

Electrocatalytic reduction of carbon monoxide to multicarbon products on copper-single atom catalysts

(¹Graduate School of Engineering Science, Osaka University) ○Keitaro Ohashi,¹ Takashi Harada,¹ Shuji Nakanishi,¹ Kazuhide Kamiya¹

Keywords: CO₂/CO Electroreduction; Single Atom Catalysts; First-Principles Calculation

The electrochemical CO₂ reduction reaction (CO₂RR) is an attractive strategy for closing the carbon cycle by converting CO₂ to value-added multicarbon products (C₂₊), using renewable electricity. Considering that C₂₊ products are formed via carbon monoxide (CO) dimerization,¹ the development of efficient electrocatalysts for CO reduction reaction (CORR) to C₂₊ products is highly required. Single-atom electrocatalysts (SAECs), which are composed of singly isolated metal sites supported on heterogeneous substrates, have attracted considerable recent attention as next-generation electrocatalysts for various key reactions from the viewpoint of the environment and energy. Our group has recently demonstrated that SAECs composed of metal-modified covalent triazine frameworks (M-CTFs) exhibit various unique electrocatalytic functions depending on the metal species.^{2,3} Herein, we attempted to apply copper-modified CTF (Cu-CTF) as the electrocatalyst to reduce gaseous CO to C₂₊.

Cu-CTF was synthesized based on the reported method,⁴ and the catalyst ink was drop-coated on gas diffusion electrodes (GDEs) (Fig. 1). The faradaic efficiency (FE) for acetate and ethylene in 1 M KOH at -1.0 V (vs. reversible hydrogen electrode) reached up to 27.2% and 16.2%, respectively. To elucidate the reaction mechanism of the selectively produced acetate, CORR was performed by changing the electrolyte to 5 M NH₃ and 1 M KCl. In this electrolyte, the formation of acetamide was observed with the FE of 4.7%, which is produced via nucleophilic attack of ammonia on ketene (C=C=O) intermediate. The density functional theory (DFT) calculation indicated that in the process of C₂₊ formation on Cu-CTF, C-C bond reaction proceeds by the insertion of a CO molecule into adsorbed *CHO intermediate, which is a one-electron reduction reaction intermediate of CO.

1) Kortlever, R. *et al. J. Phys. Chem. Lett.* **2015**, 6 (20), 4073–4082. 2) Kamiya, K. *Chem. Sci.* **2020**, 11 (32), 8339–8349. 3) Ohashi, K. *et al. J. Phys. Chem. C.* **2021**, 125 (20) 4) Kamiya, K. *et al. Nat. Commun.* **2014**, 5.

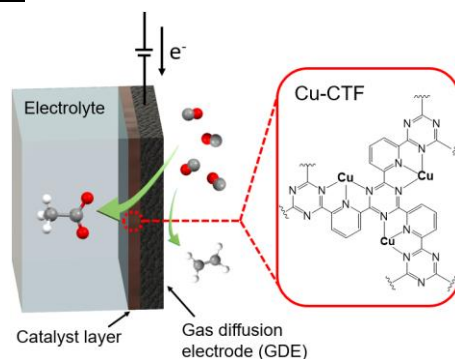


Figure 1. Schematic illustration of CORR on Cu-CTF/GDE.