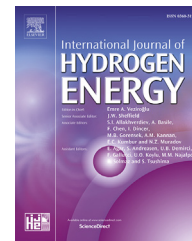




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Hydrogen production via methanol oxidation on platinum oxide thin film catalyst: Influence of methanol-to-oxygen ratio

Andrii Rednyk, Anna Ostroverkh, Viktor Johánek*

Department of Surface and Plasma Science, Charles University, V Holesovickach 2, 180 00 Prague 8, Czech Republic

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ABSTRACT

Platinum oxide (PtO_x) thin films deposited by means of radio frequency (rf) magnetron sputtering on oxidized Si substrate were investigated under realistic conditions as efficient catalysts promoting oxidation of methanol to produce hydrogen. The main focus was given to the role of reactant mixture (methanol + oxygen) composition at different surface temperatures. Freshly deposited PtO_x changes its chemical state and morphology during the initial reaction leading to strongly corrugated metallic Pt layer with small amounts of stable Pt²⁺ cations providing a crucial ingredient for its specific catalytic properties. With growing temperature or methanol-to-oxygen molar ratio the reaction selectivity of such catalyst generally shifts from pathways producing water to those generating hydrogen. The efficiency for a given reaction route can be thus maximized via independent tuning of the fuel-oxygen ratio and surface temperature. The most intensive hydrogen evolution with the lowest relative amount of CO by-product (but relatively high abundance of methanolic residuals) was achieved with mildly oxygen lean feed above 500 K. The highest selectivity for partial oxidation of methanol pathway (>80%) can be, on the other hand, obtained with stoichiometric or oxygen rich mixture.

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Introduction

Recently much emphasis has been paid to development of hydrogen-fueled combustion engines [1,2] and fuel cell devices for direct conversion of chemical energy of a fuel into electricity [3], typically using hydrogen [4,5] or methanol [6,7] as the primary energy source. Hydrogen has been recognized as a potentially major future power source for zero emission vehicles [1–3] and mobile technology [5,8,9]. When hydrogen is used as a fuel in mobile devices several problems have to be faced, such as safety, distribution, storage, and refueling

[2,10]. In order to overcome these issues a strategy of on-board hydrogen generation from a suitable liquid fuel can be utilized [8,9,11]. Methanol is considered to be a great potential resource for this purpose for its relatively high energy density, good availability, and high hydrogen-to-carbon ratio. The most rational way to convert methanol into hydrogen is partial oxidation of methanol (POM, CH₃OH + ½ O₂ → 2H₂ + CO₂) in which methanol steam and oxygen react on the surface of catalyst to yield hydrogen as a main product along with relatively harmless carbon dioxide. POM reaction is exothermic (ΔH° = –49.4 kJ mol^{–1}) and in most practical applications oxygen can be conveniently replaced by air [12]. The above

* Corresponding author.

E-mail address: viktor.johanek@mff.cuni.cz (V. Johánek).

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advantages make POM preferable reaction route over other hydrogen production processes, e.g., steam reforming of methanol (SRM, $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$), and methanol decomposition (MD, $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$). Especially the side-reactions evolving carbon monoxide have to be avoided unless an additional purification or oxidation stage is used. Apart from environmental risks associated with CO emissions there are also technical restraints, for instance, even low relative CO concentrations as little as few tens ppm can poison platinum electrodes of proton exchange membrane fuel cells (PEMFC), leading to rapid decay of cell efficiency [13,14].

Platinum and its oxides are well known as effective oxidizing catalyst [15–18]. Supported Pt is also widely used as a catalyst in PEMFCs [6,15,19–21] and for hydrogen production via methanol oxidation [17,22–25]. It has been widely discussed in recent literature on the oxidation state of Pt in such catalysts under realistic reaction conditions and the chemico-physical properties of the oxidized and reduced phases of Pt [23,26–28], including the electrochemical environment in fuel cell related applications [6,19,20,29–31]. Recently we have reported enhanced methanol oxidation activity of platinum oxide (PtO_x) layers prepared by magnetron thin-film sputtering as compared to bare platinum, which was attributed to the coexistence of highly stable Pt^{2+} cations and metallic platinum (Pt^0) with high specific surface area [25]. A key advantage of magnetron sputtering is possibility to prepare a broad range of thin films with almost any compositions deposited on either flat or high surface area substrates. Moreover, controlled growth rate of the thin films, fast and simple single-step deposition procedure makes this techniques superior compared to currently common conventional chemical (“wet”) methods. Apart from the catalyst structure and composition the reaction conditions (such as molar ratios of reactants [17]) provide another degrees of freedom in tuning the performance of a given catalyst. In this report we extend our previous analysis of methanol oxidation on PtO_x [25] by investigating the influence of oxygen content in the feed mixture on activity and selectivity of this material in the catalytic oxidation of methanol, with focus on a clean and energetically convenient hydrogen production.

Experimental

10 nm thick platinum oxide thin film catalysts were prepared by means of reactive direct current (DC) magnetron sputtering. Deposition was performed from 2"-diameter platinum target (99.95% purity) onto a naturally oxidized Si (100) wafer ($16 \times 16 \text{ mm}^2$; 0.3 mm thick) placed 90 mm away from the Pt target. The sputtering was carried out at room temperature in a vacuum chamber ($<5 \times 10^{-5}$ Pa base pressure) filled with oxygen (Linde Gas, Purity 5.6) at 4×10^{-1} Pa partial pressure. DC power applied to the Pt target was 10 W. With the above parameters a PtO_x deposition rate 2 nm/min was achieved.

The surface morphology of the $\text{PtO}_x/\text{SiO}_2$ sample was examined by means of scanning electron microscopy (SEM) using MIRA Tescan microscope operated at 30 keV electron beam energy. Elemental and chemical analysis was done by X-ray photoelectron spectroscopy (XPS) in an ultrahigh vacuum chamber (base pressure $<10^{-7}$ Pa) equipped with SPECS

Phoibos MDC 9 energy analyzer and an X-ray source operated with Al anode ($h\nu = 1486.4 \text{ eV}$).

Catalytic activity measurements at atmospheric pressure were performed in a laboratory micro-reactor system, which has been described in more detail in our previous paper [25]. Methanol vapor was produced by bubbling helium buffer gas (Linde Gas, 4.6) through liquid methanol (Penta, 99.8% purity) held at 303 K. Oxygen (Linde Gas, 5.0) was added prior to entering reaction cell. Methanol to oxygen ($\text{CH}_3\text{OH}:\text{O}_2$) molar ratios were adjusted via independent change of helium and oxygen flow rates (regulated by Alicat Scientific mass flow controllers) while keeping the total flow at a constant value of 12 sccm (standard cubic centimeter). The product stream was passed through a cold trap ($T = 190\text{--}200 \text{ K}$) to remove water vapor and unreacted methanol and sampled through a precise manual metering valve to a vacuum chamber ($P < 10^{-5}$ Pa) equipped with a quadrupole mass spectrometer (QMS; Pfeiffer Prisma Plus 220). QMS current signals of major products (H_2 , CO , CO_2 , O_2) were converted to relative molecular concentrations using sensitivity factors obtained experimentally by calibrations with pure gases. Temperature programmed reaction (TPR) experiments were performed in the temperature range between 370 and 600 K with heating rate of 2 K/min, the active area of the sample exposed to the reactants was $13 \times 13 \text{ mm}^2$.

Results and discussion

Platinum oxide thin films with thickness 10 nm were deposited on a flat Si (100) substrate by the means of DC magnetron sputtering. Methanol oxidation TPR experiments were performed under different $\text{CH}_3\text{OH}:\text{O}_2$ molar ratios covering oxygen rich, stoichiometric, and oxygen lean conditions (1:1, 2:1, and 3:1) with respect to POM stoichiometry, as well as with pure methanol (MD conditions). Two consecutive temperature programmed reactions (denoted as TPR1, TPR2) were done for each sample at identical experimental conditions. The samples were then subjected to a time-on-stream test by keeping it for several hours (>8 h) under a steady gas feed flow at constant sample temperature of 600 K.

Let us begin with POM stoichiometric $\text{CH}_3\text{OH}:\text{O}_2$ (2:1) molar ratio as a benchmark. In Fig. 1 a comparison of catalytic activities in TPR1 and TPR2 performed on $\text{PtO}_x/\text{SiO}_2$ sample under 2:1 $\text{CH}_3\text{OH}:\text{O}_2$ gas mixture is presented. H_2 , CO , and CO_2 were detected as main reaction products. Other detectable side-products such as methane and methyl formate were formed only in insignificant amounts.

Hydrogen onset in both TPR1 and TPR2 is observed around 425 K (in a good accord with [17]), while some CO and CO_2 were already present at the beginning of the experiment at 360 K. The onset of hydrogen production is determined by the appearance of the H_2 signal above the noise level of the mass spectrometer for the given mass (4 amu), which gives an equivalent of about 50 ppm of the product stream. Carbon oxide and dioxide at lower temperatures may originate from methanol combustion or complete oxidation reactions (will be discussed later) and, in the first TPR, also from an oxidative removal of carbon impurities precipitated on the surface during sample transfer. The product pattern changes significantly between the first and the second reaction run

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