

**COMPUTATIONAL STUDY
ON THE INTERACTION OF OXYGEN WITH
PALLADIUM, PLATINUM AND NICKEL CLUSTERS**

Samarasinghage Ranga Indika Ratnayake

Dissertation submitted in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE of the UNIVERSITY OF COLOMBO, SRI LANKA.

P-016791

NOVEMBER 2007



INTRODUCTION

The group 10 elements Nickel (atomic no. 28), Palladium (atomic no. 46) and Platinum (atomic no. 78) are three of the most important metals used as heterogeneous catalysts. These metals are utilized to assist in the formation of numerous products both in the field of bulk and fine chemicals. However, despite the close structural relationship between them and their proximity in the periodic table, there exist several significant differences in their Chemistry, in particular between Pt and Pd, the origins of which are still not fully understood.

Platinum is capable of promoting the hydrogenation of most functional groups under relatively mild conditions, usually at temperatures below 70 °C and hydrogen pressures of 3 to 4 atm. Esters, carboxylic acids, and amides are the only functional groups not readily hydrogenated over Pt catalysts. Palladium has greater activity for the hydrogenation of olefins and acetylenes, requiring less extreme conditions than the corresponding reactions over Pt. The commonly accepted mechanism for olefin hydrogenation, over both Pt and Pd, is the Horiuti-Polanyi reaction sequence in which the initial step is the activation of both the hydrogen and the alkene¹. For a given olefin the ease of hydrogenation over metal catalysts decreases in the order Pd > Rh > Pt > Ni >> Ru. In the mass transfer limited situations, for example low hydrogen pressures or large catalyst surface area, olefin isomerization can occur. This highlights further differences between the reactivities of Pt and Pd since Pt shows little isomerization activity whereas Pd promotes double bond migration via the formation of π - allyl intermediates¹.

Hydrogen is a chemically reactive gas that adsorbs dissociatively on most transition metal surfaces. Adsorbed hydrogen can lead to strong perturbations of the surface electronic structure. Surface electronic properties of Ni, Pd, and Pt clusters containing atomic hydrogen have been calculated by the SCF X α SW method, including relativistic effects. Hydrogen - metal bonding is dominated by d-orbitals for Pd and Pt, and s-orbitals for Ni, consistent with photoemission spectra for hydrogen chemisorbed on and dissolved in these metals. In most cases, as is the case with Pt, this results solely in a relaxation of the surface lattice. The results, in conjunction with the concept of orbital electro negativity, suggest why hydrogen solubility and catalytic reactivity vary among these metals². However, some metals, including Pd, undergo a surface reconstruction, a process leading to the absorption of hydrogen into the bulk structure of the metal which can lead to the formation of PdH.

The reduction of oxygen on a metal surface, one of the primary reactions taking place in proton-exchange membrane fuel cells, has been widely studied in electrochemistry. Palladium has been reported as the active electro catalyst for oxygen reduction in an acid electrolyte medium, and the adsorption of oxygen on the metal surface has been identified as a fundamental step of its reduction mechanism³.

Oxygen adsorption has been investigated with several experimental techniques, including low energy electron diffraction (LEED), molecular beam scattering, thermal desorption, electron energy loss spectroscopy (EELS) and Auger electron spectroscopy (AES).

The density functional theory and the cluster model approach have been used to study the adsorption of a molecule on the surfaces of platinum, palladium and nickel. For each metal surface, two adsorption sites have been considered: the atop site (π) and the bridge site (di- σ). For each case, optimized geometries and adsorption energies have been calculated. The results show that the energy difference when the atoms adsorb on the three metal surfaces. On the three metal surfaces the di- σ adsorption mode is the preferred one⁴. There is a good general agreement between the calculated results and the available experimental data. This reactivity differences can be experimentally observed by catalyzing with Palladium and Platinum. In the presence of Palladium reaction of oxygen with hydrogen in acidic medium, gives hydrogen peroxide (H_2O_2). But in the presence of Platinum it gives water (H_2O).

The study of reactivity on small clusters is important in order to elucidate the mechanisms of adsorption and reaction and to determine cluster size and shape effects on reactivity. In this work, it is expected to perform a systematic density functional theory (DFT) study of the electronic structure and properties of small Pd_n clusters and compare them with similar clusters of Pt and Ni and their interactions with atomic and molecular oxygen. The objective is to identify the evolution of electronic, geometric, and thermodynamic properties of O_2 and Pd_n upon O_2 adsorption and dissociation on Pd_n clusters.