A Quantitative Scale of Oxophilicity and Thiophilicity

Oxophilicity and thiophilicity are widely used concepts with no quantitative definition. In this paper, a simple, generic scale is developed that solves issues with reference states and system dependencies and captures empirically known tendencies toward oxygen. This enables a detailed analysis of the fundamental causes of oxophilicity. Notably, the notion that oxophilicity relates to Lewis acid hardness is invalid. Rather, oxophilicity correlates only modestly and inversely with absolute hardness and more strongly with electronegativity and effective nuclear charge. Since oxygen is highly electronegative, ionic bonding is stronger to metals of low electronegativity. Left-side d-block elements with low effective nuclear charges and electro-negativities are thus highly oxophilic, and the f-block elements, not because of their hardness, which is normal, but as a result of the small ionization energies of their outermost valence electrons, can easily transfer electrons to fulfill the electron demands of oxygen. Consistent with empirical experience, the most oxophilic elements are found in the left part of the d block, the lanthanides, and the actinides. The d-block elements differ substantially in oxophilicity, quantifying their different uses in a wide range of chemical reactions; thus, the use of mixed oxo- and thiophilic (i.e., “mesophilic”) surfaces and catalysts as a design principle can explain the success of many recent applications. The proposed scale may therefore help to rationalize and improve chemical reactions more effectively than current qualitative considerations of oxophilicity.