

VALUE-ADDED CONVERSION OF CARBON DIOXIDE TO ALCOHOL FUELS

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Selective conversion of CO₂ to alcohols has several redeeming features especially in view of the fact that large amounts of these chemicals are manufactured world-wide. However the current feedstocks for alcohol production (mainly via steam-reforming) are petroleum-based with a sizeable carbon footprint. Further, the high operating pressures and temperatures needed for steam reforming translates to correspondingly high capital investment and a long energy pay-back period. Therefore **mild** methods for producing alcohols from environmentally problematic feedstocks such as CO₂ take on added importance. It is also worth noting that in addition to applicability as transportation fuels, alcohols are commodity chemicals that have wide-ranging use in plastics manufacture, paint formulations, for making resins and electric insulation, in the pharmaceutical sector, in anti-freeze fluids, and as laboratory solvents.

In this talk, both electrocatalytic and photoelectrocatalytic (PEC) methods for converting CO₂ to alcohols will be described as milder process alternatives to steam reforming. First the use of Pt/C/TiO₂ nanocomposites will be discussed whereby CO₂ is shown to be efficiently converted to methanol and isopropanol in the presence of a pyridine co-catalyst [1]. Comparison with the behavior of a Pt disk electrode of comparable geometric area will be presented and it will be shown how the product distribution is different in the two cases. The process efficiency is also greatly enhanced with the use of a nanocomposite film while drastically reducing the amount of Pt in the latter case.

The second approach centers on the use of an inorganic semiconductor (specifically p-type) to photocatalytically drive the reduction of CO₂ without the use of a co-catalyst or an expensive noble metal such as Pt. Many inorganic p-type semiconductors have been deployed in the literature [2] for PEC reduction of CO₂ including: CdTe, GaP, GaAs, InP, Si, and FeS₂. However with the exception of the last compound (pyrite) and elements such as Si and P, all the other component elements in these semiconductors are either toxic (As, Cd)

or not earth-abundant (Te, Ga, In). Selective photoconversion of CO₂ to methanol without the use of a co-catalyst also is not commonplace in these prior studies, and in the isolated such cases, methanol was only photogenerated at very high overpotentials. Two-electron reduction products such as CO and formic acid have been reported in some cases in place of the (more difficult) six-electron conversion to methanol. With the use of semiconductor *colloids* such as CdS or ZnS, photocatalytic reduction of CO₂ yields mostly formate and/or formaldehyde as the products.

In the second part of this talk, solar photoelectrosynthesis of methanol will be described on hybrid CuO/Cu₂O semiconductor nanorod arrays for the first time at potentials ~800 mV below the thermodynamic threshold value and at Faradaic efficiencies of ~95%. The CuO/Cu₂O nanorod arrays were prepared on Cu substrates by a two-step approach consisting of the initial thermal growth of CuO nanowires followed by controlled electrodeposition of p-type Cu₂O crystallites on their walls. No co-catalysts (such as pyridine, imidazole or metal cyclam complexes) were used contrasting with earlier studies on this topic using p-type semiconductor photocathodes. The roles of the core/shell nanorod electrode geometry and the copper oxide composition were established by varying the time of electrodeposition of the Cu₂O phase on top of the CuO nanorod core.

The use of electrochemical quartz crystal microgravimetry (EQCM) to unravel the mechanistic aspects of CO₂ photoreduction on copper oxide photocathodes will be presented [3].

Finally methanol photogeneration was confirmed by GC-MS analyses of product evolved at -0.2 V vs. SHE, i.e., at an *underpotential* relative to the standard potential of CO₂/CH₃OH. This last feature is an important virtue of the p-type semiconductor based photoreduction approach. In contrast the (“dark”) electrocatalytic process counterpart for CO₂ reduction suffers from the electrical energy cost incurred from the need for considerable *overpotentials* to overcome the kinetic barrier associated with this process. This cost is simply circumvented in the solar PEC process from the energy inherent in sunlight.

Acknowledgments

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References

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