Applied Surface Science 473 (2019) 291–297

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Catalytic activity of several carbons with different structures for methane decomposition and by-produced carbons

Haruki Nishii[a], Dai Miyamoto[a], Yoshito Umeda[b], Hiroaki Hamaguchi[c], Masashi Suzuki[c], Tsuyoshi Tanimoto[a], Toru Harigai[a], Hirofumi Takikawa[a], Yoshiyuki Suda[a]

[a] Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan
[b] Toho Cryogenics Company Limited, Chita, Aichi 456-0004, Japan
[c] Aichi Center for Industry and Science Technology, Kariya, Aichi 470-0536, Japan

ARTICLE INFO

Keywords:
Methane decomposition
Raman spectroscopy
Activation energy
Hydrogen production
Carbon black
Activated carbon

ABSTRACT

Since methane decomposition has no CO_2 emissions, it is attracting attention as a hydrogen production method with a low environmental burden. Understanding the structure of the produced carbon is important for long-term stable production of hydrogen. In this study, methane decomposition was carried out on carbons with several different structures (activated carbon (AC), carbon black (CB), meso-porous carbon (MC), and carbon nanofiber (CNF)). We have found that the carbon produced by methane decomposition decreases activity by covering the catalyst, but itself also acts as a catalyst irrespective of the original carbon catalysts. All of the catalysts continued to maintain a methane conversion ratio of about 17% by catalyzing the produced carbon even after the activity was lowered. By analysis of the catalysts before and after the experiment, it was shown that the produced carbon covered the catalyst surface and resulted in a specific surface area of about 10 m^2/g and the intensity ratio of the D band to the G band in the Raman spectra (I_D/I_G) of around 1.55 irrespective of the original carbons structures. We proposed that Raman spectroscopy is an effective method for evaluating initial catalytic activity for methane decomposition because I_D/I_G of the catalysts before the experiment have a linear relationship with the methane conversion ratio per unit surface area in the early stage of the reaction.

1. Introduction

Hydrogen utilization technology including fuel cells that are characterized by high energy efficiency and no CO_2 emission at the utilization stage, can contribute to energy saving and environmental burden reduction. Furthermore, the market size of hydrogen related technology is predicted to be about 1 trillion Japanese Yen by 2030 and about 8 trillion Japanese Yen by 2050 in Japan, making it an important technology. On the other hand, there are many problems in hydrogen utilization: safety, cost, and infrastructure [1,2]. There is a possibility that part of the problem can be solved by on-site hydrogen production using natural gas. By using an existing natural gas supply line, hydrogen transportation is safe and of low cost because it does not require the direct transportation of hydrogen and the laying of new supply lines [3].

The main component of natural gas is methane. Various methods for hydrogen production using methane have been proposed: (a) steam methane reforming, (b) partial oxidation, and (c) autothermal reforming [4,5,6]. However, since all of these hydrogen production methods involve the emission of CO_2, CCS (carbon dioxide capture and storage) is required, which leads to a cost increase. Therefore, methane decomposition without CO and CO_2 emission attracts attention as a promising hydrogen production method.

Methane is decomposed into carbon and hydrogen according to the following reaction [7]:

$$CH_4 = C(s) + 2H_2 \quad \Delta H^\circ = 75.6 \text{kJ/mol} \tag{1}$$

Various noble metals such as Ni, Cu, and Fe have been used as catalysts for methane decomposition [8,9,10,11,12,13,14]. However, when these noble metals are used as a catalyst, these catalysts are covered by the deposition of carbon produced by the process, so that a regeneration process accompanied by CO_2 emission by carbon combustion is required.

In recent years, the use of carbons as a catalyst with a lower cost than metal catalysts have attracted attention [15,16,17]. Compared to metal catalysts, carbon catalysts have advantages such as high temperature tolerance, resistance to impurities such as sulfur, and possibility of further cost reduction due to commercial use of high purity carbon [18,19].

Various carbons have been used as catalysts for methane

E-mail address: suda@ee.tut.ac.jp (Y. Suda).

https://doi.org/10.1016/j.apsusc.2018.12.073
Received 9 May 2018; Received in revised form 29 August 2018; Accepted 8 December 2018
Available online 10 December 2018
0169-4332/