## Palladium Triphosphine Catalysts for CO<sub>2</sub> Reduction

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Global climate change is unquestionably one of the greatest social and scientific challenges of our time. Anthropomorphic carbon dioxide emissions, the primary culprit in the alterations to our ecosphere, are produced by the combustion of fossil fuels to produce  $CO_2$ ,  $H_2O$ , and energy. The United Nations Framework Convention on Climate Change is currently negotiating for a 25-40% decrease in  $CO_2$  emissions by 2030<sup>1</sup>, at the same time as the world population is increasing and developing nations are improving their standards of living. Energy production must begin to rely more upon carbon-neutral technologies, such as nuclear, wind, and solar power, if we are to meet these goals. Hydrocarbons, however, are easy to store and transport, and are supported by a vast worldwide infrastructure that will be functioning for decades to come. The only  $CO_2$ -neutral way to continue to use hydrocarbons as fuels is to use  $CO_2$  to produce the fuels in the first place. Using corn ethanol and other forms of biomass is one way to accomplish this, but growing plants for fuel requires land that might otherwise be used to grow plants for food. A man-made photosynthesis analog, turning solar (or wind, or nuclear) energy into liquid fuels by reducing  $CO_2$ , is therefore desirable.

The thermodynamics of  $CO_2$  reduction favor electron transfer coupled with proton addition. The single-electron-reduction of  $CO_2$  is energetically much more demanding than proton-coupled electron transfers, as shown by the following reduction potentials.<sup>2</sup>

	E <sup>0</sup>	ΔG
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.53 V	+102 kJ
$\rm CO_2 + 2H^+ + 2e^- \rightarrow \rm HCO_2H$	-0.61 V	+118 kJ
$CO_2 + e^- \rightarrow CO_2^-$	-1.90 V	+367 kJ

The kinetics of the reduction, however, are not as favorable. Direct reduction of  $CO_2$  has been achieved on many electrodes, but the reduction overpotentials are high, and mixtures of products, including CO, formate, oxalate, and H<sub>2</sub> gas, are usually produced.

The challenge of electrocatalytic production of fuels from  $CO_2$ , therefore, lies in finding stable molecular catalysts that will form just one product at economically feasible voltages. A variety of homogenous catalysts that will facilitate this have been developed. Of the molecular electrocatalysts for  $CO_2$  reduction that have been developed to date, palladium complexes with triphosphine ligands are some of the most successful. The original catalysts are square-planar Pd compounds of the type shown in Figure 1, and they reduce  $CO_2$  to CO in acidic solution with selectivity of 85% for CO over H<sub>2</sub>, second-order rate constants ranging from 50-300 M<sup>-1</sup>s<sup>-1</sup>, and overpotentials of approximately 0.3 V.<sup>3</sup>



Extensive kinetic studies on the catalyst indicate that there are two kinetic regimes. At low acid concentration the reaction is second order in acid, first order in catalyst, and unaffected by the  $CO_2$  concentration. At high acid concentration, the reaction is zero order in acid and first order in both catalyst and  $CO_2$ . The proposed reaction mechanism for the reaction is shown in Figure 2<sup>4</sup>. The turnover number for this class of catalyst, however, is low, ranging from 10-100 depending on the steric hindrance from the ligands. The major decomposition product is a Pd(I)-Pd(I) dimer.



Another Pd phosphine catalyst that shows promise for  $CO_2$  reduction is  $[Pd_2(CH_3CN)_2(eHTP)](BF_4)_4$ , shown in Figure 3<sup>5</sup>. The turnover number for the catalyst is only 8, lower than even the monomeric palladium triphosphine compounds, but the turnover rates are high enough (k> 10<sup>4</sup> M<sup>-1</sup>s<sup>-1</sup>, two orders of magnitude greater than the monomeric catalysts) to suggest that the two Pd atoms are cooperatively interacting. The kinetic data support this, since the reaction is first-order in acid at low acid

concentrations. The proposed reason for the increase in rate is the formation of a sevenmembered ring complex between the dimer and  $CO_2$  (Figure 5).



Attempts to increase turnover number produced the dimeric molecule shown in Figure 4<sup>4</sup>, with a rigid structure and sterically bulky ligands that prevent the Pd(I) decomposition pathway that affected the monomers. Kinetic studies on the molecule suggest that the two Pd atoms operate independently of each other, and the catalyst showed less than 20% decomposition after 200 turnovers, with second-order rate constants of about 50  $M^{-1}s^{-1}$ .

Electrocatalytic reduction of  $CO_2$  to usable fuels must be performed at good rate and low overpotentials with good catalytic stability. Palladium phosphine  $CO_2$  reduction catalysts have been developed that reduce  $CO_2$  with overpotentials of only 0.3 V. The research into this area is promising, but more work will be needed to find catalysts that make  $CO_2$  reduction economically practical.

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