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A Comparative study of oxygen adsorption on palladium and platinum using density functional theory calculations

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In aqueous medium oxygen and hydrogen react on palladium surfaces to produce H_2O_2. On platinum surfaces this reaction goes all the way to water. There is evidence from Laser Raman Spectroscopy that the O-O bond is not dissociated on palladium surfaces. In the present work this fascinating difference between palladium and platinum in the adsorption of oxygen was investigated using density functional theory (DFT) employing the method B3LYP/gen in Gaussian 98. The core electrons of the metals were approximated by LANL2DZ effective core potential. The outer electrons of the metal atoms were treated using LANL2DZ basis functions and the electrons of oxygen atoms were treated using 6-311G(d,p) basis functions. The geometrical parameters, energies, and bond orders of the two atom metal cluster, with and without adsorbed oxygen were calculated. For both, on palladium and platinum surfaces the adsorption was shown to be precursor mediated. A comparison of the adsorption energies and the energy barrier for dissociation of oxygen over the two metals indicated that the dissociation is more favored over platinum than over palladium, which is in agreement with experimental observations. Calculated energy barriers for oxygen dissociation over palladium and platinum are 2.832 eV and 1.531 eV respectively.

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