

Electrochemical and Photoelectrochemical Reduction of Carbon Dioxide in Metal Powder-Suspended Methanol

Yousuke Ueno,¹ Satoshi Kaneco,^{1,*} Tohru Suzuki,² Hideyuki Katsumata¹ and Kiyohisa Ohta¹

¹ Department of Chemistry for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507, Japan
² Environmental Preservation Center, Mie University, Tsu, Mie 514-8507, Japan

1. Introduction

In the past 60 years, the amount of anthropogenic carbon dioxide (CO₂) emitted to the atmosphere, primarily because of expanding use of fossil fuels for energy, has risen from preindustrial levels of 280 parts per million (ppm) to present levels of over 365 ppm. Consequently, the dire warning of severe weather perturbations and globally rising temperatures have been given. Although scientists, engineers, policy makers, and others are looking for ways to reduce the growing threat of climate change, there is no single answer. Therefore, the development of carbon capture and sequestration technologies, which has accelerated greatly in the last decade, may play a significant role in addressing this issue. Carbon sequestration can be defined as the capture and secure storage of carbon that would otherwise be emitted to or remain in the atmosphere. In order that CO₂ can be economically transported and sequestered, carbon capture prefers a relatively pure stream of the gas. Pathways for carbon capture come from potential sources such as several industrial processes which produce highly concentrated streams of CO₂ as a byproduct, power plants which emit more than one-third of CO₂ emissions worldwide and the production method of hydrogen fuels from carbon-rich feedstocks. CO₂ can be removed from the gas streams by physical and chemical absorption. Recently, the chemical absorption using amines represents the most widely deployed commercial technology for capture. However, in other commercial applications, the typical solvents for physically absorbing CO₂ include glycol-based compounds and cold methanol.

Methanol is a better solvent of CO₂ than water, particular at low temperature, because the solubility of CO₂ in methanol is approximately five times that in water at ambient temperature and eight to fifteen times that in water at temperatures below 0 °C. Therefore, methanol has been industrially used as the physical absorbent of CO₂ in Rectisol method at low temperature. Currently, over 70 large-scale plants apply the Rectisol process.

Recently, many investigators have actively studied the electrochemical reduction of CO₂ using various metal electrodes in organic solvents, because organic aprotic solvents dissolve much more CO₂ than water. It has been described that low reduced products containing carbon monoxide, oxalic acid and formic acid were produced by the electroreduction of CO₂ in dimethyl sulfoxide, N,N-dimethyl formamide, propylene carbonate and acetonitrile. However, even at a copper electrode, few hydrocarbons have been obtained in these organic solvents. Therefore, we investigated the electrochemical reduction of CO₂ with copper electrode in the methanol-based electrolyte¹⁻³.

In the present study, the electrochemical and photoelectrochemical reduction of CO₂ in metal-suspended methanol has been presented.

2. Experimental

The electrochemical and photoelectrochemical

reduction of CO₂ was performed in a custom-made, divided H-type cell. An Aldrich Nafion 117-type ion exchange membrane (0.18 mm thickness) was used as the diaphragm. The cathode potential was measured with respect to an Ag/AgCl sat. KCl electrode that was connected with the catholyte through an agar salt bridge.

The methanol (99 %, Nacalai Tesque, Inc., Japan) was used as received without further purification. Sodium hydroxide (Nacalai Tesque, Inc.) were used as the supporting salt in the methanol-based catholyte. 300 mM KOH/methanol was used as the anolyte.

Lead and zinc were used as the cathode for the electrochemical reduction, p-InP as the photocathde for the photoelectochemical reduction.

A discontinuous electroreduction procedure was used: first, CO₂ gas was bubbled into the methanol catholyte for 1 h at a rate of 30 ml/min, then the CO₂-saturated solution was reduced photo/electrolytically at cathodic polarizations. Stirring of the catholyte was provided by a magnetic bar. The Faradaic efficiencies of formation for the main products were calculated assuming that a total of 50 coulombs of charge passed through the cell. Gaseous products obtained during electroreduction were collected in a gas collector and were analyzed by gas chromatography. Products soluble in the catholyte were analyzed by using high-performance liquid chromatography and gas chromatography.

3. Results and discussion

In the electrochemical reduction of CO₂ at Pb electrode in methanol without the copper powder, the main reduction products from CO₂ were carbon monoxide and formic acid. However, in the presence of copper powder, hydrocarbons such as methane and ethylene were formed by the electrochemical reduction of CO₂ in methanol. Fig. 1 shows the effect of copper powder content on the formation of haydrocarbons in the electrochemical reduction of CO₂ at Pb electrode in methanol. The same phenomena were observed at Zn electrode.

References

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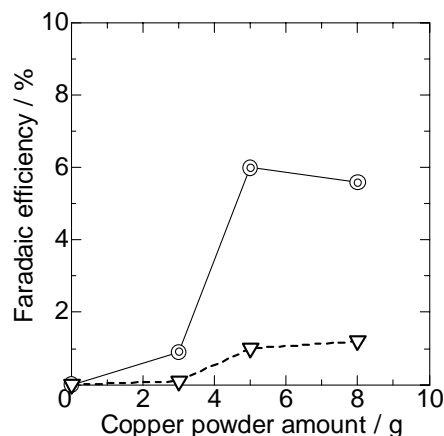


Fig. 1 Effect of copper powder amount on the formation of hydrocarbons in the electrochemical reduction of CO₂ at Pb electrode in methanol. CH₄: double circle, C₂H₄: reverse triangle.