Mechanistic Investigations of CO_2-reduction Using Supramolecular Photocatalyst Fixed on Solid Surface

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CO_2-reduction photocatalysts play a crucial role for developing artificial photosynthesis. Ru(II) metal complexes have been investigated as catalysts to reduce CO_2 and produce CO and HCOOH[1,2]. However, the reaction mechanisms of these metal complexes are still unclear. In this study CO_2 reduction mechanism of a supramolecular photocatalyst consisting of Ru(II) photosensitizer and Ru(II) catalyst units[3] was investigated (**RuRu**, Figure 1). **RuRu** was fixed on Al_2O_3 particles to prevent intermolecular collisions and its photocatalysis was investigated in detail by changing adsorbing density and photocatalytic reaction conditions for CO_2 reduction.

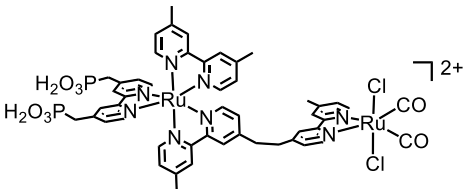

Figure 1. Structure of **RuRu**

The **RuRu** supramolecular photocatalysts were adsorbed on alumina particles by stirring in MeCN for 7 days. The adsorption density of **RuRu**/Al_2O_3 was controlled at 5 μmol g^{-1} where the distance between the neighboring **RuRu** molecules on the Al_2O_3 is much larger than the molecular length of **RuRu**. The **RuRu**/Al_2O_3 particles were dispersed into a dimethylacetamide-triethanolamine (DMA-TEOA) mixed solution containing 0.1 M of 1-benzyl-1,4-dihydronicotinamide (BNAH) as a one-electron donor and irradiated at $\lambda > 480$ nm under CO_2 atmosphere. Both CO and HCOOH was photocatalytically produced. The selectivity of HCOOH formation increased (from 91% to 94%) at lower irradiated light intensity. This strongly suggests that lower efficiency of the electron injection from the one-electron-reduced Ru photosensitizer unit to the Ru catalyst unit predominates the formation of HCOOH. On the other hand, CO selectivity (S_{CO} = CO/(HCOOH+CO) ×100) dramatically increased from 11% to 76% by decreasing the concentration of TEOA from 1.5 M to 0 M (Figure 2). We discuss about the photocatalytic reaction mechanism of CO_2 reduction.

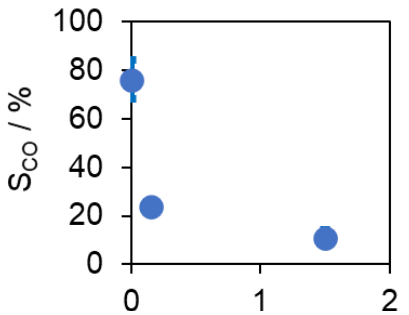

Figure 2. The relationship between TEOA concentration and CO selectivity.

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