

Available online at www.sciencedirect.com

ScienceDirect

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

Development and performance of a K–Pt/ γ -Al₂O₃ catalyst for the preferential oxidation of CO in hydrogen-rich synthesis gas

Yajun Zhang^a, Shuimu Wu^b, Lian Jin^b, Donglai Xie^{a,*}

^aMOE Key Laboratory of Enhance Heat Transfer & Energy Conservation, South China University of Technology, Guangzhou 510640, China

^bThe Key Laboratory of Fuel Cell Technology of Guangdong Province, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO

Article history:

Received 24 October 2013

Received in revised form

18 January 2014

Accepted 4 February 2014

Available online 22 February 2014

Keywords:

PEMFC

CO deep removal

Preferential oxidation

K–Pt/Al₂O₃ catalyst

ABSTRACT

Proton exchange membrane fuel cells are widely employed in micro combined heat and power cogeneration (micro-CHP) systems, and the feed to them should be essentially free of CO. CO preferential oxidation is an effective method for the thorough removal of CO from synthesis gas. A series of K–Pt/ γ -Al₂O₃ catalysts are prepared and tested for their CO cleaning capabilities. The catalyst is prepared from potassium nitrate acid, chloroplatinic acid and γ -Al₂O₃ powder by normal or ultrasonic impregnation. The catalyst performance is investigated in a micro-reactor system. The effects of K loading, Pt loading, ultrasonic processing, space velocity, O₂-to-CO ratio and operation temperature on catalyst performance are studied. A CO concentration of less than 10 ppm is achieved when the CO concentration in the feed gas is 0.45%. It was found that both ultrasonic processing and the addition of K promote the catalyst performance. The 15K1.0Pt/Al–U catalyst exhibits the best performance.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Proton exchange membrane fuel cells (PEMFCs) have received much attention because of their advantages, including low operating temperature, long life, high energy conversion density and quick start-up. This type of fuel cell demands a feed gas CO concentration below 10 ppm to avoid poisoning the Platinum-based anode catalysts. Micro combined heat and power cogeneration (micro-CHP) systems for residential and small business applications are one of the important applications of fuel cells. There are several methods to remove CO from hydrogen-rich gases, including

physical methods, such as pressure swing adsorption [1,2] and membrane separation [3,4], and chemical methods, such as water gas shift, CO methanation and CO preferential oxidation [5,6]. Considering the small scale and small footprint requirement of the micro-CHP applications, a physical method for CO cleaning may not be feasible. Preferential oxidation (PROX) is one of the most effective methods to thoroughly remove CO from the synthesis gas. PROX refers to converting CO to CO₂ with the minimal consumption of hydrogen. The catalyst plays a significant role in strengthening the CO oxidation and inhibiting hydrogen oxidation. Developing a catalyst with good performance for thorough CO cleaning from H₂-rich fuel gas at low temperatures is

* Corresponding author. Tel./fax: +86 20 22236985.

E-mail addresses: dlxie@scut.edu.cn, donglaixie@163.com (D. Xie).

crucial for the development of PEMFC-based micro-CHP systems.

Noble metals are commonly used in CO-PROX catalysts. The performance of noble metal catalysts such as Platinum (Pt), Rhodium (Rh), Ruthenium (Ru) and Iridium (Ir) has been reported in recent years [7–11]. Pt and Pt-supported catalysts are most commonly used for CO preferential oxidation reactions and have better catalytic properties than other noble metal catalysts. The addition of alkali metals over Pt/Al₂O₃ has been reported to have both positive and negative effects on the catalytic performance [12,13]. Studies on the effect of the addition of potassium (K) illustrate that the addition of K can promote the CO oxidation activity and enhance the catalyst performance, where the promotion effects are related to the catalyst preparation method and the K content [14–17]. Pt/Al₂O₃ and Cerium-modified Pt/Al₂O₃ catalysts show relatively high activity and selectivity for CO-PROX [18–20]. Studies on the Pt–Fe/mordenite catalysts indicate that Pt–Fe/mordenite catalysts have good catalytic properties, even in the presence of H₂O [21–23].

A KW-scale fuel cell based micro-CHP system consisting of a fuel-processing unit, a power generation unit and an auxiliary unit is being designed and developed in the New Energy Group of South China University of Technology [24]. Natural gas has been selected as the fuel for hydrogen production by steam reforming. The CO in the synthesis gas is cleaned by a high-temperature water gas shift reactor, in which its concentration is reduced to 2.0–4.0%, and a low-temperature water gas shift reactor, in which its concentration is reduced to 0.3–0.6%. A CO preferential oxidation reactor is selected to further reduce the CO concentration to below 10 ppm before it enters the fuel cell stack. Due to the lack of commercial CO preferential oxidation catalyst, it has to be developed in house. Aluminum supported Pt-based catalysts are selected as they are most commonly used for CO preferential oxidation reactions and have better catalytic properties than other noble metal catalysts. Studies from Minemura et al. [25] show that the additive effect of potassium on Pt catalysts was remarkable over Al₂O₃ and the CO concentration was decreased to be below 10 ppm for a typical feed gas composition of 0.2%CO, 0.2%O₂, 75%H₂ and He in balance. Hence a series of K–Pt/γ-Al₂O₃ catalysts have been prepared and tested for their CO cleaning capabilities.

Catalyst preparation, characterization and performance evaluation

Catalyst preparation

The Pt/γ-Al₂O₃ catalyst is prepared from chloroplatinic acid (H₂PtCl₆·6H₂O) and γ-Al₂O₃ powder and the K–Pt/γ-Al₂O₃ catalyst is prepared using KNO₃ as well. The Pt/γ-Al₂O₃ catalyst is prepared by impregnating the γ-Al₂O₃ powder (supplied by Tianjin Chemical Research & Design Institute, Tianjin, China) with the desired amount of an aqueous solution of H₂PtCl₆·6H₂O (Shanghai Chemical Reagent Research Institute, Shanghai, China) in a glass beaker under slow stirring for 30 min, after which the solution is allowed to stand for 24 h. When ultrasonic impregnation is preferred, the beaker is placed in the water bath of an ultrasonic cleaner for 1 h before

standing for 24 h. The catalyst is then dried in an electrically heated oven at 110 °C for 5–6 h and calcined in air at a given temperature (500, 550 or 600 °C) for 3 h in a muffle oven. The Pt/γ-Al₂O₃ catalyst can be modified with K by ultrasonically impregnating the dried sample with an aqueous solution of KNO₃ (Guangzhou Chemical Reagent Company, Guangzhou, China). The modified catalyst is then dried again at 110 °C for 12 h and calcined at 500 °C for 3 h.

All of the catalysts were reduced with hydrogen under 350 °C for 3 h in the reactor before the performance evaluation. The prepared catalysts are listed in Table 1.

Catalyst characterization

After being prepared, the catalysts are characterized by several instruments. X-ray diffraction (XRD) is performed with a D8 Advanced Bruker diffractometer. Temperature-programmed reduction (TPR) experiments are carried out on a Micrometrics tp-5080 automatic multi-purpose adsorption instrument (Xianquan company, Tianjin, China). 50 mg of a catalyst is loaded into a quartz reactor and pretreated in high purity nitrogen under 500 °C for 1 h to remove impurity. After cooling to room temperature, the flowing gas is switched to a 10 vol% H₂/N₂ mixture, and the catalyst is heated to 500 °C at a ramping rate of 10 °C per minute.

Catalyst performance evaluation

The catalyst performance is studied in a micro-reactor system, where the micro-reactor is an 8-mm-inner-diameter stainless steel tube in which the feed gas is introduced from the top and flows downward. First, 500 mg of the catalyst is loaded in the reactor. A bottle of synthesis gas (molar composition: CO 0.45%, CH₄ 0.34%, CO₂ 16.55%, H₂ 50.25% and N₂ in balance) is employed to simulate the hydrogen-rich gas downstream of the water gas shift reactors in the micro-CHP system. Bottled air is used to provide the oxidant to the reactor. Bottled nitrogen is employed to purge the evaluation system prior to experiments. Bottled hydrogen is used for catalyst reduction. All gas streams are controlled by mass flow controllers. The CO and O₂ concentrations in the outlet gas are analyzed using online gas chromatography (GC). The catalyst performance is characterized by CO conversion (X) and CO selectivity (S), which are defined as

$$X = \frac{[\text{moles of CO reacted}]}{[\text{moles of CO in the feed}]} \times 100\% \quad (1)$$

$$S = \frac{0.5 \times [\text{moles of CO reacted}]}{[\text{moles of O}_2 \text{ reacted}]} \times 100\% \quad (2)$$

Results and discussion

Influence of the preparation methods on catalyst performance

Effect of Pt loading

Pt loading is expected to have a significant impact on the catalyst performance. Catalysts with low Pt loading may not

Download English Version:

<https://daneshyari.com/en/article/1280881>

Download Persian Version:

<https://daneshyari.com/article/1280881>

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