



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Water gas shift activity of Au–Re catalyst over microstructured cordierite monolith wash-coated by ceria

Göktuğ N. Özyönüm^{a,b}, Ramazan Yıldırım^{a,*}

^a Department of Chemical Engineering, Boğaziçi University, 34342 Bebek, İstanbul, Turkey

^b TUBITAK Marmara Research Center Energy Institute, 41470 Gebze, Kocaeli, Turkey

ARTICLE INFO

Article history:

Received 4 December 2015

Received in revised form

3 February 2016

Accepted 4 February 2016

Available online 4 March 2016

Keywords:

Water-gas shift

Gold catalysts

Ceria

Monoliths

Microstructured catalyst

ABSTRACT

Water-gas shift (WGS) activity of 1.4 wt.% Au–0.2 wt.% Re/CeO₂ catalyst was investigated over microchannel cordierite monolith as a low pressure drop and easy to miniaturize reactor structure for small size applications like fuel processors. The catalyst was prepared by wash-coating the colloidal ceria, which is believed to be one of the best support for WGS, over the wall of cordierite monolith followed by depositing Au and Re using homogeneous deposition–precipitation (HDP) method; then the WGS activity of the catalyst was tested in a microflow reactor. The SEM-EDS and ICP characterization tests were also performed. Initially, the monolithic Au/CeO₂ had lower performance than the particulate catalyst but its activity improved significantly by adding Re as promoter and making some modifications in HDP method. Then 10% CO₂ and 25% H₂ was introduced to the feed (both separately and together) to simulate a realistic feed from a fuel processor, and both equilibrium and actual CO conversions were decreased as expected; however, the performance of monolithic Au–Re/CeO₂ was still satisfactory indicating that this structure could have a potential for small scale medium temperature WGS applications.

Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen is an important raw material for various applications including refineries, petrochemical industries, ammonia synthesis and hydrocarbon production through Fischer–Tropsch type processes together with CO in the form of synthesis gas [1]. It is also believed that hydrogen will play an important role in clean energy production in the future as the fuel for the fuel cells [2,3].

The water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is usually used as an additional step in hydrogen production from hydrocarbons or coal to eliminate CO in hydrogen stream (and produce additional hydrogen) or to adjust the H₂/CO ratio of synthesis gas so that it would be more suitable to produce a specific hydrocarbon product. Besides, WGS is also utilized in automobile exhaust systems to eliminate CO while the hydrogen produced during this process is used as an effective reductant for NO_x removal [4–6].

* Corresponding author. Tel.: +90 212 3597248; fax: +90 212 2872460.

E-mail address: yildirra@boun.edu.tr (R. Yıldırım).

<http://dx.doi.org/10.1016/j.ijhydene.2016.02.025>

0360-3199/Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

The WGS is an equilibrium-controlled and mildly exothermic reaction; it is an industrially well-established process which is typically executed in two stages: high-temperature shift (HTS) at 300–400 °C over Fe–Cr based catalysts and a low-temperature shift (LTS) at 200–260 °C over Cu–Zn based catalysts [7,8]. In recent years, however, there have been significant efforts to develop new catalysts to carry out WGS reaction in single stage at mild conditions to purify hydrogen stream produced in the fuel processor of fuel cell systems [9,10]. Supported gold catalysts, formed by dispersion of nano-sized gold particles over a suitable support have been extensively studied in recent years due to their remarkably high WGS activity at low temperatures; the ceria seem to be the best support that can be used for this purpose [9,11]. It is believed that the ceria affects the dispersion of active metal and enhance the WGS activity through its redox properties and oxygen storage capacity [12,13].

The studies have also shown that the WGS activity and stability increase if two metals are used together; many bimetallic systems such as Pt–V/CeO₂, Pt–Re/CeO₂–ZrO₂ and Au–M on iron (III) oxide (M = Ag, Bi, Co, Cu, Mn, Ni, Pb, Ru, Sn and Tl) have been studied for this purpose and they have been found to increase the rates of WGS reactions [14–19]. It was recently reported that Re addition also improved the WGS activity of Au/ceria catalysts [20].

The growing interest for miniaturization of the reactors seems to be also important for WGS reactions especially for fuel cell applications [21,22]. The fuel processor for mobile and small scale stationary applications should be in manageable size, and the traditional WGS reactor occupies the largest volume of the system with high pressure drops [23,24]. The use of microchannel reactors such as wash-coated monoliths may be highly beneficial for this purpose because they cause significantly lower pressure drops than the packed reactors, and they can be easily miniaturized by simply decreasing number of channels [25]. However, there are only limited number of works on WGS over monolithic Pt based catalysts [21,23,26–28]; and as far as we know, there is no work reported for WGS over monolithic Au in the presence of CeO₂, which is one of the most promising support material for this reaction; as a matter of fact we are aware of only one work in the literature for WGS over monolithic gold catalysts, which involves Fe₂O₃ as the support material [3].

In this work, a monolithic Au–Re/CeO₂ catalyst was prepared by wash-coating the colloidal ceria over cordierite monolith followed by sequentially depositing Re and Au over wash-coated monoliths by applying homogeneous deposition–precipitation (HDP) technique, then the WGS activity of the catalyst was tested in a microflow reactor; SEM-EDS and ICP characterization tests were also performed.

Experimental

Catalyst preparation

Particulate catalysts

Ceria support was prepared by deposition–precipitation (DP) of cerium nitrate using Na₂CO₃. It was then vacuum dried overnight at 75 °C and calcined at 400 °C for 4 h. Au/ceria

catalysts were prepared by DP or HDP technique. In the DP technique, which was carried out under fully controlled conditions (pH, stirring speed and temperature), ceria was suspended in deionized (DI) water at a pH of 8. The pH was adjusted by adding aqueous Na₂CO₃ solution. Subsequently, the desired amount of HAuCl₄·3H₂O solution was added dropwise under vigorous stirring and then the precipitate was aged for 1 h, filtered and washed with hot DI water. The filtrate was then dried overnight at 75 °C under vacuum and calcined at air in a muffle furnace at 400 °C for 4 h. In the HDP technique, urea was used as precipitating agent. Ceria was first suspended in DI water followed by the addition of an aqueous HAuCl₄·3H₂O solution dropwise under vigorous stirring. After heating, solution pH was gradually increased to 7 by the decomposition of urea. The solutions were aged at 70 °C for 1 h. Afterwards the catalyst was filtered, washed with hot DI water and vacuum dried. Finally, the same drying and calcination conditions were applied as the DP method.

Monolithic Catalysts

Thin-wall commercial cordierite substrates with 400 cpsi (cell per square inch) were cut into cylinders of 10 mm diameter and 20 mm length (Fig. 1) and washed with acetone in order to open the pores and remove the impurities; then they wash-coated with ceria by dipping vertically into the colloidal ceria solution (18 wt.% CeO₂ in water) for 2 min. The excess solution was evacuated from the channels of the cylinders by a flow of compressed air, and they were dried again in a microwave oven. The dipping–drying procedure was repeated until a 13–15 wt.% increase was observed in the monoliths. Finally, the coated monoliths were calcined in air at 400 °C for 4 h, after heating with a temperature ramp of 2 °C/min. The Au loading was performed using DP or HDP methods. Catalyst preparation by DP was conducted in the same way with the powder Au/ceria catalyst. In the case of HDP, two alternative preparation schemes were used. In the first scheme (method 1), the monolith samples wash-coated with ceria were first immersed in water followed by the addition of an aqueous HAuCl₄·3H₂O solution under vigorous stirring. Solution pH was gradually increased to 7 by the decomposition of urea. The solutions were aged at 80 °C for 1 h. Afterwards, the

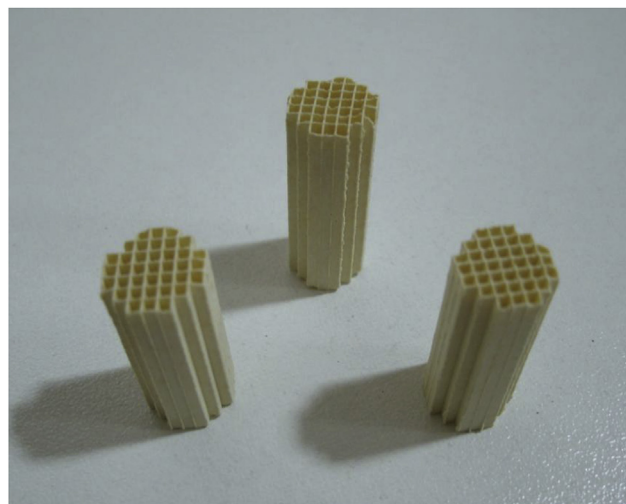


Fig. 1 – Cordierite monolith pieces used as support.

Download English Version:

<https://daneshyari.com/en/article/1268792>

Download Persian Version:

<https://daneshyari.com/article/1268792>

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