

be added to balance the halogen content of the organics, may be added to the recycle stream to give the highest practical concentration for the hydrolysis.

Conclusions

Double mediated electrochemical oxidation using the Cl(-I)/Cl(I) and Ru(IV)/Ru(VIII) couples in a cell very similar to a chlor-alkali cell has been shown to have promise for the treatment of organic waste streams, particularly halogenated or dilute, salty liquors. Currently, studies are concentrating on optimising the core process and examining the application of the system to a variety of 'real' wastes with an industrial origin.

Appendix

In a cell (193000Cb, 54 Ah) in which oxidation occurs, with cell voltage of 3V, 2 moles of electrons carry out the oxidation process, equivalent to one mole of [O] and costs ~ 1p. The same amount of oxidation delivered using hydrogen peroxide (one of the cheapest chemical oxidants) at a nominal cost of £600/te for a 35 wt.% solution (£1700/te H₂O₂, 29411 moles [O]) costs ~ 5.8 p. High-valent metal-based oxidants such as Cr^{VI} and Ce^{IV} are much more expensive. Bulk K₂Cr₂O₇ costs £1835/te (3400 moles, 10200 moles [O]) while Ce^{IV} nitrate ~ £10000/te (2300 moles Ce^{IV}, equivalent to 1150 moles [O]) and the equivalent oxidation, carried out using this reagent costs £8.68 (all costs assume 100 per cent efficiency for simplicity). Like peroxide, the electron (the oxidant itself) leaves no residues which are toxic or difficult to dispose of, while oxidants like Cr^{VI} and Ce^{IV} leave large quantities of spent oxidant for disposal.

References

- 1 F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley Interscience, New York, 1968
- 2 J. L. Courtney and K. F. Swansborough, *Rev. Pure Appl. Chem.*, 1972, 22, 47
- 3 D. G. Lee and M. van den Engh, "The Oxidation of Organic Compounds by Ruthenium Tetroxide" in "Oxidation in Organic Chemistry", ed. W. S. Trahanovsky, 1973, Academic Press, New York
- 4 C. Djerassi and R. R. Engle, *J. Am. Chem. Soc.*, 1953, 75, 3838
- 5 U. A. Spitzer and D. G. Lee, *J. Org. Chem.*, 1975, 40, 2539
- 6 D. C. Ayres, *Nature*, 1981, 290, 323
- 7 C. S. Creaser, A. R. Fernandes and D. C. Ayres, *Chem. Ind.*, 1988, 499
- 8 A. M. Couper, W. N. Brooks and D. A. Denton, "Modern Chlor-alkali Technology", 1989, 4, 71
- 9 P. C. S. Hayfield, *Platinum Metals Rev.*, 1998, 42, (2), 46
- 10 J. K. Beattie, R. W. Kaziro and P. A. Lay, *World Appl.* 89/05172

Direct Methane Oxidation by Platinum Catalyst

The conversion of natural gases into more useful alcohols is usually achieved by changing the alkane component of the natural gas into a combination of carbon monoxide and hydrogen (synthesis gas) which is then converted to higher order alkanes by the Fischer-Tropsch reaction (1). These processes require a lot of energy, so it would be less costly if the alkane component, usually methane, could be directly converted into alcohols, by selective oxidation; the main difficulty being the low reactivity of the C-H bond. One such method, from Catalytica Advanced Technologies Inc., California, used toxic mercury(II) salts, and resulted in methane being converted into a methanol ester in an approximately 43 per cent yield.

Now, however, the same group has reported the development of a successful, stable platinum catalyst (2). Platinum salts were already known to be more efficient for the oxidation of methane in strong oxidising acids, but were not stable in hot (>100°C) acid. By utilising stabilising ligands, catalysts of greater stability were devel-

oped. They found that the addition of a bidiazine ligand to a platinum(II) salt gave high stability to strong acids and oxidising conditions. One of the most effective catalysts was dichloro(η -2-{2,2'-bipyrimidyl})platinum(II), [(bpym)PtCl₂]. Three key steps were proposed for the conversion of methane: C-H activation, oxidation and functionalisation.

The present reaction, which takes place at 220°C, converts ~ 72 per cent of the methane to methyl bisulfate, and is thought to proceed via the formation of a methyl-platinum species. The authors state that the mechanism of the C-H reaction needs more investigation as the factors controlling its reactivity could lead to greater control of the reaction selectivity.

References

- 1 R. C. Everson and D. T. Thompson, *Platinum Metals Rev.*, 1981, 25, (2), 50; F. King, E. Shutt and A. I. Thompson, *op. cit.*, 1985, 29, (4), 14
- 2 R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh and H. Fujii, *Science*, 1998, 280, (5363), 560