

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SciVerse ScienceDirect

journal homepage: [www.elsevier.com/locate/ije](http://www.elsevier.com/locate/ije)

# Methanol oxidation on hybrid catalysts: PtRu/C nanostructures promoted with cerium and titanium oxides

Praveen Kolla<sup>a</sup>, Alevtina Smirnova<sup>b,\*</sup>

<sup>a</sup> Material Engineering and Science PhD Program, South Dakota School of Mines & Technology, Rapid City, SD 57701, USA

<sup>b</sup> Department of Chemistry and Applied Biological Sciences, South Dakota School of Mines & Technology, Rapid City, SD 57701, USA

## ARTICLE INFO

### Article history:

Received 13 July 2013

Received in revised form

11 September 2013

Accepted 16 September 2013

Available online 11 October 2013

### Keywords:

In-situ combustion

Methanol oxidation

Hybrid catalyst

Bi-functional mechanism

Ligand effect

Ceramic oxide promoter

## ABSTRACT

Hybrid catalysts comprising of ceramic, metal, and carbon phase were synthesized by incorporating titanium and cerium oxides into PtRu/C commercial catalyst using an in-situ combustion followed by heat treatment at 600 °C. The structure dependent electrochemical behavior of as-synthesized and heat-treated materials towards methanol oxidation, carbon dioxide (CO) tolerance and chemical stability was studied by XRD, HRTEM, BET, EDS, cyclic voltammetry, chronoamperometry, and CO-stripping method. As a result of heat treatment, amorphous phase of metal oxides was transformed into a crystalline phase with particle size of about 3–7 nm. Improved methanol oxidation activity of the hybrid catalysts was compared to PtRu/C catalyst as a baseline and explained by the changes in Pt electronic behavior and excess adsorption of OH<sup>-</sup> ions. When heat-treated at 600 °C, CeO<sub>2</sub>-PtRu/C demonstrated the highest mass activity of 580 mA/mg (~3× that of PtRu/C) compared to TiO<sub>2</sub>-PtRu/C (394 mA/mg). Heat-treated hybrid catalysts exhibited higher methanol oxidation activity at higher peak potentials than the corresponding as-synthesized materials. However, as-synthesized hybrid catalysts display higher CO-tolerance, lower CO-oxidation onset potentials, and better chemical stability in comparison to corresponding heat-treated catalysts. To explain the difference, a mechanism for ceramic oxide structure dependent electrochemical behavior of the hybrid catalysts is proposed and discussed.

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

## 1. Introduction

Direct Methanol Fuel Cell (DMFC) has potential to replace electronic devices based on rechargeable batteries and automotive power sources [1]. However, slow anode kinetics, strong adsorption of methanol oxidation intermediates onto

platinum surface and chemical instability of catalysts in acidic medium are the challenges that hinder the DMFC commercial viability. In this regard, search for inexpensive catalysts having high noble-metal utilization, greater methanol activity and better chemical stability are essential for DMFC commercialization [2].

\* Corresponding author. Fax: +1 605 394 1232.

E-mail address: [Alevtina.Smirnova@sdsmt.edu](mailto:Alevtina.Smirnova@sdsmt.edu) (A. Smirnova).

Platinum supported on carbon (Pt/C) has the highest activity towards methanol oxidation [3]. However, strong adsorption of carbon monoxide (CO), an intermediate of methanol oxidation, reduces platinum Electrochemical Surface Area ( $ESA_{Pt}$ ). The over-potential required for complete CO-oxidation limits the fuel cell operating conditions. Therefore, ruthenium (Ru) is successfully used along with platinum (Pt) as bi-functional catalyst to lower CO–Pt adsorption strength for direct CO removal and/or to provide OH-species to Pt surface for sequential CO-oxidation [4].

High noble metal loading and chemical instability of Pt–Ru catalyst can be minimized by promotion of Pt–Ru with various metals and metal oxides as they demonstrated synergistic improvements in methanol oxidation activity and CO-tolerance [5–9]. Among them, ceria and titania [10–13] are widely studied as Pt–Ru promoters and/or as a catalyst support. However, these ceramic oxides cannot provide enough electrical conductivity at ambient temperatures. Consequently, modification of these materials with carbon or metallic catalyst phases is necessary to match conductivity of carbon support. Furthermore, despite of recent efforts [14], structural dependency of these ceramic oxides towards promotional methanol oxidation and surplus CO-oxidation have not been completely understood.

Therefore, an *in-situ* combustion method is used to impregnate optimal amounts of ceria and titania into PtRu/C catalyst and synthesize hybrid catalyst comprising of metallic, ceramic and carbon phase. The method has an advantage of producing higher surface area, sufficient electrical conductivity, and better ceramic phase distribution in hybrid catalyst. Relative promotional behavior of cerium and titanium oxides on PtRu/C and their structural dependency towards methanol oxidation, CO-tolerance, and chemical stability are addressed.

## 2. Materials and methods

### 2.1. In-situ combustion synthesis

A modified sol–gel glycine-nitrate synthesis [15] was applied to impregnate metal oxides into Pt–Ru/C catalyst (Tanaka®). The initial mixtures were prepared by dissolving metallic precursors of cerium ( $Ce(NO_3)_3 \cdot 6H_2O$ ) in glycine-water solution and titanium ( $Ti\{OCH(CH_3)_2\}_4$ ) in isopropanol–water glycine solution. In the case of  $TiO_2$  mixture, 1.0 mL of concentrated  $HNO_3$  was added to dissolve precursor in the glycine solution and form glycine complex. The mixture was added to the supporting material (PtRu/C) for impregnation of ceramic oxides and dried overnight in air at 50 °C followed by combustion synthesis at 350 °C. The resulting catalyst was further heated at 600 °C for 1 h in an inert gas atmosphere ( $N_2$ ) to develop polycrystalline metal oxide nanoparticles.

### 2.2. Structural analysis

Hybrid catalyst materials structure was characterized by Rigaku Ultima Plus theta–theta XRD.  $Cu\text{-}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) was used to scan materials from 10° to 90° (2 $\theta$ ) with scan rate of 0.667 °/min. The catalyst structure was

studied using high resolution JEOL TEM-2100 using an electron beam from LaB<sub>6</sub> gun at 200 keV. For TEM analysis, catalyst powders were dispersed in ethanol by sonication and placed on square mesh copper grid coated with carbon film (CF200-Cu). Chemical composition of the catalysts was estimated with a Zeiss Supra40VP FESEM with EDX analyzer from Oxford Instruments. The X-ray counts were averaged over four spectra corresponding to different areas (0.1 mm × 0.1 mm) of the sample. Chemisorb 2720® (Micromeritics Instrument Inc.) was used for the measurements of single point BET specific surface area (SSA). The BET SSA was measured from  $N_2$  adsorption–desorption at 77 K by degassing the samples at 300 °C in  $N_2$  for 30 min.

### 2.3. Electrochemical studies

The electrochemical study of the catalysts was performed in conventional three-electrode half-cell in 0.1 M  $HClO_4$  electrolyte with Ag/AgCl/0.1 MKCl reference electrode. The catalyst inks for electrochemical measurements were prepared by mixing 0.4 mL of 5% 1100 Nafion™ solution in 20 mL of isopropanol and 79.6 mL of water with 0.6 g of dry catalyst. Catalyst inks were dispersed in ultrasonic homogenizer at room temperature. 10  $\mu$ L of the ink were transferred onto glassy carbon electrode (0.19 cm<sup>2</sup>) and dried to form a thin film. The glassy carbon electrode was then connected to a bipotentiostat (AFCBP1) from Pine Instruments.

ESA of platinum was calculated from CV hydrogen adsorption region [16]. CO-stripping voltammetry was conducted in three steps: CO-adsorption onto electrode, removal of dissolved CO-species from electrolyte, and stripping of CO-species from electrode in the process of oxidation. First, ultra-pure (99.9%) CO gas was purged through electrolyte (30 min) for adsorption of CO-species followed by  $N_2$  purge (30 min) for removal of CO-species while maintaining the working electrode at –0.2 V. Afterward, stripping voltammetry, from –0.2 V to 1.0 V was performed for oxidation of CO-species followed by two cycles from –0.5 V to 1 V at 20 mV/s to confirm that all CO-species were completely oxidized in the first oxidation cycle.

## 3. Results

### 3.1. Composition and structure

Chemical compositions of the PtRu/C catalysts impregnated with titania and ceria are presented in Fig. 1. The elemental composition derived from EDS confirms that hybrid catalysts are comprised of metallic (48–54 wt.%), carbon (20–30 wt.%), and ceramic (21–24 wt.%) phase in the amount sufficient to improve the synergistic methanol activity and stability without affecting the electrical conductivity of the PtRu/C catalyst [17].

The crystal structures of the hybrid catalysts before and after heat treatment were compared with PtRu/C catalyst structure (Fig. 2). Synthesized  $TiO_2$ –PtRu/C has amorphous titania phase along with oxide phases of Pt–Ru alloy. After heat treatment at 600 °C, oxide phase of Pt–Ru alloy was reduced to its metallic phase, while titania crystals having

Download English Version:

<https://daneshyari.com/en/article/7721023>

Download Persian Version:

<https://daneshyari.com/article/7721023>

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