

CHAPTER SEVEN

CONCLUDING REMARKS AND FUTURE DIRECTIONS

The present study was undertaken in order to characterise structural and compositional aspects of surface chirality at well-defined platinum single crystal electrodes. In addition it was hoped that the usefulness of cyclic voltammetry as a probe of surface chirality could be expanded to include a much greater range of organic species and surface types. In fact the ubiquity of voltammetry in examining surface chirality was also regarded as a crucial aspect of this investigation. Previous work in this area had been limited to glucose electro-oxidation at clean platinum monocrystalline electrodes [1-6]. Such work was also deemed relevant to problems of enantioselectivity in heterogeneous catalysis because although a substantial body of data concerning such reactions had been accumulated over the last twenty years [7,8], there was still a paucity of information concerning the subtle processes underlying the metal catalyst surface/substrate interaction [9,10].

Two key questions needed to be addressed at the beginning of the project:

- Are enantioselective interactions between metal surfaces and chemisorbate molecules observed when chiral kink sites are modified by metal adatoms?. This is important because such behaviour would hold out the possibility of 'fine-tuning' molecule-surface interactions in order to generate novel catalysts for use in the synthesis of fine chemicals.
- Do organic molecules other than glucose (aldoses) exhibit a chiral response when adsorption from the solution phase is taking place? If so, then a new way of examining chirality in two dimensions using voltammetry could yield detailed insights into asymmetric organic reactions via systematic changes in the structure and chirality of stereogenic centres on both the adsorbate and the catalyst surfaces.

If one takes the first of these questions, the answer is somewhat equivocal. In Chapter Four it was demonstrated that in order to understand the way metal adatoms attach themselves to various fundamental adsorption sites, one had to consider both differences in the work functions between the platinum substrate and the metal adsorbate (electronic effects [11]) and also surface diffusional properties of the adatom on particular vicinal planes. So, for example, bismuth deposition on platinum surfaces vicinal to the (111) plane always led to

the attenuation of hydrogen UPD processes associated with defect sites. Hence, by extension, since bismuth cannot adsorb hydrogen, such sites are deduced to be the preferred site of attachment for bismuth species adsorbing from the background electrolyte. This behaviour was confirmed for both (110) and (111)×(100) linear stepped platinum surfaces and ‘zig-zag’ or kinked surfaces. It was known previously from the work of Campbell et al. [12] that surface diffusion on Pt(111) is very rapid based on the fact that LEED superstructures for bismuth cannot be observed unless the surface is cooled below 150 K. In contrast, for bismuth deposited on Pt(100) in UHV, Stuve et al. [13] demonstrated that a well-ordered c(2×2) adlayer, at a coverage of 0.5 monolayers, was already well-developed even at 298 K (see later). Hence rapid surface diffusion on (111) planes should allow the bismuth adatom to eventually bond with the highest co-ordination sites present in the surface in order to maximise surface stability (thermodynamically stable sites). This behaviour is largely reflected for gold deposits, also the propensity of the gold atom to seek out defect sites is slightly less than that of bismuth as exemplified in the population of (111) terrace sites by gold prior to the complete blocking of linear steps for the cases of Pt(755) and Pt(533). This is postulated to be the result of the weaker interaction between the electrostatic dipole at the step and the gold atom relative to the more electropositive bismuth atom in accordance with the theory of Feliu et al. [11]. It may even be that a slightly repulsive interaction between the step and gold adatoms at ‘high’ local coverages of step site may be the mechanism by which complete blocking is prevented. In contrast, for gold and bismuth deposited on stepped surfaces vicinal to the more open (100) planes, simultaneous occupation of terrace and defect sites is always observed. Since defect sites afford the highest degree of co-ordination to a metal adatom, it is proposed that the most thermodynamically stable adsorption site remains the defect rather than the terrace. Hence there must be some kinetic barrier that prevents thermodynamic equilibrium being achieved. In the context of the previous LEED-UHV results pertaining to bismuth adsorption alluded to above [10], it is proposed that a decrease in the rate of surface diffusion on the more open (100) planes precludes the bismuth (and gold) adatoms accessing all sites on the surface prior to becoming chemisorbed and hence resulting in a random occupation of sites. For silver adatoms, the behaviour described above for bismuth and gold is modified still further since the possibility of surface alloying needs also to be considered. The strong affinity of silver for platinum has already been reported by Clavilier [14] whereby, gentle annealing of silver films on platinum single crystal electrodes leads to the spontaneous formation of surface alloys [15,16]. Attard and Al-Akl [17] have

also noted the propensity of silver to form surface alloys with platinum upon repetitively cycling electrochemical potential of a platinum electrode in the presence of silver ions. Moreover these workers demonstrated that nucleation of the surface alloy could only take place at defect sites [18]. For very flat Pt(111) and Pt(100)-(1x1) planes, little surface alloying was observed. This behaviour is in accordance with the present study in that the initial silver deposit is not stable with respect to potential cycling and a stable CV is attained only after at least 20 potential cycles. Although the kinetics of surface alloying were not investigated quantitatively, for stepped and kinked surfaces, the attainment of a 'stable' CV could be achieved with far fewer potential cycles since surface defects are present a priori. In fact it is for Pt(100)-(1x1) that the slow rate of surface alloying is highlighted in the present work. Hence although in the early stages of deposition, silver behaves very much like bismuth (silver is more electropositive than gold), at some critical coverage surface alloying takes place at defect sites leading to the generation of new electroadsorption states. These states are finally quenched as silver is adsorbed on top of the silver-platinum surface alloy.

Hence it may be expected, assuming that no other electronic mechanisms are occurring, that the population of surface kink sites by bismuth and gold should result in an attenuation in the activity of the surface (since glucose activation under acidic conditions is negligible for both metals) and perhaps also a gradual diminution in the chiral response of the chiral electrode once chiral kink sites are blocked for the same reason. For silver-induced modifications of the platinum, distinct electrochemical properties intermediate between platinum and silver may be expected based on the formation of silver alloys. For gold adsorption these speculations are largely born out. All activity is quenched at precisely one monolayer coverage and enantioselectivity is found to be negligible once all kink sites are blocked. For silver too, expectations are met with enantioselectivity being observed over a much greater range of silver coverage together with new electroadsorption features giving rise to a chiral response, similar to the behaviour of bulk Pt-Pd single crystal alloys. It is only when all platinum atoms are blocked, that glucose activity falls to zero. Bismuth adsorption however caused both an increase in activity as defect sites were blocked together with a switching in the sense of enantioselectivity. It is well known that increasing the surface density of linear steps leads to an attenuation in the glucose electro-oxidation current on platinum [2] and hence these sites have been ascribed to sites of surface poison formation. Therefore, if bismuth is adsorbed in such defect sites, it is expected that electro-oxidation of glucose

should increase since surface poison formation cannot take place. This indeed was observed. However, subsequent adsorption of bismuth at terrace sites caused a decrease in glucose electro-oxidation, presumably due to the blocking of active sites. It is concluded therefore that silver and gold, although adsorbed in defect sites, in contrast to bismuth do not stop poison formation occurring. Since it is unlikely that glucose decomposition is taking place at the already blocked defect site, it is deduced that bismuth also exhibits some sort of electronic influence to prevent poison formation even at (111) terrace sites which is not observed for silver and gold-modified surfaces. The switching of the sense of enantioselectivity in glucose electro-oxidation may also be linked to this electronic influence of bismuth as signified by the coincidence of chiral electro-oxidation features and new bismuth induced hydrogen UPD peaks for (111) terraces containing (100)×(111) steps. An interesting departure from the present work therefore would be to contrast bismuth, gold and silver with adatoms capable of activating C-H bonds on glucose. Palladium, rhodium and ruthenium would be the metals of choice in this regard. All of these metals are catalytically active although strong adsorption of oxygenated species at ruthenium in aqueous environments [19-21] may lead to a deactivated surface at high coverages. However at low coverages, as of methanol electro-oxidation [19], ruthenium is expected to accelerate strongly the rate of glucose electro-oxidation since it can activate water at rather low overpotentials. Could ruthenium dosed platinum give rise to a strong chiral response? In the form of a bulk alloy the answer is undoubtedly 'yes' since platinum contained within the alloy surface ensures that kink sites present still give rise to surface chirality (see above for Ag/Pt [14] and reference [22] for Pd/Pt). However the growth mode of ruthenium deposited on platinum is seldom Frank-van der Merwe. Rather, because of the high surface energy of ruthenium relative to platinum the growth mode is reported to be almost Volmer-Weber like with small three dimensional ruthenium crystallites forming even at relatively small coverages [23]. Hence whether or not chiral kinks will be sites of adsorption for ruthenium would still be an open question. For palladium at rhodium, a similar growth mode to gold is expected based on differences in work function between adatom and platinum and similarities in surface energy. However in contrast to gold, palladium and rhodium should interact more strongly with components of the double layer leading to new observations in relation to glucose electro-oxidation, particularly if adsorbed in chiral kink sites. However, the fact that rhodium and palladium adsorb anions very strongly could also lead to a loss of surface enantioselectivity in sulphuric acid (since defects are blocked by both adatoms and

attached anion) but strong enantioselectivity in electrolytes free of specifically adsorbing anions [24].

It would be prudent also to examine the bismuth, silver and gold overlayers on the various platinum single crystal surfaces studied under UHV conditions with various electron-based spectroscopies in order to confirm surface coverages and proposed epitaxial structures. It would be difficult to confirm step decoration although thermal desorption of carbon monoxide and hydrogen is known to be sensitive to defect sites and the disappearance of thermal desorption peaks associated with defects as metal adatoms deposit might be useful. Surface alloying of silver would be revealed readily by AES and XPS via changes in the relative intensities of bulk and surface signals as a function of time, particularly at slightly elevated temperatures. However, in situ STM would most likely offer the best method of confirming many of the findings reported here, particularly if the tunnelling current from platinum and adatom sites leads to significant chemical contrast.

The answer to the second question posed at the beginning of this chapter is slightly disappointing although crucial for understanding circumstances in which enantioselectivity becomes important. Of the fifteen different chiral molecules chosen for investigation of diastereomeric interactions with chiral platinum surfaces, only glucose gave rise to a clear enantioselective response, with proline affording a very small effect. The distinguishing feature of glucose with respect to the other molecules studied is that it undergoes weak molecular adsorption but strong reactive adsorption leading to the generation of large electric currents. All of the other molecules undergo strong chemisorption with eventual blocking of all platinum sites in an indiscriminate manner (no enantioselection or discrimination between steps and terraces). It is therefore postulated, in the light of recent findings that similar surface enantioselective processes can only be observed in UHV for weakly chemisorbed or physisorbed species [25], that strong chemisorption precludes chiral discriminatory effects. In addition, it may be expected that in the absence of strongly directional hydrogen bonding between surface and molecule that enantioselectivity may not be observed. Hence electrode surfaces should not be thought of as 'clean' in the surface science sense but rather covered with ionic and dipolar species capable of adsorbing at particular kink, step and terrace sites yet able to hydrogen bond strongly with other molecules unless 'overwhelmed' by chemisorbed entities leading to their displacement from the electrode surface. Molecular modelling would be a useful way of interpreting the findings presented here. For example,

the calculation of adsorption enthalpy differences for enantiomers at R- and S- sites would help rationalise these empirical findings. If this difference was only a small fraction of the total adsorption enthalpy, then enantioselectivity may not be expected [26,27]. Theories of enantioselection based on differences in adsorption sites for a variety of chiral auxiliaries could also be tested in this context although for cinchona modified Orito-type reactions, in the absence of other reacting species (particularly hydrogen and ethyl pyruvate) meaningful deductions may not be possible. In order to get close to the UHV findings it could be argued that simple chiral hydrocarbons adsorbing from an organic electrolyte might lead to a much wider range of weakly interacting chemisorbates to be investigated. The problem here would be to find a solvent that was pure, would not decompose on platinum to give adsorbed intermediates and yet would dissolve readily any chiral probe molecule. Finally, it is clear that the present study has lacked any spectroscopic fingerprinting of the adsorption modes of the chiral molecules studied. Hence, in future work it is essential that such studies be undertaken in order to assess whether the species randomly adsorbing at the surface may indeed be behaving chirally with respect to kink sites. This could manifest itself as differences in the relative intensity of particular vibrational modes on the chiral molecule associated with the kink site as reported recently by Gellman [28] or by intermolecular hydrogen bonding between different chiral molecules adsorbed on the surface (so-called 'docking' mechanisms of enantioselection [8]). Whatever will be found over the next ten years concerning chirality at metal surfaces, it is hoped that in some small measure, the present study has contributed. After all, further understanding of one of the most subtle, yet important aspects of the natural world (chirality) is a great prize, seldom granted but essential to the future development of new materials and pharmaceuticals for the benefit of all humanity.

7.1. References

1. J. Llarca, J. Feliu, A. Aldaz, J. Clavilier, A. Rodes, *J. Electroanal. Chem.*, **316** (1991) 175.
2. A. Rodes, M. Llarca, J. Feliu, J. Clavilier, *Anales de Quimica international Edition*, **92** (1996) 118.
3. K. Popovic, A. Tripkovic, R. Adzic, *Journal of Serbian Chemical Society*, **59** (1994) 677.
4. K. Propvic, A. Tripkovic, R. Adzic, *J. Electroanal. Chem.*, **339** (1992) 227.
5. G. Attard, C. Harris, E. Herrero, J. Feliu, *Faraday Discussions*, **121** (2002) 253.
6. G. Attard, *J. Phys. Chem.*, **B 105** (2001) 3158.
7. P. B. Wells, S. P. Griffiths, P. Johnston, *applied Catalysis, A: general* **191** (2000) 193.
8. A. Baiker, T. Mallet, *Fine Chemicals Through Heterogeneous Catalysis*, (2001) 449.
9. H. U. Blaser, H. P. Jalett, M. Muller, M. Studer, *Catal. Today*, **37** (1997) 441.
10. A. Baiker, H. U. Blaser, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Vol. 5, VCH, Weinheim, 1997, p. 2422.
11. E. Herrero, V. Climent, J. Feliu, *Electrochem. Comm.*, **2** (2002) 636.
12. M Paffett, C. Campbell, T. Taylor, *J. Chem. Phys.*, **85** (1986) 6176.
13. E. Stuve, N. Kizhakevariam, *Journal of Vacuum Science and Technology, A: Vacuum Surfaces and Films*, **8** (1990) 2557.
14. J. Clavilier, L. Klein, A. Vaskevich, A. El-Shafei, *J. Chem. Soc., Faraday Trans.*, **92** (1996) 3777.
15. B. Koel, M. Batzil, Abstracts of papers, 223rd ACS, National Meeting, Orlando, FL, United States, 2002.
16. C. Shern, S. T Say, *Journal of Vacuum Science and Technology, A: Vacuum, Surfaces, and Films*, **14** (1996) 2522.
17. A. Al-Akl, Ph.D Thesis, Cardiff, 1997.
18. V. Rooryck, C Buess-Herman, G. Attard, F. Reniers, *Journal of Vacuum Science and Technology, A: Vacuum, Surfaces, and Films*, **17** (1999) 1647.
19. C. Lu, C. Price, R. masel, P. Babu, P. Waszczuk, H. Kim, E. Oldfield, A. Wieckowski, *J. Phys. Chem.*, **B 106** (2002) 37CHECK.

20. H. Massong, S. Tillman, T. Langkau, E. Abd El Meguid, H. Baltruschat, *J. Electrochem. Acta*, 44 (1998) 1379.
21. F. Vigier, F. Gloaguen, J. Leger, C. Lamy, *Electrochimica Acta*, 46 (2001) 4331.
22. G. Attard, R. Price, *Surf. Sci.*, 345 (1996) 236.
23. A. Crown, C. Johnston, A. Wieckowski, *Surf. Sci.*, **506** (2002) L268.
24. V. Topolev, O. Petrii, *Mosco, Elektrokhimiya*, **6** (1970) 1726.
25. A. J. Gellman, C. F. McFadden, P. Cremer, M. Beulow, Book of Abstracts, 212th ACS, National Meeting, Orlando, FL, (1996) 25.
26. C. F. McFadden, P. S. Gremer, A. J. Gellman, *Langmuir*, **12** (1996) 2483.
27. A. Gellman, J. Horvath, M. Buelow, *J. Mol. Cataly A: Chemical*, **167** (2001) 3.
28. A. J. Gellman, J. D. Horvath, M. T. Buelow, *Journal of Molecular Catalysis A: Chemical*, **167** (2001) 3.
29. A. Baiker, T. Mallat, *Fine Chemicals Through Heterogeneous Catalysis*, (2001) 449.