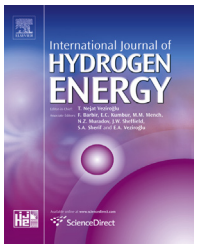
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Low-temperature steam reforming of methanol to produce hydrogen over various metal-doped molybdenum carbide catalysts

Yufei Ma [a], Guoqing Guan [a,b,*], Chuan Shi [c,**], Aimin Zhu [c], Xiaogang Hao [d], Zhongde Wang [d], Katsuki Kusakabe [e], Abuliti Abudula [a,b,*]

[a] Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan
[b] North Japan Research Institute for Sustainable Energy, Hirosaki University, 2-1-3 Matsubara, Aomori 030-0813, Japan
[c] Laboratory of Plasma Physical Chemistry, Dalian University of Technology, No.2 Linggong Road, Ganjingzi District, Dalian City, Liaoning 116024, China
[d] Department of Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China
[e] Department of Nanoscience, Sojo University, 4-22-1 Ikeda, Nishi-ku, Kumamoto 860-0082, Japan

ARTICLE INFO

Article history:
Received 18 June 2013
Received in revised form
7 September 2013
Accepted 30 September 2013
Available online 6 November 2013

Keywords:
Steam reforming of methanol
Molybdenum carbide
TPR method
Transition metal
Hydrogen production

ABSTRACT

Various transition metals (M = Pt, Fe, Co, and Ni) were selected to support on molybdenum carbides by in-situ carburization metal-doped molybdenum oxide (M-MoO_x) via temperature-programmed reaction (TPR) with a final temperature of 700 °C in a reaction gas mixture of 20% CH_4/H_2. XRD analysis results indicated that β-Mo_2C phase was formed in the case of Fe, Co, or Ni doping while α-Mo_2C phase was appeared with the β-MoC_{1-x} phase in the case of Pt doping. With the increase in Pt doping amount, more α-MoC_{1-x} phase was produced. As-prepared metal doped molybdenum carbides were investigated as alternative catalysts for the steam reforming of methanol. Comparing with the undoped molybdenum carbide such as β-Mo_2C, metal-doped one showed higher methanol conversion and hydrogen yield. It is found that Pt doped molybdenum carbide had the highest catalytic activity and selectivity among the prepared catalysts and methanol conversion reached 100% even at a temperature as low as 200 °C, and remained a long-time stability with a stable methanol conversion.

Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

In order to solve environmental problems, development of clean energy technology is becoming more and more important from now. Hydrogen is considered one of ideal and clean energy carriers. However, since it is difficult to store compressed hydrogen safely and economically, production of hydrogen using on-board reformers by the steam reforming of

* *Corresponding authors*. North Japan Research Institute for Sustainable Energy, Hirosaki University, 2-1-3 Matsubara, Aomori 030-0813, Japan. Tel.: +81 17 762 7756; fax: +81 17 735 5411.
** *Corresponding author*.
E-mail addresses: guan@cc.hirosaki-u.ac.jp (G. Guan), chuanshi@dlut.edu.cn (C. Shi), abuliti@cc.hirosaki-u.ac.jp (A. Abudula).

0360-3199/$ – see front matter Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijhydene.2013.09.150

hydrogen carrier is required. Among the different liquid hydrogen carriers available, methanol has the greatest potential when comparing with other hydrocarbon fuels because it has many advantages: it is a liquid fuel at ambient condition with a low activation temperature, a high hydrogen-to-carbon ratio, but coke (without C–C bond) and sulfur free (no sulfur) [1–3]. Hydrogen can be produced from methanol by steam reforming, auto-thermal reforming, partial oxidation or even decomposition ways. Among these methods, the steam reforming of methanol (SRM) is considered the best way due to its high hydrogen yield. The SRM reaction can be expressed as:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad \Delta H^0_{298\ K} = 49.3\ kJ/mol \tag{1}$$

In the case of using stoichiometric feed, only H_2 and CO_2 will be produced from the steam reforming of methanol theoretically. However, other gases such as methane and carbon monoxide are usually produced together with H_2 and CO_2 in the product stream, relying on the types of catalysts and the reaction conditions due to the following reactions [4–6].

$$CH_3OH \leftrightarrow CO + 2H_2 \quad \Delta H^0_{298\ K} = 91\ kJ/mol \tag{2}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H^0_{298\ K} = -41\ kJ/mol \tag{3}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H^0_{298\ K} = -206\ kJ/m \tag{4}$$

Various catalysts have been developed for SRM reaction. Cu- and Pd-based catalysts are generally used because of their low CO production [4]. It is found that addition of Zn into the Cu-based catalyst can improve the Cu dispersion [5]. However, Cu-based catalysts have poor thermal stability when the reaction temperatures are over 300 °C due to the sintering of Cu, and they also are easily deactivated by H_2S contaminates and chloride in the reactant stream [6,7]. Noble metal based SRM catalysts such as Pd/CeO_2, Pd/ZnO, Pd/Ga_2O_3, Pd/SBA-15, Au/$Ce_{1-x}Zr_xO_2$, Au/CeO_2, and Pd/Ga_2O_3 have also widely investigated and showed high activities at a temperature between 200 and 400 °C [8–14]. Recently, transition metal carbides such as tungsten carbide and molybdenum carbide have been attracted much attention because they show catalytic activities similar to those of noble metals in various reactions such as hydrogenation reactions, hydrocarbon isomerization, and methane and alcohol reforming [15–18]. Széchenyi and Solymosi prepared Mo_2C by the carburization of MoO_3 with C_2H_6/H_2 mixture and found that it is an effective catalyst for the decomposition of ethanol and methanol with a high thermal stability [19]. When Mo_2C was supported on carbon Norit, carbon nanotube, ZrO_2 and Al_2O_3, a higher catalytic activity than an unsupported catalyst was identified [1,20–22]. Furthermore, when carbides are served as supports, they could stabilize the formation of small, flat metal particles, leading to unique catalytic properties from the synergistic interaction of admetal particles and carbide substrates [23]. For instances, Lewandowski et al. dispersed Pt on the molybdenum carbide for simultaneous hydrodenitrogenation and hydrodesulfurization and found that the catalytic activitiy and stability were greatly enhanced when compared with the pure, non-modified one [24]. Griboval-Constant et al. supported Ru and Co on the molybdenum carbide for Fischer–Tropsch synthesis and also found the promotion effects [25]. However, in these studies, it should be noted that the metal was in fact supported on the passivated surface of the molybdenum carbide (i.e., oxide surface), but not on the carbide surface. In order to synthesize and characterize metal-doped carbide materials where the metals interact directly with the native surfaces of carbides, Schweitzer et al., directly deposited Pt onto the carbide surface using aqueous wet impregnation method, avoiding exposure of the carbide surface to O_2. When this catalyst was applied for water gas shift reaction, they found that it had high activity for this reaction due to the strong metal–carbide interactions and uniform Pt particle dispersion on the carbide surface [26]. When it was used for the SRM in the presence of 5 ppm H_2S, a higher degree of tolerance to sulfur during SRM was found [27]. However, this method is very complex, and it cannot be used in practical process.

In the present study, a facile method was developed to support various metals on molybdenum carbide by in-situ carburization metal-loading molybdenum oxide (M-MoO_x)

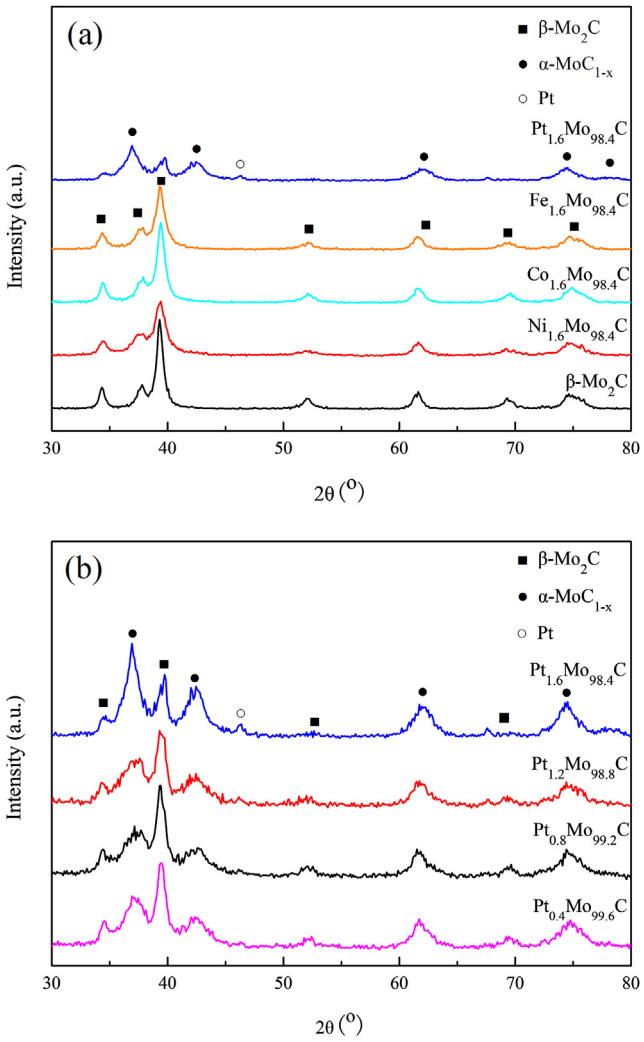


Fig. 1 – (a) XRD patterns of metal doped molybdenum carbide catalysts; (b) XRD patterns of Pt doped molybdenum carbide with different doping amount.

Download English Version:

https://daneshyari.com/en/article/1273937

Download Persian Version:

https://daneshyari.com/article/1273937

Daneshyari.com