

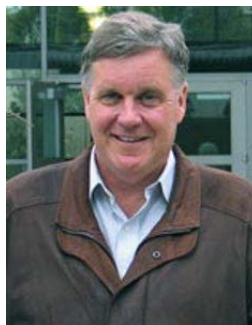
The electrocatalytic reduction of CO₂ and oxidation of formate and formaldehyde

Frontiers in Catalysis Science and Engineering Seminar Series

Presented by...

Clifford Kubiak

- Distinguished Professor of Chemistry and Biochemistry
- Harold C. Urey Chair in Chemistry
- UC San Diego



Abstract

Catalysis of the conversion of carbon dioxide to liquid fuels using solar and electrical energy is a global challenge that could impact the carbon balance by recycling CO₂ as fuels. A related challenge is the direct conversion of chemical energy contained in liquid fuels to electrical energy in fuel cell applications. Recent results in the study of artificial catalysts for the chemical reduction of CO₂ will be reviewed. The improvement in the activities of several rhenium based catalysts of the type Re(CO)₃(4, 4'-R₂bipy)Cl, and infrared spectroelectrochemical studies that probe the mechanism of catalysis will be described. The importance of proton coupled mechanisms will be discussed with respect to lowering the potentials for CO₂ reduction. Recent studies of the selectivity for H⁺ vs. CO₂ reduction pathways by UV-Vis and FTIR stopped flow kinetics studies will also be described. In the reaction of the reduced form of the rhenium CO₂ reduction catalyst, Re(CO)₃(*t*-Bu₂bipy)Cl, the anionic complex [Re(CO)₃(*t*-Bu₂bipy)]⁻ was found to react with CO₂ with a 2nd order rate constant >50-fold greater than those for the reactions with H₂O or various weak acids such as trifluoroethanol at the same concentrations. These studies together with high resolution X-ray spectroscopy (XANES) have shown that the high kinetic selectivity for CO₂ reduction to CO over H⁺ reduction to H₂ by Re(CO)₃(4, 4'-R₂bipy)Cl catalysts has its origins in a formally Re(0)bipy(-1) ground state of (dz²)¹(π*)¹ electronic structure. These findings provide clear guidance in the design of both catalysts for selective reduction of CO₂ to CO vs. H⁺ to H₂. They also provide a mechanistic understanding that enables the simultaneous formation of synthesis gas in various CO:H₂ ratios. The mechanistic principles also provide a basis for extending high rates of catalytic activity to the less expensive group VII metal, manganese. Our recent studies of the manganese catalysts will be presented. Recent studies of systems of interest to PNNL scientists and our research group, particularly the use of Ni and Pd complexes of the "P2N2" type ligands and their use in the electrocatalytic oxidation of formate and formaldehyde will be presented. Two new syntheses of the P2N2 ligands will also be described.

More info: <http://kubiak.ucsd.edu/>

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9:00 am