Iridium Catalysts for Water Oxidation, CH Hydroxylation and Alcohol Dehydrogenation

Abstract
Alternative energy requires electrocatalysis, for example of water oxidation. Homogeneous oxidation catalysis is harder to arrange than reduction or redox-neutral cases. For one thing the ligands must be oxidation-resistant, hence our choice of pyalk\(^n\). In the protonated form, pyalkH, this binds to the low valent metal precursor but on oxidation it loses the proton to become an exceptionally strong donor, both σ and π. Another feature of our best complexes is coplanar binding of the alkoxides or other anionic ligands. By raising the energy of just one of the d\(\pi\) orbitals, filled in d\(6\) octahedral Ir(III), we destabilize one pair of electrons so that oxidation with loss of these two electrons gives d\(4\) octahedral Ir(V). We also apply the same ideas to Rh, but here only Rh(IV) was accessible. Our catalytic solutions for water oxidation to O\(_2\) are too complex to characterize but model compounds were fully characterized in III, IV and V states. A Cu(pyalk)\(_2\) catalyst has also proved effective but this is still under study. The Ir catalyst can be attached to surfaces but depending on the case, the activity is sometimes reduced. Several new techniques for crystallizing these intermediates have proved valuable. These complexes are also active for CH oxidation in alkanes (or alkyl groups) with retention of configuration at carbon. Finally, we look at oxidation by dehydrogenation as applied to biomass conversion.