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The roles of metals and their oxide species in hydrophobic Pt–Ru catalysts for the interphase H/D isotope separation

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ARTICLE INFO

Article history:

Received 1 July 2010

Received in revised form

1 August 2010

Accepted 3 August 2010

Keywords:

Hydrophobic catalyst

Liquid phase catalytic exchange

Hydrogen isotope separation

Pt–Ru/C

ABSTRACT

Liquid phase catalytic exchange is mainly used for separation of hydrogen isotopes from liquid water. Based on the carbon-supported Pt and Pt–Ru catalysts with different metal and oxide species distributions, several hydrophobic catalysts, used in the reaction, were fabricated. The characterization results indicated that alloy and amorphous nanoparticles were formed in the Pt_{0.5}Ru_{0.5}/C catalyst using the microwave-irradiated polyol method. After reduction, the content of metallic species increased and that of hydrous Ru oxide species significantly decreased. A Pt_{0.5}Ru_{0.5}O₂/C catalyst containing more oxide species was also synthesized by the microwave-irradiated oxidation precipitation method. Performance tests demonstrated that the presence of more metallic Pt species in both the hydrophobic Pt and Pt–Ru catalysts resulted in higher catalytic activity. The addition of Ru, as an alloy or as a hydrous oxide, can improve the catalytic activity of pure Pt. These experimental results were explained by the reaction mechanisms.

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1. Introduction

Liquid phase catalytic exchange (LPCE) between liquid water and gaseous hydrogen is an important reaction for separation of hydrogen isotopes from liquid water. LPCE processes have been developed for various applications, such as tritium recovery from waste water in some nuclear facilities, moderator detritium in heavy-water reactors, heavy-water production, etc [1–9]. LPCE usually occurs between ambient temperature and 80 °C. The waterproofing properties of hydrophobic catalysts, used in the reaction, prevent liquid water from entering the catalyst micropores. Thus, the reactants and production channels remain unblocked and the reaction can proceed smoothly. However, a catalyst “poisoning” [4–13] in conventional hydrophilic catalysts will occur in LPCE.

Hydrophobic Pt catalyst has the most catalytic activity for LPCE, compared with other metal catalysts [10]. Consequently, single Pt catalysts, which are high cost, are the most frequently

reported. Efforts have been devoted to increasing the catalytic activity of the Pt catalyst and reducing its high cost. A major approach is to decrease the average particle size of the active metal. It has been reported [11,12] that Pt and Pt–Ir catalysts with smaller particle sizes, which have a larger reaction interface, show higher LPCE catalytic activities. The catalytic activity of Pt catalyst can also be improved by appropriate addition of other components such as Cr, Ti, and Ir [10,11].

Recently, Pt–Ru-based catalysts have been intensively studied for use in direct methanol fuel cells [13–18]. The CO poisoning of single Pt catalysts can be effectively impeded by introducing Ru, as an alloy or as an oxide [13]. The presence of a second material such as Ru or Ru oxide can significantly improve the electrocatalytic activity for methanol oxidation. Some researchers [16–20] have emphasized that hydrous Ru oxide species, which has high electron and proton conductivities, is important in Pt–Ru-based catalysts. Our preliminary research [21] has also revealed that hydrophobic Pt–Ru

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doi:10.1016/j.ijhydene.2010.08.009

bimetallic catalysts with appropriate Pt/Ru atomic ratios have higher activities than pure Pt for LPCE. The carbon-supported Pt–Ru catalysts were prepared by the modified microwave-irradiated polyol method. X-ray photoelectron spectroscopy (XPS) characterization indicated that Pt and Ru metals and their oxides coexisted in the Pt–Ru catalysts. However, it still remains unclear how these metal species affect the catalytic activities. The reason for the increased activity was not investigated in detail.

The purpose of the present work is to obtain insight into the roles of metals and their oxides species in hydrophobic Pt–Ru catalysts for LPCE. First, carbon-supported Pt and Pt–Ru catalysts with different metal and oxide species distributions were obtained by different methods. The hydrophobic catalysts were then fabricated, based on these carbon-supported catalysts. Finally, the catalytic activities of the Pt and Pt–Ru hydrophobic catalysts for LPCE were investigated. The roles of different Pt and Ru species were discussed in detail.

2. Experimental

2.1. Preparation of carbon-supported catalysts

Pt_{0.5}Ru_{0.5}O₂/C and RuO₂/C catalysts were prepared using a microwave-irradiated oxidation precipitation (MIOP) method. Vulcan-XC 72R carbon black (300 mg; Cabot Corporation) was ultrasonically dispersed in 25 mL of an aqueous solution of H₂PtCl₆ and RuCl₃, or of RuCl₃. Then 15 mL of concentrated hydrogen peroxide aqueous solution was added dropwise, with stirring, at a rate of 20 mL/min at ambient temperature, followed by constant stirring for 15 min. The Ru³⁺ cations were oxidized to Ru⁴⁺ cations by the hydrogen peroxide. The synthesis was then performed in a closed PTFE vessel using an ETHOS T microwave labstation (Milestone Corp.). The synthesis solution was heated to 120 °C at a microwave heating rate of 7 °C/min, and lasted for 30 min. The Pt and Ru species were precipitated on the carbon support.

The Pt and Pt–Ru depositions on the carbon or RuO₂/C were performed using a modified microwave-irradiated polyol (MIP) process as described elsewhere [11,21]. Vulcan-XC 72R or RuO₂/C (300 mg) was ultrasonically dispersed in 30 mL of ethylene glycol (EG), followed by addition of an EG solution of H₂PtCl₆, or of a mixture of H₂PtCl₆ and RuCl₃, to the suspension under constant stirring. The pH of the synthesis solution was adjusted to 12 using a 1 mol/L NaOH aqueous solution. The reaction mixture was heated to 190 °C at a heating rate of 12 °C/min in the ETHOS T microwave labstation, and then kept at 190 °C for 5 min. After cooling to ambient temperature, the resulting powder catalyst was filtered, washed, and dried. Pt_{0.5}Ru_{0.5}/C and Pt/RuO₂/C catalysts were obtained. For comparison, a 20 wt % Pt/C catalyst was prepared by the same method. The total Pt and Ru contents with an atomic ratio of 1/1 remained at 20 wt% for the Pt_{0.5}Ru_{0.5}O₂/C, Pt/RuO₂/C, and Pt_{0.5}Ru_{0.5}/C catalysts.

2.2. Heat treatment of the Pt/C and Pt_{0.5}Ru_{0.5}/C catalysts

The as-prepared Pt/C or Pt_{0.5}Ru_{0.5}/C catalysts were loaded into a long quartz tube and the tube was placed in the center of

a tube furnace; N₂ gas was allowed to flow into the quartz tube at a rate of 500 mL/min for 30 min at ambient temperature. The tube furnace was then heated to 500 °C at a fast ramping ratio of 30 °C/min under a flow of 15% H₂/N₂. After 1 h at 500 °C, the quartz tube was removed from the tube furnace and cooled to room temperature in a 15% H₂/N₂ atmosphere. The resulting catalysts are denoted as Pt/C–H and Pt_{0.5}Ru_{0.5}/C–H.

2.3. Physical characterization of the carbon-supported catalyst

X-ray diffraction (XRD) analysis was performed using a DX-2600 SSC diffractometer (CuK α radiation, $\lambda = 1.5405 \text{ \AA}$) at a scanning rate of 1.2° min⁻¹ from 10° to 90°. The Scherrer and Bragg formulae were employed to calculate the mean diameter and the lattice parameter of the catalysts. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM 3010 transmission electron microscope operated at an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) analyses were carried out on an ESCALAB 250 spectrometer. Narrow scan photoelectron spectra of Pt 4f and Ru 3p were recorded and deconvoluted by XPSPEAK (version 4.1).

2.4. Preparation of hydrophobic catalysts

As described in our previous work [11,12,21], a porous FN material (2.5 mm thick, 110 PPI, 500 g m⁻²) was used as an inert carrier for the hydrophobic catalysts. In the first step, a stable slurry of the carbon-supported catalyst and PTFE was prepared under sonication, and the hydrophobic PTFE was used to waterproof the catalyst. The mixed slurry was then loaded onto the unpretreated FN carrier by natural impregnation. Finally, the coated FN was dried and calcined at different temperatures to obtain the hydrophobic catalysts.

2.5. Activity measurements of the hydrophobic catalysts

Hydrophobic catalyst performance tests were performed in a jacketed glass column of internal diameter 16 mm and height 450 mm. Thermostatically controlled water (50 °C) was passed through the glass jacket to maintain a constant temperature over the column. The as-prepared hydrophobic catalyst and an inert packing of Dixon phosphor bronze gauze rings were mixed homogeneously and used to fill the column. The Dixon gauze rings were used to promote surface area for the phase exchange reaction between the H₂O liquid and HDO vapor [6–12]. The total height of the catalyst–packing layer was 240 mm.

Deuterated water (D/H atomic ratio = 2.3×10^{-2}) and natural hydrogen steam were fed into the reaction column counter-currently, with deuterated water flowing from the top to the bottom of the column. The HD concentrations in the hydrogen gas at the reaction column inlet and outlet were analyzed with an Agilent 6890N gas chromatograph (HP Corp.). The catalytic activity was evaluated by the column efficiency η of the isotopic exchange column. The column efficiency calculation was in accordance with the literatures [11,12].

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