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Tuning metal support interactions enhances the activity and durability of TiO_2-supported Pt nanocatalysts

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ABSTRACT

A facile approach to enhance catalytic activity and durability of TiO_2-supported Pt nanocatalysts by tuning strong metal support interaction (SMSI) is investigated in this work. No need for a high temperature treatment, the strong metal-support interaction (SMSI) in TiO_2-supported Pt can be induced at 200° C by H_2 reduction. Moreover, electrochemical methods (methanol oxidation reaction and cyclic voltammetry) are first reported ever to be effective characterization tools for the coverage state caused by SMSI. In addition, the SMSI has also been confirmed by X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and Transmission Electron Microscopy. It is found that the encapsulation of TiO_{2-x} species on the surface Pt clusters was induced and modified by thermal reduction and fluoric acid treatment. The catalytic activity and durability of the TiO_2-supported Pt nanocatalysts are strongly dependent of the state of SMSI. The proposed SMSI-tunable approach to enhance the ORR activity and stability is also proved applicable to $Pt/Ti_{0.9}Nb_{0.1}O_2$ nanocatalysts. We believe that the reported approach paves the way for manipulating the activity and stability of other TiO_2-supported metal nanocatalysts. Furthermore, the suggested electrochemical methods offer facile and effective ways to verify the presence of coverage state before combining with other physical analysis.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are well known as a clean, highly efficient energy source to produce energy from hydrogen. Platinum is mainly used as a fuel cell catalyst material, but high price and scarcity limit its wide use. To further increase the activity and dispersion of Pt nanoparticles, carbon has been widely used as the support material for catalyst nanoparticles. Despite carbon support has several advantages such as large surface area, high conductivity, low cost and good accessibility, it still has shortcomings of corrosion and weak interaction with Pt, which would cause Pt agglomeration or detachment in the operation of the fuel cell, resulting in loss of activity catalyst after long-term operation [1]. In order to enhance the stability of the platinum catalyst, using metal oxide as the platinum catalyst support has attracted great interest. In addition to the benefits of improved stability, in some studies, researchers found that the metal oxide support and Pt nanoparticles can form a strong metal-support interaction (SMSI) [2–4]. Metal oxide supports provide electron to Pt nanoparticles and affect the unfilled d band vacancies of Pt, so that the adsorption, dissociation and desorption of oxygen species could be facilitated. Consequently, the oxygen reduction reaction rate increases and the SMSI effect significantly enhances the activity of the Pt nanocatalyst.

However, scientists found that the activity of metal-oxide supported catalysts decreases after heat treatment at high temperature. Tauster et al. suggested that phenomenon was attributed to the strong metal-support interaction (SMSI) which causes the Pd/TiO_2 catalysts lose it H_2 and CO adsorption ability after reduction at 773K [5]. Since then, SMSI effects in several metal nanoparticles (Pt, Pd, Rh, Co, etc.) on metal oxide surface (TiO_2, CeO_2, etc.) systems have been discussed after annealing at high temperature in reducing atmosphere [6–13]. This effect can be explained by the formation of reduced oxide species which

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migrate onto the surface of metal nanoparticles to form a thin film blocking the active sites on metal particles. As mentioned above, SMSI effect can be either beneficial to the enhancement of the catalyst activity and stability, or adversely affect the catalyst activity. Hence, an effective way is still needed to control and adjust the SMSI effect, so the positive effect prevails on catalyst and will not cause loss of activity. Also, establishing a simple and rapid way to observe SMSI effect will be necessary for further research [6–13].

In this work, we induced SMSI effect on Pt/TiO_2 catalyst at 200 °C in pure hydrogen atmosphere. Interestingly, we found that cyclic voltammetry (CV) and methanol oxidation reaction (MOR) can be used to clarify the coverage state caused by SMSI. Hydrofluoric acid was used to remove the reduced TiO_2 thin film on the Pt surface, followed by the oxygen reduction reaction (ORR) test. After facile acid treatment and the removal of oxide species on Pt, the catalyst's performance was significantly enhanced. This unusual effect has been also found on $Pt/Ti_{0.9}Nb_{0.1}O_2$ catalyst.

2. Experimental section

2.1. Materials

The TiO_2 supports used in this study were based on P-25 (Degussa). This material has 99.5% purity and main crystalline structure in anatase phase. The average particle size is 25 nm with a surface area of 50 m^2/g.

2.2. Synthesis of Pt/TiO_2 catalyst

A microwave-enhanced process was performed to synthesize Pt nanoparticles. 0.1 g TiO_2 support and 20 ml of ethylene glycol were put into a round-bottom flask and stirred by a magnetic stirrer for 30 minutes. The suspension was ultrasonicated for 1 hour to ensure all of the TiO_2 nanoparticles were well dispersed in ethylene glycol. Then this round-bottom flask was put into the 0 °C water bath to cool down the temperature to 5 °C. At the same time, 0.0664 g of H_2PtCl_6 was dissolved by 5 °C ethylene glycol to form an orange color solution. This solution will then be poured into the TiO_2 suspension that we already prepared in the previous step. This suspension was continuously stirred by a magnetic stirrer for 30 minutes, followed by the addition of 0.8 M NaOH ethylene glycol solution to adjust pH to 11.0. Next, the suspension was put into a microwave oven and heated to 160 °C with 300 W for 1 hour. After the reaction was complete, the solution was cooled down to room temperature in air. The black precipitate was centrifuged and washed with acetone and deionized water. The obtained 20 wt% Pt/TiO_2 was dried at 80 °C in oven for 12 hours. Finally, this black Pt/TiO_2 powder was collected and sealed in a glass bottle for further characterization and tests.

2.3. Hydrogen treatment

0.1 g of Pt/TiO_2 catalyst was put into a quartz filter tube purged with pure hydrogen gas at a flow rate of 10 mL/min. Then the sample was heated to 200 °C and kept for 1 hour. After hydrogen treatment, the sample was naturally cooled down to room temperature. This hydrogen treated Pt/TiO_2 (denoted as Pt/TiO_2-HT) was collected and sealed in a glass bottle for further characterization and tests.

2.4. Hydrofluoric acid treatment

0.04 g of Pt/TiO_2-HT was moved to a Teflon bottle and mixed with 5 ml deionized water. This suspension was ultrasonicated for 1 hour to ensure that all Pt/TiO_2-HT nanoparticles were well dispersed in water. After that, 2% hydrofluoric acid was slowly dropped into the bottle with continuous magnetic stirring. The suspension was continuously stirred for 24 hours at room temperature. Next, the black suspension was centrifuged and washed with deionized water, dried at 80 °C in oven for 12 hours. Finally, this hydrofluoric acid treated black Pt/TiO_2-HT powder (denoted as Pt/TiO_2-HFT) was collected and sealed in a glass bottle for characterization. For comparison, Pt/TiO_2 without any hydrogen heat treatment was directly washed with an HF solution by following the same procedure (denoted as Pt/TiO_2-FT).

2.5. Synthesis of $Pt/Ti_{0.9}Nb_{0.1}O_2$ catalyst

For more experiments, $Pt/Ti_{0.9}Nb_{0.1}O_2$, $Pt/Ti_{0.9}Nb_{0.1}O_2$-HT and $Pt/Ti_{0.9}Nb_{0.1}O_2$-HFT were synthesized. First, $Ti_{0.9}Nb_{0.1}O_2$ nanoparticles were synthesized by a hydrothermal process. Appropriate amount of $TiCl_4$ and $NbCl_5$ with atomic ratio 9:1 was dissolved in 8 °C water and ethanol respectively with continuous stirring. After stirring for 10 minutes, $TiCl_4$ and $NbCl_5$ solution were mixed together in Teflon bottle and stirred for another 10 minutes. The Teflon bottle was then sealed in stainless steel autoclave reactor and heated to 200 °C at 10 °C/min in an oven and kept at 200 °C for 2 hours. After that, the reactor was naturally cooled down to room temperature. $Ti_{0.9}Nb_{0.1}O_2$ suspension was taken out from the Teflon bottle and centrifuged. The particles were washed with deionized water for 3 times and dried at 80 °C for 12 hours afterwards. Pt loading of $Pt/Ti_{0.9}Nb_{0.1}O_2$, $Pt/Ti_{0.9}Nb_{0.1}O_2$-HT, and $Pt/Ti_{0.9}Nb_{0.1}O_2$-HFT were synthesized with the similar procedure as Pt/TiO_2, Pt/TiO_2-HT, and Pt/TiO_2-HFT above.

2.6. Material characterization

High-resolution Transmission Electron Microscopy (HRTEM) image and Energy-dispersive X-ray spectroscopy (EDX) elemental profiles were taken by Spherical-Aberration Corrected Field Emission Transmission Electron Microscope from National Tsing Hua University and Field Emission Gun Transmission Electron Microscopy from National Taiwan University of Science and Technology. X-ray photoelectron spectroscopy (XPS) was performed using the wide-range beamline (BL24A) of the NSRRC in Taiwan. The XPS binding energy scale was referenced to the bulk Au $4f_{7/2}$ core level located at 84.00 eV relative to the Fermi level. X-ray diffraction (XRD) patterns were acquired using a Bruker D2 Phaser XRD machine equipped with a Cu-Kα irradiation photon source, λ = 1.5406 Å, Ni filter, 40 kV and 100 mA. All samples were analyzed in the range 2θ = 20°–80°, with a scanning speed of 0.1° s^{-1} and 0.05°/step, at room temperature. X-ray absorption spectroscopy (XAS) spectra were recorded at the Beamline 17C and 07A1 at NSRRC in Taiwan. Measurements were made at room temperature.

2.7. Electrochemical Measurements

All electrochemical measurements were carried out by a three electrode cell connected to a potentiostat. Platinum foil was used as counter electrode, and Ag/AgCl electrode was used as the reference electrode. All potentials in this work are referred to normal hydrogen electrode (NHE). The working electrode was a glassy carbon electrode (GCE) with a 5 mm diameter (0.196 cm^2). The catalyst ink was prepared by dispersing a known amount of catalyst and 10% ECP300 carbon black in ethanol. This catalyst ink was then ultrasonicated for 3 hours. The glassy carbon electrode was cleaned by ethanol and washed by DI water. 1.4 μL of the ink contain 0.00784 mg Pt was dropped on the glassy carbon electron surface uniformly and dried in air to form a uniform thin film with Pt loading of 0.04 mg_{Pt}/cm^2. 0.5 wt% Nafion solution was dropped on the electron surface and air-dried. Methanol oxidation reaction