Research Project for Master Students

Metal Activation of CO for Energy Production

Early studies on the chemistry of transition metal carbonyls, that is, complexes of CO, showed that in certain conditions coordinated CO is activated to react with H2O.
Depending on the reaction system two types of processes may occur:

$CO + H_2O \rightleftharpoons CO_2 + H_2$ (1)

$CO + H_2O \longrightarrow CO_2 + 2H+ 2e$ (2)

Equation (1) is called the water-gas shift reaction which can be catalyzed by homogeneous and heterogeneous catalysts. However, the kinetic and thermodynamic parameters of this reaction have largely prevented its more widespread use for the production of H_2 (see Kolb et al, 2005 and refs therein).
On the contrary, equation (2) has been adopted by CO-trophic organisms to feed on CO and produce energy or Hydrogen by processing the protons and electrons produced by different enzymes than those that catalyze equation (2), e.g. Hydrogenase.

There are a number of organometallic systems capable of reacting according to eq (2). In these reactions, the electrons and protons produced may be used to produce either H_2 or to generate an electrical current when associated or supported on appropriate electrodes (see Kim et al, 2004 and Rodriguez-Rivera et al, 2005).
The aim of this project is to use the new generation of water solubilizing ligands to produce metal carbonyl complexes that may undergo reaction (2) under homogeneous conditions and/or facilitate their support to modified electrodes.
This work will be done in collaboration with one of the leading Electrochemistry laboratories in Portugal.

The proposed research plan will contemplate:

- synthesis and chemical characterization (IR, NMR, MS) of some transition metal carbonyl complexes bearing water solubilizing ligands involving inert atmosphere techniques;
- study of the reaction of these complexes with water in search of conditions of catalytic turnover;
- characterization of the electrochemical behavior of the complexes including, when feasible the preparation of electrochemical devices driven by the above reactions..

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Area: Chemistry, Electrochemistry, Green Chemistry, Sustainable Energy

Location: ITQB, Laboratory of Organometallic Chemistry

Kim et al. Powering fuel cells with CO via aqueous polyoxometalates and gold catalysts. Science 2004, 305, 1280-1283
Rodriguez-Rivera et al. Hydrogenation of benzene using aqueous solution of polyoxometalates reduced by CO over gold catalysts. J Am Chem Soc 2005, 127, 10790-10791
Kolb et al. Water-gas shift reaction in micro-channels - Results from catalyst screening and optimisation. Catalysis Today 2005, 110, 121-131