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Low-temperature hydrocarbon combustion over proton conductor/metal–mixed catalysts

Kota Tsuneyama [a], Shinya Tetanishi [a], Takashi Hibino [a,*], Satoshi Nagao [b], Hirohito Hirata [b], Shin-ichi Matsumoto [b]

[a] *Graduate School of Environmental Studies, Nagoya University, Nagoya, Aichi 464-8601, Japan*
[b] *Higashifuji Technical Center, Toyota Motor Corporation, Susono, Shizuoka 410-1193, Japan*

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ABSTRACT

Catalytic combustion of hydrocarbons is a highly active field of research, particularly in relation to the reduction of pollutant emissions from automobiles. In this study, we report on hydrocarbon oxidation at the internal interfaces of a mixed catalyst consisting of $Sn_{0.9}In_{0.1}P_2O_7$ and Pt powders. In a gaseous mixture of propane, H_2O, and O_2, the H_2O dissociates into protons, electrons and active oxygen species at anodic interface sites, leading to oxidation of the hydrocarbon to CO_2. On the other hand, O_2 reacts with protons and electrons to form H_2O at cathodic interface sites. As a consequence, local electrochemical cells are formed at the interfaces, and undergo self-discharge. It was shown that the mixed catalyst had a high turnover frequency for Pt, yielding high catalytic activity for Pt contents of as low as 0.1 wt% and an initiation temperature for hydrocarbon oxidation of 150 °C.

1. Introduction

Uncombusted hydrocarbons, in addition to CO and NO_x, emitted from gasoline engines are commonly removed by three-way catalysts (TWCs). However, the TWCs available to date require a combustion temperature of 300–500 °C, especially for saturated hydrocarbons, which is much higher than typical exhaust temperatures of <200 °C during cold-start transients. This gap makes it difficult to maintain emission restrictions that are becoming increasingly stringent worldwide, because considerable amounts of hydrocarbons are released into the atmosphere under such low-temperature conditions [1]. Thus, in recent years, there has been increasing interest in low-temperature hydrocarbon combustion as a potential approach to achieve ultra low-emission vehicles [2–5].

The activation of C–H bonds in saturated hydrocarbons is considered to be the key initial step in hydrocarbon oxidation and is accomplished over platinum group metals such as Pt and Pd [6–8]. While the precise nature of the active site is not yet clear, due to the complexity of their operating conditions, there seems to be little doubt regarding the role of chemisorbed or combined oxygen species (so-called active oxygen) in the extraction of hydrogen by breaking of the C–H bond in hydrocarbons [9,10]. In addition, the presence of Ce–Zr–mixed oxides stabilizes the oxidation state of the metal catalyst and therefore, contributes to a reduction in the combustion temperature of the hydrocarbons [11,12]. Although several transition-metal oxides [13] and perovskite-type oxides [14] can also activate O_2 in the gas phase or oxide ions in the lattice due to their redox properties, such oxygen-activating species are not commercially viable for low-temperature hydrocarbon combustion, because of their relatively low levels of activity.

In this study, we focused on H_2O vapor as an active oxygen source and a mixture of proton conductor and electrocatalyst powders as a catalyst. We recently reported that in a proton exchange membrane fuel cell using $Sn_{0.9}In_{0.1}P_2O_7$ and Pt/C as the electrolyte and electrode, respectively, light hydrocarbons, including ethane, propane, and butane, could be directly used as fuels, even in the temperature range of 100–300 °C [15]. More importantly, the hydrocarbons were oxidized to CO_2 with very high faradic efficiency, so that the following reaction proceeded at the Pt/C anode:

$$C_nH_{2n+2} + 2nH_2O \rightarrow nCO_2 + (6n+2)H^+ + (6n+2)e^- \quad (1)$$

It is known that HO· is formed by the anodic polarization of H_2O [16,17]; therefore, such a radical is likely to be an important active species for breaking the C–H bond in Reaction (1). On the other hand, the following oxygen reduction reaction occurred at the Pt/C cathode as a counter-reaction to Reaction (1):

$$(1.5n+0.5)O_2 + (6n+2)H^+ + (6n+2)e^- \rightarrow (3n+1)H_2O \quad (2)$$

As a result, the fuel cell exhibited power densities ranging from 10 to 60 mW cm^{-2}, which were dependent on the temperature and the hydrocarbon species.

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[*] Corresponding author. Fax: +81 52 789 4894.
E-mail address: hibino@urban.env.nagoya-u.ac.jp (T. Hibino).

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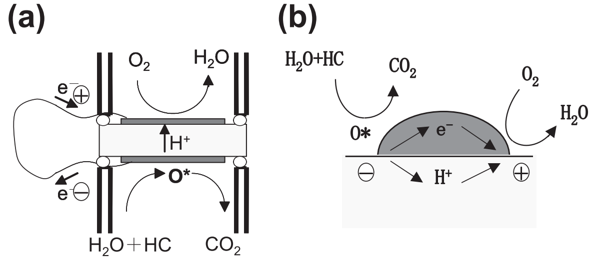

Scheme 1. Schematic illustrations of (a) fuel cell and (b) local electrochemical cell.

Based on these observations, it is expected that an electrochemical reactor for hydrocarbon combustion can be developed through Reactions (1) and (2) at temperatures of 100 °C or higher by short-circuiting the fuel cell, as shown in Scheme 1a. Moreover, if micro-scale electrochemical cells can be successfully produced by mixing the proton conductor powder with the electrocatalyst powder as illustrated in Scheme 1b, then the reaction area for hydrocarbon oxidation can be drastically increased. This paper demonstrates that Reactions (1) and (2) are applicable to hydrocarbon oxidation on solid catalysts, which opens up new possibilities for the development of low-temperature hydrocarbon combustion systems.

2. Experimental

2.1. Materials

$Sn_{0.9}In_{0.1}P_2O_7$ and Pt were used as proton conductor and electrocatalyst, respectively, in the manner previously reported [15]. $Sn_{0.9}In_{0.1}P_2O_7$ was prepared as follows. SnO_2 and In_2O_3 were mixed with 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 crucible at 650 °C for 2.5 h, and the product was then ground in a mortar. For electrochemical cell studies, the $Sn_{0.9}In_{0.1}P_2O_7$ powder was uniaxially pressed into pellets (12 mm diameter, ca. 1.5 mm thick) under a pressure of 200 MPa and used as the electrolyte. A Pt/C anode (10 wt% Pt/C, 4.0 mg Pt cm^{-2}) and a Pt/C cathode (10 wt% Pt/C, 0.6 mg Pt cm^{-2}) were purchased from BASF. For catalyst studies, commercially available platinum black was used as a component of the catalyst. The Pt powder was mixed with $Sn_{0.9}In_{0.1}P_2O_7$ and α-Al_2O_3 powders in a mortar for a few minutes. For comparison with the $Sn_{0.9}In_{0.1}P_2O_7$ + Pt-mixed catalyst, a Pt/γ-Al_2O_3 (1 wt% Pt) catalyst, which is used as a standard catalyst at Toyota Motor Corporation, was also tested.

2.2. Electrochemical cell studies

Reactions (1) and (2) were investigated using an electrochemical cell. The two Pt/C electrodes (area: 0.5 cm^2) were attached on opposite sides of the electrolyte without the use of any special binder. In both cases, a Pt mesh was employed as a current collector. (It is reasonable to consider that this mesh does not influence hydrocarbon oxidation because there is a gas diffusion layer between the Pt mesh and Pt/C catalyst layer.) An Au reference electrode was attached to the side surface of the electrolyte. In all experiments except the cyclic voltammetry (CV) measurements, the reference electrode was exposed to atmospheric air. Two gas chambers were set up by placing the cell assembly between two alumina tubes, as illustrated in Fig. 1a. Unless otherwise stated, a mixture of propane and H_2O in Ar (1000 ppm–7% propane and 3% H_2O) was supplied to the anode at a flow rate of 30 mL min^{-1}, and O_2 diluted with Ar (5000 ppm–21% O_2) was supplied to the cathode at a flow rate of 30 mL min^{-1}. The concentrations of propane, COx (CO_2 and CO), and O_2 in the outlet gas from the anode chamber were analyzed using an on-line gas chromatograph. The gas concentrations were obtained after the reaction had achieved a steady state. CV curves were measured between 0 and 1.2 V vs. reversible hydrogen electrode (RHE) at a scan rate of 10 mV s^{-1}. Anodic and cathodic polarization curves were measured by controlling the potential of the working electrode vs. the reference electrode with a potentiostat. Raman analysis was carried out by setting up the electrochemical cell in a spectrophotometer, as shown in Fig. 1b. Raman spectra of the anode surface were recorded during the application of constant current to the electrochemical cell with visible (532 nm) laser excitation. All Raman measurements were conducted at room temperature in air.

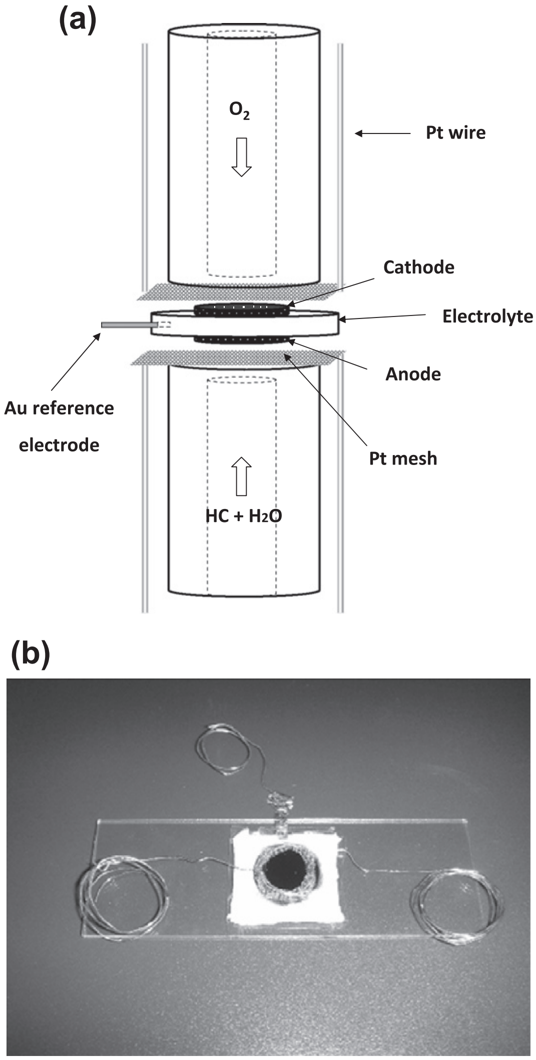

Fig. 1. Electrochemical cells for (a) gas composition, CV, and polarization curve measurements and (b) Raman analysis.

2.3. Catalyst studies

The catalytic activity of the $Sn_{0.9}In_{0.1}P_2O_7$ + Pt-mixed catalyst (0.1–10 wt% Pt) for hydrocarbon oxidation was evaluated under various conditions. The dispersion state of each component in the mixed catalyst was analyzed using scanning electron microscopy (SEM) in conjunction with energy dispersive X-ray (EDX) spectroscopy. The number of reaction sites on the Pt surface was measured by the CO pulse method at room temperature. Catalytic tests were conducted in a fixed-bed flow reactor. Unless otherwise