Oxidation of Methanol using Carburized Molybdenum Catalyst

Shamsul Izhar*1,2 and Masatoshi Nagai1

1Graduate School of Bio-applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24 Nakamachi, Koganei, Tokyo 184-8588, Japan
2Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, UPM Serdang 43400, Selangor, Malaysia

Abstract: Molybdenum catalysts carburized in CH4/H2 exhibited activity for methanol electrooxidation (MOR) in half cell measurements. Mo carburized at 773 and 873 K showed high electrooxidation of methanol compared to carburization at other temperatures. Catalyst characterization was carried out by XRD and TPC. The active carbide species responsible to facilitate the MOR was the Mo oxy carbide and β-Mo2C species.

Keywords: Molybdenum carbide, Methanol oxidation reaction.

1. INTRODUCTION

Fuel cells have been well thought-out as substitute power source for the near future. Amongst the fuel cells that are currently applied today is the direct methanol fuel cell (DMFC), which has gained attention for use in electronic applications. Since the DMFC is made of membrane electrode assemblies consisting of precious Pt-metal alloy electrocatalysts, the expenditure to manufacture and marketable fuel cells is high. Thus, the foremost challenges in fuel cell research are to lessen the cost of the electrocatalyst either by lowering the Pt loading or by developing a non-precious catalyst. Especially in the latter case, it is essential to note that methanol oxidation reaction (MOR) catalyst requires a material with high electronic conductivity and electrocatalytic activity (because of the high 6-electron transfer), passive towards corrosion in acidic electrolytes, and tolerant towards poisoning from the intermediates formed during the reaction [1].

Since transition metal carbides have been stated to have Pt-like chemical reactivities and electronic properties [2], there have been many studies related to the development of transition metal carbides for use as hydrogen fuel cell electrocatalysts. Tungsten and molybdenum carbide have been shown to have some electrocatalytic activity towards the MOR [3] and hydrogen oxidation reaction [4]. The reason for their good activity is their ability to dissociate water then subsequently acts as a good oxygen donor, which according to Iwasita [5] is an important requirement in MOR. Zellner et al. [6] reported that methanol dissociates on the tungsten carbide (WC) film to produce the methoxy intermediate (CH3O), which is stable on the WC surface. Hwu et al. [7] also reported the possible role of molybdenum carbides as promoters for WC electrocatalysts in methanol fuel cell applications.

Although carburized catalysts have found to be a catalyst for MOR, there has been only little study on the catalysts active sites. In this work, various carbide phase was defined by varying the of carburization temperature during the catalyst preparation, in order to study the activity Mo carbide during MOR. The activity for MOR was performed using a half-cell electrode. Characterization of the carburized catalysts was carried out using XRD and temperature programmed carburization apparatus equipped with a quadrupole mass spectrometer.

2. MATERIALS AND METHODOLOGY

2.1. Preparation of Mo Carbine Catalyst

Mo carbide was prepared by a similar method reported by Izhar et al. [8]. In brief, MoO3 (Kishida) oxidic precursors were mounted into a quartz bed micro reactor and heated to 773 K in air for 1 hour at a heating rate of 10 K/min. After the temperature dropped to 573 K, the gas was changed to a continuously flowing stream of 20% CH4/H2 mixture. The temperature was increased to 773, 873, 973 or 1073 K, preserved at its final temperature for 2 h, at a ramping rate of 1 K/min. The reducing mixture was then cooled to room temperature and passivated under a stream of 1% O2/He gas for 12 h. Mo carbides dispersed on Ketjenblack (KB) was prepared by solving the catalysts in methanol with weight ratio of 30:70. The blend is then stirred until methanol is vaporized and dried in air at 393 K overnight. An ethanol based catalyst ink was prepared by adding ethanol to the catalyst. Then a water-based 5 wt% Nafion solution (Aldrich) is directly added to the catalyst/ethanol slurry. Nafion content is set to 35 wt% and stirred in an ultrasonic mixer.

2.2. Activity Screening and Catalyst Characterization

Half-cell measurement was carried out based on a previous method [8], using a ring-disc electrode in 1.0 M H2SO4 as the working electrolyte at room temperature. Methanol solution concentration dissolved with the working electrolyte was 1.5 mol/L. The working electrode and
H2O (m/z = 18) were qualitatively analyzed using the quadrupole mass spectrometer (Quastar 422, Balzers Co.) products in the gas phase that was analyzed using a carburization (TPC) was performed to obtain the desorbed donor of the reaction, thus probably producing CO2. RHE), dissociation of water occurred, which is the oxygen sites becoming free from H adsorption. At 500 mV (vs RHE), all three carburized catalysts showed current densities of 9 mA/cm², while the non-carburized MoO3/KB showed less than 1 mA/cm². The carburized Mo catalyst undoubtedly demonstrated better catalytic activity than the non-carburized MoO3/KB.

The capacitive currents between 0.4 and 0.6 V (vs RHE) was determined by integration of the voltammogram in Fig. (1) between the 0.4–0.6 V (vs RHE) potential region. A commercial analysis program (OriginLab, Microcal Corp.) was used to determine the area using a non-linear peak fitting function. As shown in Fig. (2), the 873 K-carburized Mo catalyst showed the highest capacitive current with 1310 mC/cm², followed by those carburized at 773 (822 mC/cm²) and 973 K (518 mC/cm²). This demonstrates that carburization temperature is an important factor in producing active carburized catalyst for methanol oxidation. This phenomenon is in agreement with a result by our group using cobalt molybdenum carbides for hydrogen oxidation reaction [9].

3. RESULTS AND DISCUSSION

3.1. Activity Screening of Mo-C/KB in Half-Electrode Cell Electrode

Fig. (1) illustrates the cyclic voltammetry of Mo carbide catalysts supported by KB. In the forward sweeps, a clear peak at 500 mV (vs RHE) and 150mV (vs RHE) during the reverse sweep can be observed with the presence of fuel in the electrolyte. However a small peak at 200 mV (vs RHE) during forwards sweeps was observed only for the Mo carburized at 873 K. This could be due to the carbide active sites becoming free from H adsorption. At 500 mV (vs RHE), dissociation of water occurred, which is the oxygen donor of the reaction, thus probably producing CO2.

Mo carburized at 773, 873 and 973 K showed higher anodic activity with dissolved methanol compared to the activity in argon without fuel. At 500 mV (vs RHE), all three showed highest current density between 10 and 20 mA/cm² respectively. However the 1073 K-carburized catalyst showed current densities of 9 mA/cm², while the non-carburized MoO3/KB showed less than 1 mA/cm². The carburized Mo catalyst undoubtedly demonstrated better catalytic activity than the non-carburized MoO3/KB.

3.2. XRD measurement was performed over the carburized catalyst to give a wide view of the active species for MOR. The XRD analysis of the bulk Mo carburized at various temperatures are shown in the Fig. (3). The high intensity of β-Mo2C becomes clear as the carburization temperature increases to 973 K. Small peaks at 2θ = 12°, 33°, 38°, 42° and 62° for the 773, 873 and 973 K carburized Mo carbides were assigned to the oxycarbide species according to Oshikawa et al. [10] and Oyama [11]. Broad peaks at 2θ = 25° for all the supported catalyst is probably due to the presence of KB. For Mo carburized at 873 K that exhibited the highest activity, peaks of β-Mo2C and MoOxCy were observed. This consequently illustrates the key to active species of Mo carbide for MOR was β-Mo2C and MoOxCy. This result is in agreement with Izhar et al. who revealed that oxycarbides are the active species for hydrogen oxidation reaction [9].
the formation of CO at 967 K was related to the complete transformation of MoO$_3$ to the β–Mo$_2$C since XRD for 973 K carburized MoC showed peak intensity for the oxyxcarbide. Therefore, based on the TPC measurement, it can be concluded that the principle reactions taking place during the carburization are the reduction of MoO$_3$ to β–Mo$_2$C by CH$_4$/H$_2$, the deposition of carbon by the decomposition of methane, and the dissolution of carbon into the Mo system.

Since the activity towards the MOR is the highest for 873 K carburized MoC and the TPC showed the presence of MoO$_3$C$_y$ and β–Mo$_2$C at 873 K, the amount of oxygen-containing species (oxyxcarbide) in the catalyst is one of the factors to take into consideration as the active species. The oxyxcarbide species facilitated the reaction of the resulting residue with some O-containing species to form CO$_2$ (or HCOOH). On the other hand, at above 973 K, XRD demonstrated the presence of free carbon in the surface layer that resulted in a remarkable reduction of catalytic activity. Okamoto et al. [12] in their study on the role of oxygen in tungsten carbide has also shown that the MOR activity was significantly enhanced over tungsten carbide that included the most oxygen in the catalyst.

4. CONCLUSION

Molybdenum carbide catalysts prepared by carburization in a mixture of 20% CH$_4$/H$_2$ at various temperatures was studied as catalysts for MOR. The carburized catalyst exhibited higher activity for methanol electrooxidation in half cell electrode measurements as compared to that without carburization. Furthermore, carburization of molybdenum at 773 and 873 K showed high electrooxidation of methanol compared to carburization at other temperatures. XRD and TPC were used to identify the active species for MOR. The active carbide responsible to facilitate the MOR was the Mo oxycarbide and β–Mo$_2$C species.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

Declared none.

REFERENCES


