Elucidating the interplay between shape, chemical composition and catalytic activity is an essential task for the rational design of novel nanocatalysts. We present a systematic analysis of molecular oxygen (O\(_2\)) chemisorption trends on bimetallic Pt-Ni clusters supported on MgO(100), by means of first-principles calculations for sizes between 25 up to 86 atoms. We studied O\(_2\) chemisorption on a variety of inequivalent sites for different structural motifs: from truncated octahedral (TO), cuboctahedral (CO), icosahedral (Ih) and decahedral (Dh) ones. For small clusters (< 58 atoms) we found that O\(_2\) prefers to bind on top of two metal atoms, parallel to the cluster, with an average chemisorption energy of 1.09 eV (Pt-Ni), 1.07 eV (Pt) and 2.09 eV (Ni), respectively. The largest chemisorption energy values is found to be along edges between two neighbouring facets while sites located on the (111) facets may show a chemisorption < 0.3 eV, where often O\(_2\) dissociation easily occurs. Our results show that, even though it is difficult to disentangle both geometrical and electronic effects on O\(_2\) adsorption, there is a strong correlation between the chemisorption map and the generalized coordination numbers (GCN) at each site. For the larger clusters (82 and 86 atoms), we show that site GCN can be tuned by changing the chemical composition at the interface with the support. The GCN descriptor has been shown to be as robust as the commonly used d-band center, both in terms of classifying the chemisorption sites and to predict catalytic activity. The inclusion of dispersion corrections (PBE+vdW) leads to an overall increase on the calculated adsorption energy values but with a negligible alteration on the general O\(_2\) chemisorption trends. Finally, we hope this work will stimulate and eventually can drive the rational synthesis of Pt-based nanoparticles to target ORR catalytic applications.

**Keywords:** Density Functional Theory, Pt-Ni clusters, oxygen chemisorption

**References:**


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