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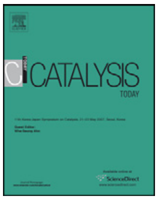

Enhanced activity of methanol electro-oxidation on Pt–V_2O_5/C catalysts

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ABSTRACT

The Vulcan carbon-supported vanadium oxide (V_2O_5) was prepared by solid-state reaction under intermittent microwave heating (IMH) method. Pt nanoparticles were dispersed by microwave-assisted polyol process over Vulcan carbon and V_2O_5/C. The catalyst samples were characterized by PXRD, TEM, CO-TPD and electrochemical methods. The TEM images showed homogeneous dispersion of ~3 nm size Pt metal crystallites embedded over Vulcan carbon support. The activities of Pt/C and Pt–V_2O_5/C for electrochemical oxidation of methanol were studied in 1.0 M KOH solution by cyclic voltammetry, chronoamperometry and chronopotentiometry. The influence of V_2O_5 component on the activity of Pt–V_2O_5/C was screened for catalytic oxidation of methanol. The results show that Pt–V_2O_5(4:3)/C composite catalyst performed better than Pt/C catalyst for methanol oxidation. The temperature programmed desorption (TPD) with CO was carried out to assess the CO tolerance of Pt–V_2O_5/C electrocatalyst. The formation of oxygen-containing species at lower potential can transform CO-like poisoning species on Pt to CO_2 in the presence of V_2O_5 which helps in regenerating active sites on Pt for further electrochemical oxidation of methanol. The enhanced electrode response is attributed to synergistic effect between Pt and V_2O_5.

1. Introduction

Direct methanol fuel cells (DMFCs) have been documented as promising power sources for compact, high-power density energy conversion [1,2]. Methanol has low-theoretical oxidation potential ($E^\circ = 0.03$ V) comparable to that of hydrogen ($E^\circ = 0$ V). Methanol is considered as an efficient fuel which can be obtained from natural gas, coal and biomass. It is an excellent energy carrier in the form of liquid at room temperature and atmospheric pressure. Unlike hydrogen, storage and utilization of liquid methanol does not need extensive modification of the existing fuel infrastructure. Despite these advantages, high over potentials for methanol oxidation and methanol crossover from anode to cathode through membrane prevent the use of DMFCs in practical applications. The strong adsorption of carbon monoxide on Pt anode inhibits the methanol oxidation reaction [3]. The electrocatalytic activities of anode are significantly enhanced when Pt is alloyed with Ru, Os, Ir, Rh, Mo and Sn either by modifying the electronic properties of Pt or by modifying the surface chemistry in which bifunctional reaction mechanism has been invoked to promote the oxidation of CO to CO_2 [4–10]. The multicomponent catalysts have exhibited superior performance relative to Pt metal, and so far, the incorporation of Ru into the Pt catalyst has yielded the best results. However, there is a need to reduce the loading of expensive noble metals and also improve the susceptibility of bimetallic electrocatalyst towards CO poisoning [11,12].

The anodic oxidation of methanol in alkaline media is more feasible than in acidic media. The open circuit potential of oxygen reduction is more positive in alkaline media than in acidic media [13]. In addition, the CO poisoning of the Pt catalyst is less likely in alkaline solution than in acidic solution. However, the problem with alkaline media is the progressive carbonation of solution due to CO_2 from air or the oxidation product of the fuel. The progressive carbonation of alkaline media has been addressed by the application of alkaline anion exchange membranes (AAEM) [14–16] and/or fuel-flexible, media-flexible laminar flow fuel cells [17,18]. Recently, Pt promoted oxides such as CeO_2 [19], ZrO_2 [20] and MgO [21] have been used as electrocatalysts for direct oxidation of alcohol in alkaline medium which significantly improved the electrode performance by enhanced activity and poison resistance. Although recent reports have demonstrated that Pt-based catalysts have higher activity for methanol oxidation, both in alkaline and acidic media, there is scope to reduce the catalyst loading for economic viability.

The supported vanadium oxides find catalytic applications in oxidative dehydrogenation (ODH) of propane [22] and selective catalytic reduction of NO_x by ammonia [23]. The vanadium-modified Pt catalysts have been applied for diesel engine exhaust gas conversion [24], and oxidation of organic compounds [25]. Various morphologies of vanadium oxide (V_2O_5) in the nano-regime

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have been synthesized and their utility as electrode materials is tested for lithium-ion batteries [26], electrochemical capacitors [27] and electrochemical sensors [28]. Surnev et al. have recently reviewed the surface and structural chemistry of vanadium oxide nano-layers in the context of catalysis [29]. Vanadium oxide layers exhibit redox and Lewis acid/base properties which are important for catalyzing surface reactions. In this communication we present the results on V_2O_5 incorporated Pt/C catalysts for direct electrochemical oxidation of methanol in alkaline solutions. A systematic electrochemical characterization of Pt–V_2O_5/C electrocatalysts for methanol oxidation is reported in this paper. The specific issues related to the CO tolerance of Pt metal-based fuel cell catalysts, the optimum Pt metal/V_2O_5 ratio, the possibility of improving catalytic activity, and the utilization of Pt metal are presented in this paper.

2. Experimental

2.1. Preparation of Pt/C or Pt–V_2O_5/C electrocatalysts

The V_2O_5/C used in this study was prepared by a solid-state reaction under intermittent microwave heating (IMH) method. In brief, the V_2O_5 (99.9% purity, Thomas Baker, India) powder was well dispersed over Vulcan XC-72R carbon (Cabot Corp., USA) using 2-propanol as solvent and the mixture was dried in oven at 80 °C. The mixture was then introduced into a microwave oven (Sharp NN-S327 WF, 2450 MHz, 1100 W) and heated six times, each time for 20 s followed by a 60 s pause. The Pt nanoparticles are supported over Vulcan carbon or V_2O_5/C by microwave-assisted polyol process [30]. Typically 1.0 ml of 0.05 M $H_2PtCl_6{\cdot}6H_2O$ (Aldrich, A.C.S. Reagent) was mixed with 25 ml of ethylene glycol (AR grade) in 100 ml beaker. 0.4 M KOH (in ethylene glycol) was added drop wise to adjust the pH of the solution to about 10 in order to induce the formation of small and uniform Pt nanoparticles. This mixture was sonicated after adding Vulcan carbon (in the case of Pt/C catalyst) or V_2O_5/C (in the case of Pt–V_2O_5/C catalyst) and the resulting mixture was subjected to microwave heating for 50 s. The sample under microwave irradiation was boiling at temperature approximately <300 °C since the boiling point of ethylene glycol is 197.3 °C. The resulting suspension was filtered and the residue was washed with acetone and dried at 25 °C in a vacuum oven overnight. The amount of V_2O_5 is varied at fixed amounts of Pt (0.01 g) and Vulcan carbon (0.04 g) in all four samples (Table 1).

2.2. Characterization of Pt/C and Pt–V_2O_5/C electrocatalysts

The reduction of Pt from their salts was monitored in the region of 200–800 nm by JASCO V 530 UV–vis spectrophotometer employing 1 cm path length quartz cuvettes. The phases and lattice parameters of catalyst samples were characterized by powder X-ray diffraction (PXRD) patterns employing Shimadzu XD-D1 diffractometer using Cu Kα radiation (λ = 1.5418 Å) operating at 30 kV and 20 mA. The particle morphology, size, and size distribution of catalysts were characterized by JEOL JEM-3010 transmission electron microscopy (TEM) at 200 kV operating voltage. Temperature-programmed desorption of carbon monoxide measurements were carried out using Micromeritics Chemisorb 2750 instrument under He flow (10 cm^3/min) at atmospheric pressure. Prior to the experiment, catalyst samples were activated at 200 °C in 5% H_2 in Ar for 1 h. The sample was cooled to room temperature in the same atmosphere and flushed with pure He for 15 min before CO chemisorption was carried out at room temperature for 1 h using 10.85% CO in He. The CO desorption profiles were recorded from room temperature to 300 °C at a heating rate of 10 °C/min.

2.3. Electrochemical measurements

The working electrodes for electrochemical measurements were fabricated by dispersing Pt/C or Pt–V_2O_5/C powders in 1.0 ml of distilled water and 5 wt% Nafion (75 μL). Ultrasonic treatment was given for 15 min to achieve uniform dispersion of the mixture at room temperature. A known amount of suspension was deposited on the surface of a glassy carbon electrode and the solvent was slowly evaporated. Finally, a drop of 1.0 wt% Nafion in ethanol solution was covered on top to prevent damage of the catalyst layer. The Pt loadings on Pt/C and Pt–V_2O_5/C electrodes were normally controlled at 0.3 mg cm^{-2}. Electrochemical measurements were carried out in a conventional three-electrode cell by using CHI 660B electrochemical workstation. A platinum foil and 1.0 M KOH|Hg/HgO (CHI Instruments, USA) were used as counter and reference electrodes, respectively. The test solution consists of 1 M CH_3OH and 1 M KOH. The dissolved oxygen was removed by purging the solution with pure nitrogen for 30 min before starting the electrochemical experiment.

3. Results and discussion

3.1. Physicochemical characterization of Pt/C and Pt–V_2O_5/C catalysts

The formation of Pt nanoparticles using microwave dielectric heating has been monitored by UV–vis spectroscopy. The H_2PtCl_6 solution before microwave irradiation is pale yellow and shows an absorption band at 264 nm due to ligand-to-metal charge-transfer transition in $PtCl_6{}^{2-}$ ion [31]. The pale-yellow color solution has become colorless after completion of the reaction. The disappearance of the band at 264 nm is verified suggesting complete reduction of $PtCl_6{}^{2-}$ ions (Eq. (1)):

$$PtCl_6{}^{2-} + CH_2OH - CH_2OH \rightarrow Pt^0 + CHO - CHO + 4H^+ + 6Cl^- \tag{1}$$

Table 1
Onset potentials and peak current densities obtained for the oxidation of methanol with different V_2O_5 loadings, and comparison of surface areas obtained from electrochemical and PXRD measurements

Catalyst	Onset potential (V)	i_p[a] (mA cm^{-2})	Q_H[b] (mC g^{-1} Pt)	EAS[c] (m^2 g^{-1} Pt)	S[d] (m^2 g^{-1} Pt)
Pt/C	−0.35	101	56.6	90 ± 10	107 ± 12
Pt–V_2O_5(4:1)/C	−0.35	121	–	–	–
Pt–V_2O_5(2:1)/C	−0.39	179	–	–	–
Pt–V_2O_5(4:3)/C	−0.42	200	59.8	94 ± 10	111 ± 12
Pt–V_2O_5(1:1)/C	−0.37	110	–	–	–

[a] Peak current density from cyclic voltammetry.
[b] Charge exchanged during the electroadsorption of hydrogen atoms on Pt particles.
[c] Surface area of Pt particles from electrochemical measurement.
[d] Surface area of Pt crystallites obtained from PXRD.