Ultra-low loading Pt–Rh/$Sn_{0.9}In_{0.1}P_2O_7$ three-way catalyst for propane + NO + O_2 reaction

Xue Dong, Kota Tsuneyama, Takashi Hibino*

Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

ABSTRACT

Propane oxidation and NO reduction at the proton conductor–electrocatalyst interface were investigated using electrochemical cells and impregnated catalysts. $Sn_{0.9}In_{0.1}P_2O_7$ and Pt or Pt–Rh were used as the proton conductor and electrocatalyst, respectively. In a gaseous mixture of propane, H_2O, and NO, H_2O is dissociated into protons and electrons at anodic sites at the interface and the resultant active oxygen oxidizes propane to CO_2. Separately, NO reacts with protons and electrons to form N_2O at cathodic sites at the interface. Under stoichiometric conditions, including 1000 ppm propane, 1000 ppm NO, 3% H_2O, and 4500 ppm O_2, the temperatures at which the above series of reactions could successfully achieve 50% conversion ($T_{50\%}$) was reduced to 310 and 385 °C for propane and NO, respectively, over a 0.01 wt.% Pt/$Sn_{0.9}In_{0.1}P_2O_7$ catalyst. These were much lower than $T_{50\%}$ of 430 and 535 °C for propane and NO, respectively, over a 0.01 wt.% Pt/γ-Al_2O_3 catalyst. Moreover, the addition of 0.005 wt.% Rh to the Pt/$Sn_{0.9}In_{0.1}P_2O_7$ catalyst enhanced NO reduction by promoting the dissociative adsorption of NO, thus providing a further reduction of $T_{50\%}$ for the NO reaction to 355 °C.
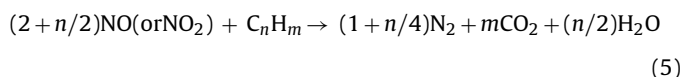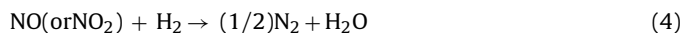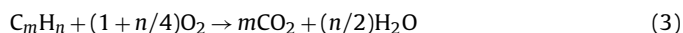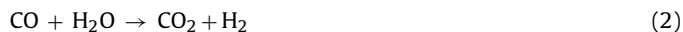
© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Three-way catalysts (TWCs) have been widely used to purify gasoline engine exhaust of hydrocarbons (HC), CO, and NO_x [1,2]. This is accomplished by controlling the air/fuel ratio of the exhaust close to a stoichiometric value of 14.6. However, the commonly used Pt and Rh catalysts are very expensive, and worldwide Pt and Rh sources are unevenly distributed, which places limitations on the numbers of vehicles produced. One approach for reducing the Pt and Rh contents while maintaining high catalytic activity is to use ceria-based compounds as catalyst supports or promoters. Ceria have multiple effects on the activity of TWCs. Ceria can easily release or uptake oxygen in the reaction environment, due to the low Ce^{4+}/Ce^{3+} redox potential [3–5]. Moreover, ceria stabilizes well-dispersed noble metals in operating conditions [6,7]. In addition, reductive pre-treatments of ceria-supported noble metals induce considerable changes in the reactivity through the so called strong metal-support interaction (SMSI) [8]. For instance, Papavasiliou et al. decreased the Pt content to 0.5 wt.% over γ-Al_2O_3 by using $Ce_{0.4}Zr_{0.5}La_{0.1}O_{1.9}$ as a catalyst promoter [9]. Although the other catalyst supports, including Si_3N_4 [10] and $La_{7.33}BaYSi_6O_{25.5}$ [11], have also been investigated for TWCs, the reported Pt loading is as high as 1 wt.%. A further reduction in the use of precious met-

als would enhance the position of TWCs as the preferred emission control technology.

TWCs promote the following reactions for CO, HC, and NO_x removal in the exhaust [12]:

$$CO + (1/2)O_2 \rightarrow CO_2 \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

$$C_mH_n + (1 + n/4)O_2 \rightarrow mCO_2 + (n/2)H_2O \tag{3}$$

$$NO(orNO_2) + H_2 \rightarrow (1/2)N_2 + H_2O \tag{4}$$

$$(2 + n/2)NO(orNO_2) + C_nH_m \rightarrow (1 + n/4)N_2 + mCO_2 + (n/2)H_2O \tag{5}$$

Typically, the CO reaction occurs first, followed by the HC and NO_x reactions. Therefore, the ability of TWCs is determined by the catalytic activity for the HC and NO_x reaction. The activation of C–H bonds in HC is considered to be the key initial step in HC oxidation. There seems to be little doubt regarding the role of chemisorbed or combined oxygen species (so-called active oxygen) in the extraction of hydrogen from the C–H bond in HC [13,14]. We recently reported that H_2O dissociated into protons, electrons, and active oxygen species at a Pt/C anode in a Pt/C|$Sn_{0.9}In_{0.1}P_2O_7$|Pt/C elec-
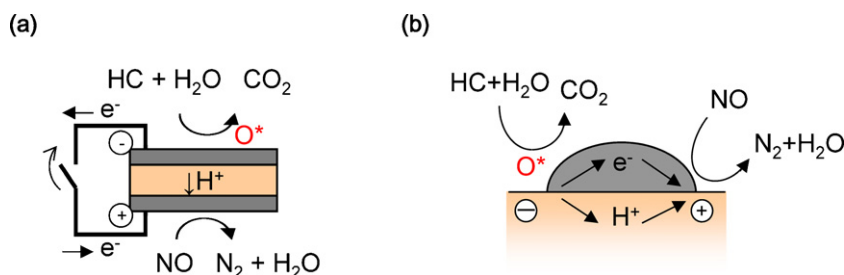
Scheme 1. Reaction schemes for propane oxidation and NO reduction in a (a) fuel cell and (b) local electrochemical cell.

trochemical reactor, which led to the oxidation of propane to CO_2 [15,16]:

$$C_3H_8 + 6H_2O \rightarrow 3CO_2 + 20H^+ + 20e^-. \tag{6}$$
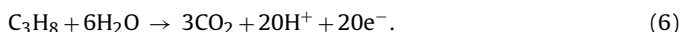
$Sn_{0.9}In_{0.1}P_2O_7$ (SIPO) has a cubic structure with SnO_6 octahedra and P_2O_7 units at the corners and the edges, respectively, wherein 10 mol% In^{3+} cations are substituted for Sn^{4+} cations [17]. Such closely packed P_2O_7 units provide many proton bonding sites and transport pathways, showing high proton conductivities above $0.1\,S\,cm^{-1}$ in the temperature range of 100–400 °C. On the other hand, the dissociation of NO_x into $N_{(ad)}$ and $O_{(ad)}$ on the surface of Pt is promoted by previously adsorbed $H_{(ad)}$ [18]. We also recently reported that NO reacts with protons and electrons to form N_2 and H_2O at the Pt/C cathode in the Pt/C|SIPO|Pt/C electrochemical cell [19,20].

$$NO + 2H^+ + 2e^- \rightarrow (1/2)N_2 + H_2O \tag{7}$$
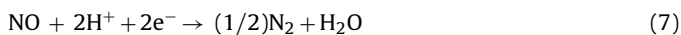
More importantly, propane oxidation and NO reduction proceeded according to Eqs. (6) and (7), respectively, at temperatures of 200 °C or lower, which suggests that the Pt/C electrode has high activities for these reactions even at reduced Pt content.

Based on these observations, it is expected that an electrochemical reactor for the HC and NO_x reactions shown in Eqs. (6) and (7) can be developed by short-circuiting the reactor, as illustrated in Scheme 1(a). Moreover, if nanoscale electrochemical reactors can be successfully produced by impregnating the surface of the SIPO powder with Pt clusters, then the reaction area for the HC and NO_x reactions would be significantly increased, as illustrated in Scheme 1(b). The purpose of the present work is to: (1) inspect the HC and NO_x reaction through Eqs. (6) and (7) using an electrochemical cell with Pt/C anode and cathode, (2) demonstrate the advantage of using nanoscale electrochemical reactors with ultra-low Pt loadings for the HC and NO_x reactions, and (3) effectively enhance the reactions shown in Eq. (6) and especially Eq. (7) by the addition of a promising Rh promoter to the Pt/SIPO catalyst.

2. Experimental

2.1. Materials and characterization methods

SIPO was prepared in the same manner as that reported previously [17]. SnO_2 (C. I. Kasei) and In_2O_3 (Wako) were mixed with 85% H_3PO_4 and ion-exchanged water, and stirred at 300 °C until a high viscosity paste was formed. The paste was calcined in an alumina pot at 650 °C for 2.5 h and then ground in a mortar. The final P/(Sn + In) molar ratio of the compounds was confirmed to be 2.0 (±0.02) from X-ray fluorescence (XRF) measurements. The BET surface area of SIPO was measured using an automated particle analyzer system (Micromeritics). The sample was degassed under vacuum at 100 °C for 1 h and then at 250 °C for 3 h prior to BET surface area measurements.

For electrochemical cell studies, the SIPO powder was uniaxially pressed into pellets (12 mm diameter, ca. 1 mm thick) under

a pressure of 200 MPa for use as the electrolyte. A Pt/C (10 wt.% Pt/C, 0.6 mg Pt cm^{-2}) electrode with a gas diffusion layer was purchased from BASF. For catalyst studies, Pt/SIPO (0.01–1.00 wt.% Pt content) and Pt–Rh/SIPO catalysts (0.01 wt.% Pt content and 0.0025–0.0100 wt.% Rh content) were prepared by impregnation of the SIPO powder surface with Pt ($Pt(NH_3)_4Cl_2 \cdot H_2O$) and Rh (($NH_4)_3RhCl_6 \cdot H_2O$) precursors. The SIPO powder was suspended in ion-exchanged water, and an aqueous solution of $Pt(NH_3)_4Cl_2 \cdot H_2O$ or two aqueous solutions of $Pt(NH_3)_4Cl_2 \cdot H_2O$ and $(NH_4)_3RhCl_6 \cdot H_2O$ were added dropwise to the suspension using micropipettes while stirring at approximately 60 °C. After aging at this temperature overnight, the catalyst powder was oxidized in an air feed at 300 °C for 1 h and then reduced in a 10 vol.% H_2 (Ar balance) feed at 450 °C for 1 h. The dispersion state of each component in the catalyst was analyzed using transmission electron microscopy (TEM: JEOL JEM2100F) in conjunction with energy dispersive X-ray (EDX: JEOL JED-2300T) spectroscopy. Specimens for TEM and EDX measurements were prepared by ultrasonic dispersion in n-butanol, and a drop of the resultant suspension was evaporated on a Cu grid. For comparison with the Pt/SIPO catalyst, a Pt/γ-Al_2O_3 (0.01–1.00 wt.% Pt) catalyst, which is used as a standard catalyst at Toyota Motor Corporation, was also tested.

2.2. Electrochemical cell studies

The reactions in Eqs. (6) and (7) were investigated using an electrochemical cell. Two Pt/C electrodes (area: 0.5 cm^2) were attached on opposite sides of the electrolyte and Au mesh was employed as a current collector at both electrodes. Two electrode chambers were set up by placing the cell assembly between two alumina tubes, as illustrated in Fig. 1(a). A mixture of 1000 ppm propane and 3 vol.% H_2O in Ar was supplied to the anode at a flow rate of 30 mL min^{-1}, and 1000 ppm NO diluted with Ar was supplied to the cathode at a flow rate of 30 mL min^{-1}. A current was applied using a galvanostat (Hokuto Denko HA-501). The concentrations of propane, CO_x (CO_2 and CO), and O_2 in the outlet gas from the anode chamber were analyzed using an on-line gas chromatograph (Varian CP-4900), and the concentration of NO_x (NO and NO_2) in the outlet gas from the cathode chamber were monitored using an on-line NO_x gas analyzer (Horiba PG-225). Propane oxidation and NO reduction were also evaluated using a half-cell with the Pt/C electrode, as illustrated in Fig. 1(b). Besides SIPO, silica and yttria-stabilized zirconia (YSZ) pellets were also used as the electrolytes in the half-cell. The silica (1 mm thick) and YSZ (8 mol% yttria, 1 mm thick) disks were purchased from Matsunami glass and Tosoh, respectively. The electrode was supplied with a mixture of 1000 ppm propane, 1000 ppm NO, and 3 vol.% H_2O vapor in Ar at a flow rate of 30 mL min^{-1}. Analysis of the outlet gas was conducted as previously described.

2.3. Catalyst studies

The activity of the Pt/or Pt–Rh/SIPO catalyst for the HC and NO_x reaction was measured under various conditions. The number of