



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

The significant role of oxygen vacancy in Cu/ZrO₂ catalyst for enhancing water–gas-shift performance

Chongqi Chen, Chunxiao Ruan, Yingying Zhan, Xingyi Lin, Qi Zheng*, Kemei Wei

National Engineering Research Center of Chemical Fertilizer Catalysts, Fuzhou University, Gongye Road 523, Fuzhou, Fujian 350002, PR China

ARTICLE INFO

Article history:

Received 8 August 2013

Received in revised form

30 September 2013

Accepted 14 October 2013

Available online 16 November 2013

Keywords:

Cu/ZrO₂

Water gas shift

Oxygen vacancy

Preparation method

ABSTRACT

Three Cu/ZrO₂ catalysts were synthesized utilizing co-precipitation (CP), deposition–precipitation (DP) and deposition–hydrothermal (DH) methods, respectively. The micro-structure and texture of those catalysts are characterized by means of XRD, SEM, N₂-physisorption, Raman and EPR characterizations. It is demonstrated that different morphologies and textures of ZrO₂ are formed, and the micro- and crystal structure of Cu nanoparticles as well as the concentration of oxygen vacancies of ZrO₂ are distinguish from each other. In addition, H₂-TPR technique is employed to investigate the reducibility properties of the as-synthesized Cu/ZrO₂ catalysts. It is found that the synergy interaction between Cu–ZrO₂ obtained by the DH method is the strongest, owing to the possession of the largest amount of oxygen vacancies. Furthermore, their catalytic activities with respect to the water gas shift reaction are also performed, and the Cu/ZrO₂-DH shows high catalytic activity, the reasons are the well dispersion and small crystallite size of Cu, the largest amount of oxygen vacancies, as well as the strongest interaction between Cu–ZrO₂.

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

1. Introduction

The three-pronged challenges for the 21st century are risking environment pollution, irreversible global climate change and uncertain oil supply [1]. Hydrogen is one of the promising energetic carriers for mobile and/or residential fuel cell, and possesses the merits of: (1) sustainable fuel resource, i.e. steam reforming of biomass and electrolysis of water; (2) much easier to be stored and transported compared with wind or solar energy; (3) no air pollutant and greenhouse gas emissions [2,3] during the burning of hydrogen. Therefore, widespread attentions have been focused on it, aiming to

reduce our dependence on fossil fuels and environment pollution [4,5].

As concerning with the hydrogen generation, a number of methods have been explored that can roughly be cataloged as: (1) hydrolysis of borohydride [6]; (2) reaction of Al with water [7]; (3) photocatalytic water-splitting [8]; (4) steam reforming of natural gas and/or biomass [9]. Among all these methods, steam reforming of natural gas, to date, is still the predominant way for hydrogen generation [10]. For the steam reforming of natural gas, water gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, $\Delta H = -41.1 \text{ kJ/mol}$) is implemented to enrich H₂ concentration and eliminate CO. In the recent two decades, due to the keen

* Corresponding author. Tel.: +86 591 8373 1234 8112; fax: +86 591 8373 8808.
E-mail address: zhengqi@fzu.edu.cn (Q. Zheng).

demand of hydrogen for fuel cells, renewing interests have been focused on exploring promising catalysts that are suitable for the WGS reaction in fuel cell applications [11,12].

Both precious metal (e.g. Pt, Au or Ru) and non-precious metal (e.g. Cu or Ni) based catalysts have been widely examined. Various oxides are chosen as support, such as CeO₂ [13], Al₂O₃ [14], TiO₂ [15], ZrO₂ [16], and their complex, like CeO₂–ZrO₂ [17], CeO₂–La₂O₃ [18] and so on. Considering the high cost of the precious metals, more and more attentions have been focused on the non-precious ones. The Cu-based catalysts have found to be shown high WGS activity and stability in low and medium temperature (200 °C–300 °C) [13,19], and have also been widely employed. Besides, ZrO₂ has also been widely used as a support for Cu-based catalysts in the field of methanol synthesis [20], steam reforming of methanol [21], etc. because it can activate and stabilize copper particles; meanwhile, the used of ZrO₂ as a support for precious metal, like Pt [22] and Au [23], in the WGS reaction has also been well documented. Therefore, it is reasonable to consider that the ZrO₂ supported Cu catalyst would show good catalytic performance for the WGS reaction.

Cu/ZrO₂ catalyst for the WGS reaction was first reported by Ko et al [24], it was found that the catalytic performance of Cu/ZrO₂ catalyst was depending on the loading amount of Cu. The influence of the crystalline structure of ZrO₂ on the activity of Cu/ZrO₂ catalyst in the WGS reaction was investigated by Agulia and co-workers [25], and it was concluded that the activity of copper supported on tetragonal ZrO₂ is much higher than the one supported on monoclinic ZrO₂. DFT calculation of Cu/ZrO₂ catalyst was performed by Tang et al. [26] for the WGS reaction, and the catalytic active site was supposed to be in the vicinity of Cu/oxides interfaces and the ZrO₂ support acts as a charge buffer to accept/release electrons from/to the Cu particle. It was reported that oxygen coordinatively unsaturated Zr sites, i.e. oxygen vacancy, is easy to be generated by calcination of ZrO₂, especially in the reduction atmosphere [27], however, the function of oxygen vacancy in the Cu/ZrO₂ catalyst for the WGS reaction has not been well studied.

Herein, in an attempt to develop efficient binary Cu/ZrO₂ catalysts with different amount of oxygen vacancies for the WGS reaction, a series of Cu/ZrO₂ catalysts were fabricated by means of three different preparation methods including Co-precipitation (CP), Deposition–precipitation (DP) and Deposition–hydrothermal (DH) method, and their catalytic performances for WGS reaction were also investigated. The chemical and physical properties of those catalysts were characterized by XRD, SEM, Raman, N₂-physisorption, EPR and TPR techniques, special attention is paid to the effect of preparation methods on the generation of oxygen vacancy for Cu/ZrO₂ catalysts and the relationship between the physico-chemical properties and catalytic performances.

2. Experimental method

2.1. Catalysts preparation

2.1.1. Materials

Zirconium oxychloride (ZrOCl₂·8H₂O), Copper (II) nitrate (Cu(NO₃)₂·3H₂O) and Potassium hydroxide (KOH) are all analytical grades and used without further purification.

2.1.2. Synthesis

The Cu/ZrO₂ catalysts with copper content of 25 wt% (calculated by CuO) were prepared by three different methods. **For the co-precipitation method (CP)**, a certain amount of ZrOCl₂·8H₂O and Cu(NO₃)₂·3H₂O were dissolved in 300 mL deionized water in a four-neck flask, and then KOH solution (0.5 mol/L) was added dropwise at 65 °C under vigorous stirring until the pH = 10, after that, the suspension was maintained at 65 °C for another 1.5 h, washed with deionized water until pH value of supernatant is neutral. **For the Deposition–precipitation method (DP)**, the support was firstly synthesized by co-precipitation method, typically, 150 mL ZrOCl₂·8H₂O solution was first put in a four-neck flask, following by adding KOH aqueous solution (0.5 mol/L) dropwise at 65 °C under vigorous stirring until the pH = 10, subsequently by maintaining the suspension at 65 °C for another 1.5 h, washing with deionized water until pH value of supernatant is neutral, dried at 120 °C for 8 h, and then calcined at 350 °C for 4 h; **secondly**, the CuO was deposited: 4.5 g of the above-synthesized ZrO₂ was dispersed in 300 mL of deionized water, and a certain amount of Cu(NO₃)₂·3H₂O was added, and then KOH aqueous solution (0.5 mol/L) was added dropwise at 65 °C under vigorous stirring until the pH = 10, after that, the suspension was maintained at 65 °C for another 1.5 h, washed with deionized water until pH value of supernatant is neutral. **For the Deposition–hydrothermal method (DH)**, the support was prepared by hydrothermal method according to the literature protocols [16], in detail, 60 mL ZrOCl₂·8H₂O aqueous solution (0.4 mol/L) was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 150 °C for 6 h, the resultant precipitate was then washed thoroughly with deionized water, dried at 120 °C for 8 h and calcined at 350 °C in static air for 4 h; afterwards, CuO was deposited same as the DP method. All the as-prepared precursors were further dried at 120 °C for 12 h, and then calcined at 300 °C for 2 h (heating rate was 5 °C/min) purging with hydrogen. The as-obtained products are denoted as Cu/ZrO₂-CP, Cu/ZrO₂-DP and Cu/ZrO₂-DH, respectively.

2.2. Characterizations

The powder X-ray diffraction (XRD) patterns of the samples were recorded by a PANalytical X' Pert Pro diffractometer using Co K α radiation ($\lambda = 0.179$ nm) at 40 kV and 40 mA. Their morphologies were investigated by Field Emission Scanning Electron Microscope (FE-SEM, Hitachi-S4800). Raman spectra were collected at room temperature on a Renishaw Invia Plus instrument using a semiconductor laser as an illumination source (532 nm). To determine the textural properties of the as-prepared samples, nitrogen adsorption–desorption measurements were carried out at 77 K using a Micrometrics ASAP 2020 system after the sample was degassed at 200 °C in a vacuum for 4 h. Temperature-programmed reduction (TPR) measurement was carried out on an AutoChem 2910 instrument. The H₂-TPR was performed by passing 10 vol.% H₂/Ar (flowing rate = 30 mL/min) on 50 mg catalyst at a heating rate of 10 °C/min. Prior to the measurement, the samples were pretreated under Argon atmosphere at 200 °C for 30 min, then the system was cooled to ambient temperature purging

Download English Version:

<https://daneshyari.com/en/article/1273943>

Download Persian Version:

<https://daneshyari.com/article/1273943>

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