

Mechanisms of (Photo)Electrochemical Reduction of Carbon Dioxide from First Principles

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An alarming milestone was reached recently: the measurement of 400 ppm CO₂ in the Earth's atmosphere. It is more than past time that we recycle CO₂ formed from fossil fuel burning back into fuels or fuel precursors. My group is participating in this urgent research effort by working to uncover the mechanisms by which known catalysts actually operate so that, armed with such knowledge, we can hope to improve them or come up with new ones. Current reduction catalysts are inefficient, nonselective, expensive, or some subset of the three, hence the need for improvement or alternatives. Our theoretical work is performed in close collaboration and consultation with experimentalists, as indicated next. Two avenues of inquiry will be discussed:

- (i) homogeneous electrocatalytic reduction of CO₂ to CO by rhenium and manganese complexes made by Kubiak and coworkers

and

- (ii) heterogeneous photoelectrocatalytic reduction of CO₂ to methanol by GaP electrodes and pyridinium catalysts first observed by Bocarsly and coworkers.

Once CO is made and a renewable and efficient process for water electrolysis to hydrogen is established, the combination can be used in standard syngas routes (Fischer-Tropsch) to fuel. Once methanol is made, standard zeolite catalysis (the Mobil process with ZSM-5) converts methanol to gasoline. Efficient, selective, and inexpensive routes to CO and methanol can contribute greatly to recycling CO₂ rather than elevating our CO₂ emissions further. Understanding the mechanisms of these two reaction classes will help achieve this goal. We will report insights gleaned from calculating reduction potentials, acidities, and activation barriers related to electron and proton transfer reactions in solution, as well as mechanisms related to adsorption and reaction on a GaP electrode surface. The latter is likely a non-innocent bystander in the chemistry, as we shall discuss.

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