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Electrochemical behaviors of dimethyl ether on platinum single crystal electrodes. Part I: Pt(1 1 1)

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ABSTRACT

The electrochemical behaviors of dimethyl ether (CH_3–O–CH_3, DME), which is regarded as a promising fuel for the fuel cell, on platinum single crystal electrode in acidic solutions have been investigated in detail by electrochemical measurements. In 0.5 M H_2SO_4 solution, DME is dissociatively adsorbed on Pt(1 1 1) electrode surface in the low potential region between 0.2 and 0.5 V (vs. RHE) and further oxidized to CO_2 around 0.8 V. One of the stable adsorbed intermediates for DME decomposition on Pt(1 1 1) is carbon monoxide (CO) and its coverage is approximately constant (ca. 0.37) between 0.3 and 0.5 V. The adsorption of hydrogen and anion significantly affects the DME dissociation process. The kinetic analysis on DME decomposition process shows that the apparent reaction rate of DME decomposition on Pt(1 1 1) in the initial stage reaches a maximum around 0.35 V. No direct oxidation of DME has been observed on Pt(1 1 1) electrode surface. As a model reaction system, cyanide-modified Pt(1 1 1) electrode surface shows no activity on both decomposition and oxidation of DME.

1. Introduction

Dimethyl ether (DME, CH_3–O–CH_3) is expected to have high electrochemical activity due to its unique chemical structure (two C–O bonds without C–C bond) and is now regarded as a promising alternative fuel for the direct oxidation fuel cell [1–7]. It has several advantages in comparison with methanol in terms of high energy density and low toxicity. To improve the performance of the DME fuel cell, many fundamental studies on the electrochemical behavior of DME, mainly on platinum electrodes have been carried out since 2000 [8–16]. Muller et al. reported that DME in anode side crossed over Nafion® 117 membrane to the cathode side in a significant amount but was not oxidized there [8]. They suggested that one of the methyl groups in DME was firstly oxidized on platinum anode and further hydrolyzed to methanol as a reaction intermediate. Recently, Mizutani et al. reported that the main product of DME fuel cell was CO_2 with a small amount of by-products of methanol and methyl formate, where methanol coming from hydrolysis of DME and methyl formate producing by electrochemical oxidation of the molecule [9]. By *in situ* infrared (IR) spectroscopic measurements, Shao et al. reported a number of reaction intermediates during DME electro-oxidation on a platinum electrode surface, such as, linearly adsorbed CO (–CO_L), bridge adsorbed CO (–CO_B), –CH_2OCH_3, and adsorbed formaldehyde [13]. They also reported that the reaction products could depend on the concentration of DME. Kerangueven et al., however, showed fairly different *in situ* IR spectra for the similar system and claimed that –CO_L, –CO_B and –COOH were the most possible intermediates adsorbed on the platinum electrode surfaces during the DME electro-oxidation process [14]. Electro-oxidation of DME on Pt polycrystalline electrode has also been investigated in our group by electrochemical and *in situ* IR measurements in acidic solutions [16]. A reaction intermediate species, $(CH_3OCH_2–)_{ad}$, has been observed in the low potential region, which is subsequently decomposed to adsorbed CO and finally oxidized to CO_2 in higher potential region. This species has been assigned to an initial product for dehydrogenation process of DME on Pt electrode surface.

As shown above, there is a little agreement in the experimental results reported for DME electro-oxidation even they were carried out under similar conditions. The surface structure of the electrodes used is a possible explanation for the differences in these results. Since electrochemical reactions are very sensitive to the surface structure of electrode [17,18], it is difficult to compare electrochemical behaviors without considering their surface structure. The use of single crystal electrodes with well-defined surface structure is expected to be an ultimate choice to solve this problem. In fact, many valuable information about the electro-oxidation processes of small organic molecules, such as methanol [18–22], formic acid [23–26] and formaldehyde [27–29], has been

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obtained successfully by using noble metal single crystal electrodes such as platinum and palladium.

Recently, we reported for the first time that the electro-oxidation activity of DME on platinum single crystal electrodes depends significantly on the surface structures [30]. The (1 0 0)-terrace shows a particularly high activity for DME electro-oxidation in comparison with other basal planes. In the present paper, the electrochemical behaviors of DME on Pt(1 1 1) electrode in acidic solutions are systematically investigated for a full understanding of the mechanism for DME electro-oxidation under various experimental conditions, such as adsorption potential, sweep rate, bulk concentration and anion adsorption effect. The kinetics of dissociative adsorption of DME on Pt(1 1 1) surface has been quantitatively analyzed as a function of adsorption potential. Furthermore, in order to understand the role of atomic ensembles on Pt(1 1 1) electrode surface, DME electro-oxidation behavior on a cyanide-modified Pt(1 1 1) electrode, where certain surface sites of Pt(1 1 1) are blocked by a stable cyanide adlayer [31,32], has been characterized. It is found that at least three contiguous Pt atoms are needed for the initial decomposition reaction of DME molecules on Pt(1 1 1) electrode. Furthermore, the electro-oxidation scheme of DME on Pt(1 1 1) electrode is briefly discussed in comparison with methanol.

2. Experimental

The platinum single crystal electrodes were prepared according to Clavilier's method [33–36]. A platinum single crystal bead with a diameter of ca. 2.5 mm was prepared by melting a platinum wire of 0.8 mm in diameter (99.99%, Tanaka Noble Metal Corp.). The platinum single crystals were cut parallel to a (1 1 1) facet on the platinum bead surface by the aid of a home-made diode laser system and polished by alumina powders until 0.05 μm [35]. Before each electrochemical measurement, the platinum electrode was annealed in an H_2/air flame for a few seconds and then cooled down in an H_2/Ar mixed atmosphere, finally quenched in Milli-Q water saturated with the H_2/Ar mixed gas [36]. The electrode was transferred to the electrochemical cell by protecting surface with a droplet of water and then immersed into the solution under potential control, typically at 0.05 V. A meniscus configuration was made between the Pt(1 1 1) surface and the electrolyte to avoid any possible contact of other part of the platinum bead to the solution.

A three-compartment electrochemical cell was used for all the experiments. Reference electrode was a reversible hydrogen electrode (RHE), and counter electrode was a platinum foil. The electrolyte solution, 0.5 M H_2SO_4 or 0.1 M $HClO_4$ solution, was deaerated with Ar (99.99%, Hokkaido Air Water Inc.) for at least 15 min before each experiment. After checking the CV of the electrode in the blank solution, DME (99.99%, Sumitomo Chemicals Corp.) was bubbled through the solution until saturation (≈1.65 M) [8]. Influence of DME concentration was also investigated by diluting a freshly prepared DME-saturated solution with a certain volume of electrolyte solution. It is assumed that the DME concentration does not change soon after preparation. All electrochemical experiments were carried out using a potentiostat (TOHO Technical Research, POT/GAL 2020) and a function generator (TOHO Technical Research, Function Generator 2230) at room temperature (ca. 20 °C). The current and potential output from potentiostat was collected by a multifunction data acquisition module (USB-6211, National Instruments) controlled by LabVIEW, which allowing us to capture electrochemical response with a sampling rate as high as 15 μs at a signal resolution of 0.3 mV.

Cyanide-modified Pt(1 1 1) electrode was prepared by immersion of a clean, well-ordered Pt(1 1 1) electrode in 0.1 M KCN solution for approximately 3 min [31,32]. The electrode was rinsed with Milli-Q water and transferred to the electrochemical cell containing cyanide-free electrolyte solution.

3. Results and discussion

3.1. Electrochemical behaviors of DME on Pt(1 1 1) electrode in 0.5 M H_2SO_4

3.1.1. Voltammetric characterization in 0.5 M H_2SO_4

Fig. 1 (dashed trace) shows cyclic voltammogram (CV) of Pt(1 1 1) electrode in 0.5 M H_2SO_4, in which two typical features of a squared wave (0.05–0.3 V) and a "butterfly" wave (0.3–0.45 V) with a sharp spike at 0.45 V are observed. The CV is almost identical with that reported previously for Pt(1 1 1) in the same solution [33–36], indicating a well-defined structure of Pt(1 1 1). The current plateau and "butterfly" wave have been attributed to the adsorption/desorption of hydrogen and bisulfate (HSO_4^-), respectively [37–39]. The spike is ascribed to a disorder–order phase transition of the HSO_4^- adlayer on Pt(1 1 1) surface [40–42]. Existence of small peaks (0.13 V and 0.27 V) on the hydrogen adsorption/desorption wave indicates a small amount of defects on the surface [43]. A pair of redox peak is observed around 0.65 V which is used to be ascribed to the hydroxyl (OH)adsorption on the Pt(1 1 1) surface [40,41]. Recently, based on the thermodynamic analysis of charge density curves on Pt(1 1 1) electrode surface, Feliu et al. proposed that the small redox peak should be associated with the reorientation of the rotational domains of bisulfate adlayer to form a more ordered adlayer with an increase of the bisulfate adsorption on Pt(1 1 1) surface [44]. This CV is stable in the blank electrolyte solution for the experiment time scale (typically ca. 1–2 h). These results confirm the quality of the single crystal electrode and the cleanliness of the electrochemical system.

The voltammetric behaviors of Pt(1 1 1) electrode significantly change when DME is introduced into the solution. The solid and dash dotted traces in Fig. 1 are the first and second potential cycles starting from 0.05 V (scan rate, 50 mV/s), respectively, in 0.5 M H_2SO_4 solution saturated by DME. In the first positive-going potential sweep, the hydrogen wave with a square shape is almost the same with the blank solution, indicating that DME is more or less inactive in the potential region of hydrogen adsorption. The anodic current in the "butterfly" region (0.3–0.45 V) is clearly increased while the sharp spike at 0.45 V is depressed. Furthermore, an anodic peak is newly observed at +0.8 V. In the negative-going

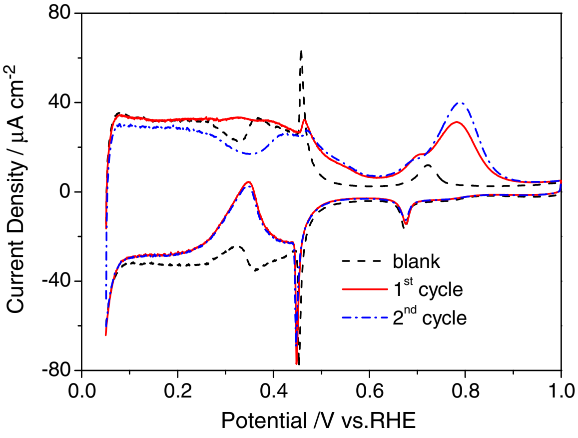

Fig. 1. The first (solid traces) and second potential cycles (dash dotted traces) starting from 0.05 V, respectively, in 0.5 M H_2SO_4 solution saturated by DME. CV of Pt(1 1 1) electrode in 0.5 M H_2SO_4 is also shown in the same figure (dashed trace). Scan rate, 50 mV/s.