Abstract

This thesis focuses on the physical and chemical behavior of atomic clusters comprising both metallic and non-metallic components. Heteronuclear clusters represent a unique regime of matter whose physical properties cannot be explained by either bulk material models or conventional molecular models. The physical properties of such clusters result from a combination of bonding interactions between component atoms and the distribution of charge among them, making them suitable for studying reactivity, stability, and unusual bonding at the atomic level. One of the main challenges in cluster science is that the stable structures of clusters are unknown before they are identified. For a given cluster composition, there may be numerous low-energy structural forms on the potential energy surface, and small changes in this surface could lead to significant differences in chemical behavior. To overcome this challenge, a methodology for the global exploration of cluster structures was employed throughout this thesis, implemented using the PyAR software. Using this approach, a variety of structurally meaningful and energetically competitive structures were identified and subsequently subjected to detailed electronic and chemical analysis.

Chapter 1 presents the general introduction, including the background, motivation, research gap, and research objectives of the study. The theoretical foundations and computational methodologies are presented in **Chapter 2**. In **Chapter 3**, boron–aluminium–gallium clusters are investigated as heteronuclear catalysts for the oxygen reduction reaction, combining density functional theory with conceptual descriptors and free-energy analysis. **Chapter 4** examines lithium–sulfur clusters to understand structural evolution and bonding changes during lithiation, supported by high-level correlated calculations. **Chapter 5** addresses the fundamental problem of stabilising planar pentacoordinate carbon through metal–carbon interactions and multicentre bonding. **Chapter 6** summarises the methodological framework and major scientific insights of the thesis. The findings indicate that the combination of global structural exploration, electronic structure analysis, and density functional theory provides insight into the relationships among structure, stability, and reactivity in heteronuclear clusters. These findings have potential implications for oxygen reduction catalysis, lithium–sulfur chemistry, and unconventional bonding in hypercoordinate carbon systems.

Collectively, the results presented in this thesis demonstrate a unified cluster-based framework that relates structure, reactivity, and bonding across chemically diverse metal–nonmetal systems.

Keywords: Heteronuclear clusters, PyAR, Density functional theory, Oxygen reduction reaction, Hypercoordinate carbon