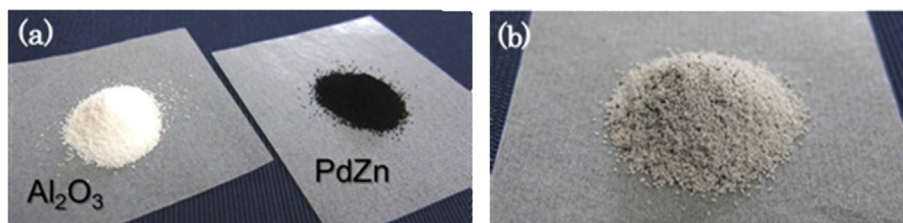


Fig. 1 –  $\text{Al}_2\text{O}_3$  and PdZn powders prepared (a) and a composite catalyst prepared by physically mixing these powders in a weight ratio of 9/1 ( $\text{Al}_2\text{O}_3/\text{PdZn}$ ) (b).

Download English Version:

<https://daneshyari.com/en/article/1275616>

Download Persian Version:

<https://daneshyari.com/article/1275616>

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