Renewable sources for CO₂ valorization through reductive processes

Paolo Stufano*
Department of Chemistry, CIRCC and University of Bari “Aldo Moro”,
Via Celso Ulpiani, 27 - 70126 Bari - IT

Two different strategies were investigated in order to address the energetic demand in CO₂ reduction to useful chemicals and fuels.

The first approach was based on the use of bio-glycerol, a byproduct of bio-diesel production process, as renewable H-donor for the hydrogenation of CO₂. Ruthenium catalysts have been proved to have high activity in CO₂ hydrogenation to formic acid, and interestingly these catalysts are in some cases the same which are used for homogenous hydrogenation of organic substrates with 2-propanol as hydrogen donor.[1] In order to use glycerol in the place of 2-propanol and to combine the processes of glycerol oxidation and CO₂ reduction a Ru(II) mediated Hydrogen transfer was performed under controlled conditions. A Ru(II) precursor, i.e. RuCl₂(PPh₃)₃ or RuCl₂(COD)/PPh₃ (COD = 1,5-cyclooctadiene) was reacted with aqueous glycerol in basic ambient affording a dihydrido-carbonyl Ru(II) complex, i.e. RuH₂(CO)(PPh₃)₃. The complex was isolated and characterized by multinuclear NMR analysis. RuH₂(CO)(PPh₃)₃ is known to catalyze the hydrogenation of CO₂.[2] The product of glycerol simultaneous decarbonylation and dehydrogenation was identified by ¹³C-NMR to be glycolic acid in form of potassium salt.[3] The overall process represents an interesting reaction for the conversion of two waste into added value products.

The second strategy concerned the photo-electrochemical regeneration of NADH for the enzymatic CO₂ to methanol through the dehydrogenase enzyme cascade: F₅₆₅DH, F₅₆₅DH and ADH.[4] Although, this process occurs under very mild conditions (water, 37°C, pH=7) and with optimal yield and selectivity (close to 100%), there still is a limitation associated with the consumption of the cofactor NADH. Enzymatic, chemical and photo-chemical approaches have been attempted,[5] but over these, electrochemical regeneration is considered the most attractive solution.[6] We have employed p-type semiconductor electrodes in order to utilize solar energy for photoelectrochemical NADH regeneration. While bare semiconductors were shown to produce only enzymatically inactive dimers (NAD₂), modification of the surface by electro-deposition of a thin layer of Pt or Ru metal caused the formation of 1,4-NADH as the main product. In particular red-light illuminated (>600 nm) Pt/p-GaAs showed an increased efficiency at low overpotentials (-0.75V vs Ag/AgCl) when compared to metal electrodes (> 7 fold), with no dimer detection. This study represents the first example of NADH regeneration at an illuminated semiconductor electrode. The absence of a mediator allows the direct coupling of this regeneration system with the enzymatic CO₂ reduction apparatus, modeling the light and dark reactions occurring in a chloroplast.

References


*Corresponding author: Paolo Stufano Tel: +39 0805442078; e-mail address: paolo.stufano@uniba.it