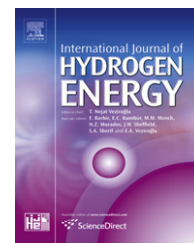


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Carbon nanotube supported Pt–Ni catalysts for preferential oxidation of CO in hydrogen-rich gases

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ARTICLE INFO

Article history:

Received 31 August 2010

Received in revised form

12 October 2010

Accepted 9 November 2010

Available online 16 December 2010

Keywords:

Preferential oxidation

Carbon nanotube

Platinum

Nickel

Carbon monoxide

Hydrogen

ABSTRACT

A series of carbon nano-tubes supported platinum-nickel catalysts were prepared and used for CO preferential oxidation in H₂-rich streams. The catalysts were characterized by using N₂-adsorption, XRD, HRTEM, H₂-TPD and H₂-TPR techniques. Effects of platinum and nickel loading amount, CO₂ and H₂O in the feed stream on the activity and selectivity over the catalysts were investigated. The results of catalytic performance tests show that the carbon nano-tubes supported Pt–Ni catalysts are very active and highly selective at low temperature for CO preferential oxidation in 1 vol. % CO, 1 vol. % O₂, 50 vol. % H₂ and N₂ gases. Adding 12.5 vol. % of CO₂ into the feed gases has slight negative influence on CO conversion. Adding 15 vol. % of H₂O leads to a little decrease of CO conversion at the temperature range of 100–120 °C, which is proposed to be caused by capillary wetting of water in the micro-pores of carbon nano-tubes. As the reaction temperature is higher, adding water can improve CO conversion. The characterization results indicate that platinum species are in nano-particles uniformly dispersed on the carbon nano-tubes surface. There are two kinds of nickel species, one is interacted with platinum and likely to form Pt–Ni alloy in reduction process, the other is much highly dispersed on carbon nano-tubes and strongly interacted with the supports. The high activity of the catalysts is attributed to the interaction between Pt and Ni with the formation of Pt–Ni alloy.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) with hydrogen-rich gases as the fuel have been attracted great attention as a kind of clean and efficient energy equipment [1]. The H₂-rich gases are mainly produced via catalytic reforming of hydrocarbons and followed by water–gas-shift (WGS) process [2–4]. The resultant H₂-rich gases generally contain 0.5–1.0 vol.% of CO due to the thermodynamic limitation of WGS reaction [5]. Unfortunately, small amount of CO has a significant negative effect on the anodic Pt electrode of PEMFCs. Thus, purifying CO to ppm level is required prior to introduction of hydrogen to

PEMFCs [6]. Among the methods for CO removal, the preferential oxidation of CO (CO-PROX) is recognized as a simple and cost-effective way [7].

So far, the catalysts studied for CO-PROX can be clarified into base metal oxide catalysts, such as CuO–CeO₂ [8], Co/SrCO₃ [9], and Co₃O₄–CeO₂ [10], and noble metal catalysts, such as Pt [11], Au [12,13], Rh [14], Ru [15] and Pd [16]. The base metal oxide catalysts are generally highly active and selective, however they are sensitive to the deactivation by H₂O and CO₂ [17]. Among the noble metal catalysts, Pt-based catalysts [18–23] especially nickel or cobalt promoted platinum catalysts [24,25] are the most promising. Pt-based catalysts exhibit

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doi:10.1016/j.ijhydene.2010.11.029

high activity at comparatively higher temperature of around 200 °C, and their resistance to H₂O and CO₂ deactivation is also need to be further improved [21].

The supports reported for Pt-based catalysts include CeO₂, Al₂O₃, SiO₂, and zeolite [20,23,26,27]. Activated carbon as the support has also been investigated [28,29]. Although these oxides supported Pt-based catalysts show very good catalytic performance for the CO removal, it is still a hard work for the removal of CO to under 10 ppm. A main reason is that CO oxidation is an exothermic reaction which may lead to generate hotspots in the catalysts, and on the hotspots reverse WGS reaction may be induced. Reverse WGS reaction is endothermic and produces CO so influencing the net removal of CO. Şimsek et al. [29] have reported that activated carbon supported Pt–SnO_x and Pt–CeO₂ exhibited very good catalytic performance for CO-PROX, over which CO could be purified to lower than 100 ppm in H₂-rich gases containing CO₂ and H₂O, suggesting that developing catalysts to purify CO to ppm level is still a significant work.

Carbon nano-tubes (CNTs) have attracted much attention from both a fundamental and an applied perspective since their discovery [30,31], owing to their special structure, high mechanical strength, unique electronic properties and high thermal conductivity. Using these new materials as catalyst supports for some reactions has already been reported [32,33]. Owing to the high thermal conductivity of CNTs, hotspots formation in the CNTs supported catalysts may be restrained and thus reverse WGS reaction may be mitigated. However, carbon nano-tubes as catalyst supports for CO-PROX reaction have been rarely reported. Tanaka KI and co-workers found that CNTs supported platinum catalysts with high loading of platinum of 15 wt.% are very active for CO-PROX reaction at room temperature in reaction mixture of 2.5 vol.% CO, 2.5 vol.% O₂, 25 vol.% H₂ and N₂ balance [34,35]. In their work, the influence of CO₂ and H₂O on the catalytic performance was not shown.

In this work, CNTs supported Pt–Ni catalysts were prepared and used for CO-PROX. The influences of CO₂ and H₂O, the loading amount of platinum and nickel in the catalysts on the catalytic performance were investigated. The catalysts exhibited high activity at low reaction temperature and very good resistance to CO₂ and H₂O.

2. Experimental

2.1. Preparation of catalysts

The aligned multi-wall carbon nano-tubes with purity higher than 95 wt.% were purchased from Shenzhen Nanotech Port Co. Ltd. The diameter and length of the CNTs are 10–20 nm and 5–15 µm, respectively. The as-received CNTs were refluxed at 100 °C for 4 h in concentrated H₂SO₄/HNO₃ (3:1, v/v, 98 wt.% and 67 wt.%, respectively), so as to increase its hydrophilicity by forming carboxyl functional groups. Then, the oxidized CNTs were filtered and washed with distilled water until the pH value reached 7 and then dried overnight at 60 °C. Thus resultant carbon nano-tubes were signed as CNTs-OX.

Pt–Ni/CNTs-OX catalysts were prepared by wet co-impregnation with aqueous solutions of Pt(NH₃)₂(NO₃)₂ and Ni(NO₃)₂·6H₂O. The atomic ratio of Pt/Ni is 1:5 in all the samples.

Typically the catalysts were prepared as follows. 200 mg of the CNTs-OX was dispersed into 40 mL of distilled water and sonicated for 40 min. Then solution containing desired amount of Pt(NH₃)₂(NO₃)₂ and Ni(NO₃)₂·6H₂O was added into the CNTs-OX suspension. The resultant mixture was sealed and then placed into a water bath at 70 °C, being stirred for 20 h. Subsequently, the mixture was frozen to 0 °C and maintained at 0 °C for 12 h. Then, it was freeze-dried for 12 h in vacuum for further use. Samples with different loading amounts of platinum were prepared, namely 1 wt.%, 2 wt.% and 4 wt.% of Pt in the catalysts and the corresponding weight amounts of Ni are 1.5%, 3% and 6%, respectively. For comparison, 2 wt.% Pt/CNTs-OX and 3 wt.% Ni/CNTs-OX were also prepared with the same procedures.

2.2. Catalyst characterizations

Nitrogen adsorption and desorption isotherms were determined on a Micromeritics apparatus of model ASAP-2020 at –196 °C. The specific surface areas were calculated by the BET method and the pore size distributions were calculated from the desorption branches of the isotherms by using BJH model. Before analysis, the prepared catalysts were pre-reduced at 300 °C in 62.5 vol.% H₂/N₂ for 2 h with a heating rate of 10 °C min^{–1}.

X-ray diffraction (XRD) patterns of the reduced catalysts were obtained on a Rigaku D/max 2500v/Pc X-ray diffractometer with Ni filtered Cu-Kα radiation (λ = 0.15406 nm).

The morphology of the catalysts was observed with transmission electron microscopy (TEM) on a Technai G² F20 microscope operated at 200 kV. Samples were pre-reduced at 300 °C in 62.5 vol.% H₂/N₂ for 2 h, then finely grounded in a mortar to fine particles and dispersed ultrasonically in ethanol. The well dispersed samples were deposited on a Cu grid covered by a holey carbon film for measurements.

The temperature-programmed reduction (TPR) equipment is consisted of a thermal conductivity detector (TCD) connected to a flow-control system and a programmed heating unit. In each test, 20 mg of sample was placed in a quartz reactor, reduced in 5% H₂ in Ar at a flow rate of 20 mL min^{–1} with a heating rate of 10 °C min^{–1}. Before analysis, samples were calcined at 300 °C for 2 h in air.

Hydrogen temperature-programmed desorption (H₂-TPD) tests were conducted on a TP-D/R/O 1100 SERIES (Finnigan) instrument. For each measurement, 100 mg of samples was loaded in a quartz reactor, reduced from room temperature to 300 °C in pure hydrogen at a flow rate of 20 mL min^{–1} and held at this temperature for 2 h. After the reduction, the sample was swept with pure N₂ at 300 °C for 0.5 h to remove the hydrogen on sample surface. The H₂ chemisorption test was then carried out at room temperature with pulses of H₂ (50 µL) passed over the samples until the TCD signals being constant. Then, H₂-TPD test was conducted at a heating rate of 10 °C min^{–1} from 30 °C to 800 °C with pure N₂ as the carrier gas and TCD as the detector. Water derived from dehydroxylation of the sample was removed by soda lime.

2.3. Catalyst activity measurements

Catalytic performance tests were carried out on a continuous-flow fixed tubular quartz micro-reactor of 450 mm in length

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