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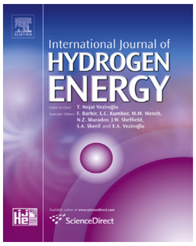

Methanol oxidation on sputter-coated platinum oxide catalysts

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ABSTRACT

Platinum oxide (PtO_x) and metallic platinum (Pt) layers deposited by means of radio frequency (rf) magnetron sputtering were examined as potential catalysts for partial oxidation of methanol (POM) reaction ($CH_3OH + 1/2O_2 \rightarrow 2H_2 + CO_2$) under realistic conditions. Flat Si(100) support and oxygen-plasma etched amorphous carbon films (a-C) were used as substrates for PtO_x. Elemental composition and morphology of the catalysts were characterized by x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). XPS analysis of PtO_x demonstrates change in its chemical state during the reaction leading to metallic layer with small amounts of stable Pt^{2+} cations which turns out to be crucial for its catalytic properties, while SEM reveals significant cracking and roughening of the oxide thin films. A reference Pt/Si catalyst, on the contrary, shows no significant differences prior and after the methanol oxidation reaction but lacks to PtO_x in both activity (in terms of H_2 production rate) and selectivity for POM, generating relatively high amounts of CO which can poison the catalyst surface. PtO_x deposited on the porous a-C outperforms the same oxide grown directly on Si, especially in its POM selectivity exceeding 90%. Both oxidic systems, however, require an initial conditioning under real reaction conditions to reach their optimal catalytic capability.

Introduction

The importance of hydrogen for energy production and energy storage applications has been continuously growing in recent years [1–5], mainly because it represents a clean-burning fuel with relatively high energy density. Hydrogen is being used mainly as a fuel in internal combustion engines or to supply proton exchange membrane fuel cells (PEMFC) which generate electricity directly by electrochemical oxidation of hydrogen [6,7]. Since hydrogen fuel cells produce only electricity and water vapor, their widespread application may lead to reduced consumption of oil and contribute to reduction of environmental pollution. Moreover, thermal efficiency of hydrogen fuel cells is higher than that of petrol-fueled combustion engines (35–40% versus 25–30%) [8,9]. The main problems of hydrogen as a combustible in fuel-cell-powered vehicle are safety, refueling, and storage. One of the strategies [10] to solve these drawbacks is on-board hydrogen generation from a suitable liquid fuel. Among different liquid fuels methanol is considered as one of the most viable options due to its high energy density, high hydrogen to carbon ratio,

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and good availability [11]. Hydrogen can be obtained from methanol by many different processes [12] such as methanol decomposition (MD, reaction (1)), steam reforming of methanol (SRM, reaction (2)) and partial oxidation of methanol (POM, reaction (3)):

$$CH_3OH \rightarrow 2H_2 + CO \quad (1)$$

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad (2)$$

$$CH_3OH + 1/2\ O_2 \rightarrow 2H_2 + CO_2 \quad (3)$$

When used in mobile technologies POM has some advantages over MD and SRM. MD (1) produces substantial amount of carbon monoxide thus such reaction is hard to be adopted for PEMFC without further treatment, because even very small traces of carbon monoxide can poison the noble-metal electrodes [13–15]. Steam reforming (2) is an endothermic reaction requiring a heat supply typically (on a large scale) realized by burning a fossil fuel, which has negative impact on the environment and reduces overall efficiency of the electricity production process. POM reaction (3), on contrary, requires oxygen or air instead of steam and since it is an exothermic reaction it does not need any external source of heat. Indeed, the overall POM reaction (3) involves several elementary steps where the undesirable carbon monoxide acts as one of the intermediates but it can be removed from the product stream by its preferential oxidation (PROX) [16]. Therefore an efficient catalyst for PEMFC and other applications demanding pure hydrogen should provide not only high hydrogen yield but also high activity for CO oxidation (to CO_2) and, at the same time, low activity for H_2 oxidation to prevent its conversion to water. However, both of the latter requirements are difficult to meet because on most noble metal catalysts hydrogen oxidation is faster than CO oxidation [17].

Platinum is among the most widely used transition metal catalyst for oxidation processes [18,19]. Recently, much emphasis has been paid to the oxidation state of the metal catalyst and differences between oxidized and reduced phases. In the case of platinum, there has been a debate regarding the advantages of Pt oxide over metallic platinum in fuel cell technology [20,21] and for CO oxidation reactions [22–24]. In this paper we report on methanol oxidation of model PtO_2 and Pt catalysts deposited on a flat Si(100) substrate and on a porous amorphous carbon interlayer (a-C) [25], which was deposited by the means of radio frequency (rf) magnetron sputtering. We demonstrate the superior reactivity and good selectivity of the platinum oxide based catalyst over the metallic one with the same thickness. The extreme versatility and tunability of the sputtering technique allows for straightforward preparation of virtually any arbitrary composition and structure in a single-step process unlike wet chemistry methods commonly used nowadays. It also provides excellent control in depositing low loadings of the active component (typically a noble metal) in a perfectly clean manner, which makes this technique very environmentally friendly and low-cost way of catalysts fabrication.

Experimental

Sample preparation

The catalyst thin films (PtO_x, Pt) with average thickness of 10 nm were prepared by means of DC magnetron sputtering at room temperature using a 2″-diameter platinum (99.95% purity) target and DC power of 10 W. We used naturally oxidized Si (100) wafer (0.3 mm thick, P-type, 6–12 Ω cm resistance) as a substrate. The choice of working gas (argon or oxygen) determined the growth of either metallic platinum or platinum oxide. With constant gas pressure in magnetron chamber at 4×10^{-1} Pa the deposition rate was approximately 3 nm/min for metallic platinum and 2 nm/min for platinum oxide layers. Platinum oxide was deposited not only directly on Si(100) but also on oxygen plasma treated amorphous carbon films (a-C) interlayer supported on Si(100). The amorphous carbon was grown by using a commercial modular high vacuum coating system MED020 (BALTEC). First, a-C thin film was deposited using direct current (DC) magnetron from a 2″-diameter graphite target (Goodfellow, 99.997% purity) onto a Si(100) in argon atmosphere, followed by oxygen plasma etching which was carried out the same device [25].

SEM

Morphology of samples have been characterized by means of scanning electron microscopy (SEM) using MIRA 3 (Tescan) microscope operating at primary energy of electron beam 30 keV.

XPS

X-ray photoelectron spectroscopy (XPS) was performed in an ultrahigh vacuum chamber operating at base pressure lower than 10^{-7} Pa equipped with SPECS Phoibos MDC 9 energy analyzer. Al X-ray source was used (total energy resolution $\Delta E = 1$ eV; photon energy $h\nu = 1486.4$ eV) for all measurements.

Micro-reactor

Partial oxidation of methanol (POM) over PtO_x and Pt catalysts sputtered on different substrates was examined in a laboratory micro-reactor system. All experiments were done at atmospheric pressures in the sample temperature range between 360 and 600 K, with heating rate of 2 K/min. Analyzed sample (16 × 16 mm) was sandwiched between a PID regulated resistive heater at the bottom and silicate glass with two feeding holes and a network of channels for better gas distribution over the sample surface, forming a micro-reactor cell volume. Silicon rubber sealing (100 μm thick) was placed around the perimeter of the sample to prevent leakage. The reactor cell was encapsulated in a relatively massive metal block to assure good thermal stability and spatial homogeneity.

Methanol vapor was introduced by bubbling helium buffer gas (Linde Gas, 4.6) through a saturator filled with methanol

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