The influence of the first series of transition elements in the electronic properties of Pd clusters: a study based on Density Functional Theory

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INTRODUCTION

Palladium, in particular is a promising material as catalyst in various applications. Small clusters of Pd are used in automotive exhaust systems to reduce toxic pollutants such as CO, NO and hydrocarbons[1]. In this present work was carried out a series of calculations based on Density Functional Theory (DFT) to study the adsorption of NO molecule was used as prototype to interact on the molecular clusters and pure palladium doped with transition metals of the first transition series (Pd_3M and Pd_9M). In this context, the scope of this study was obtained information about possible changes in structural, electronic and energetic parameters of palladium clusters when doped with the first series of transition metals (TM).

METHODS

As a first step, was obtained the preferential spin state for clusters containing four atoms of Pd_4 and Pd_3M (M =Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu) with a tetrahedral arrangement with Pd—Pd and Pd—M distances of palladium bulk (2.751Å). After, these clusters were optimized in the multiplicity of lowest energy. On Pd_4 and Pd_3M clusters a molecule of NO was optimized on two kind of tetrahedral agglomerates: with Pd—Pd (or M) of 2.751 Å and with Pd—Pd(or M) optimized. Following, the palladium cluster was increased to ten atoms, Pd_9M (figure 1b). In all calculations, the transition metal M doesn't interact directly with the molecule of NO. All calculations were performed using the Gaussian 03W program employing BP86/LANL2DZ method for metal clusters and BP86/LANL2DZ/6-311+ G(d) method for complexes with NO molecule.

RESULTS AND DISCUSSION

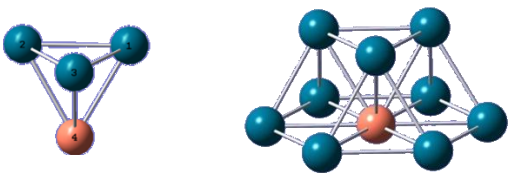

Figure 1. Clusters of Pd_3M and Pd_9M.

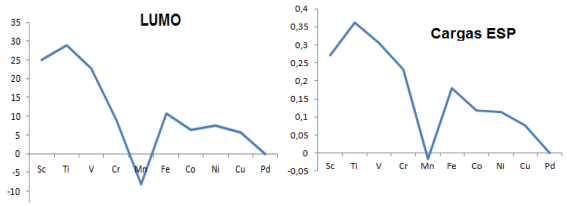

Figure 1. Comparison of trends in atomic charges on the first series atoms and the stabilization energies of the frontier orbitals, for Pd_3M clusters. a) ESP charge, b) LUMO

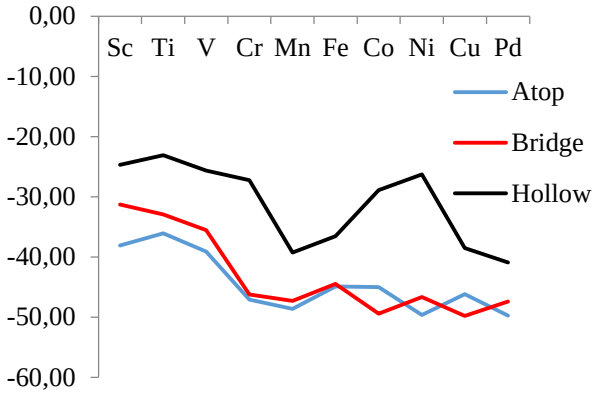

Figure 2: Adsorption energy (kcal.mol^{-1}) for the adsorption modes of NO molecule on Pd_3M.

CONCLUSIONS

The LUMO of the Pd3M presents the same behavior of the charge ESP on metal dopant M. The NO molecule adsorbs more favorably in Atop mode, regardless of which metal is doping the Pd_3M cluster.

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[2] J. A. Alonso, Science, 100, 637, (2000).