X-Ray Photoelectron Spectroscopy of Metal Clusters

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Clusters of gold, silver and tin have been characterised via x-ray photoelectron spectroscopy (XPS) using x-rays produced at a synchrotron facility. Gold and silver clusters were exposed to bromobenzene vapour to assess the extent to which adsorption of the vapour occur. Clusters of tin were produced under the presence of several oxygen concentrations in order to determine the onset of tin clusters in their fully oxidised state. The difference in energy required to eject a specific electron (called the binding energy) from this oxidised state and from the metallic state was then found.

Clusters are particles which consist of a finite number of atoms/molecules and have properties between those of atoms and bulk materials. For the work presented in this thesis free clusters have been produced in order to study their properties, free of interfering substrates, using XPS at the MAX-lab synchrotron facility in Lund, Sweden. Clusters have many applications in technology, both realised and potential, which may depend on the unique properties of clusters or upon their much greater surface area to volume ratio with regards to the bulk material. The high surface area to volume ratio of clusters is of interest in catalysis, as they provide many sites on the surface where reactions can occur while using little of the required material.

Adsorption of bromobenzene to gold and silver clusters has been studied because it is a volatile chemical, released during the incineration of waste circuit boards, and there has been a political movement to develop catalytic processes which would mitigate this hazard. The process under discussion could involve gold or silver catalysts, for which adsorption would be a first step. In this work adsorbed molecules were found to cover 60-80% of the surface of the cluster.

Tin oxides are a topic of intense study in nanoscience, with applications in gas sensors & transparent wide gap semiconductors. There are two stable forms, namely tin (II) oxide and tin (IV) oxide, which are often present together in samples. Their different electronic structures should make them readily identifiable by XPS. This has not been the case however and for tin (IV) oxide a change in binding energy of 2.0 eV from the metallic state has previously been quoted: very different to the 4.0 eV change observed for similar electrons in germanium (IV) oxide. The discrepancy has not been clearly explained and studies of free tin and tin oxide clusters were conducted to clarify the change in binding energy between metallic tin and tin (IV) oxide. The results of this work ascertain a value of 4.2 eV.

Further work, following from the results of this thesis, could involve depositing gold/silver clusters with adsorbed bromobenzene and exposing them to other reactants in the cross-coupling reaction. The products of the reaction could then be controlled using a mass-spectrometer to determine whether the desired product has emerged. Further experiments with tin could involve depositing tin clusters on transparent substrates and measuring their absorption spectrum in the infrared, visible and ultraviolet regions. This would permit one to establish the bandgap for the clusters: an important feature for potential applications such as semiconductors.