

## The influence of dopants elements at the electronic properties of Pd<sub>12</sub>M Clusters: A DFT study

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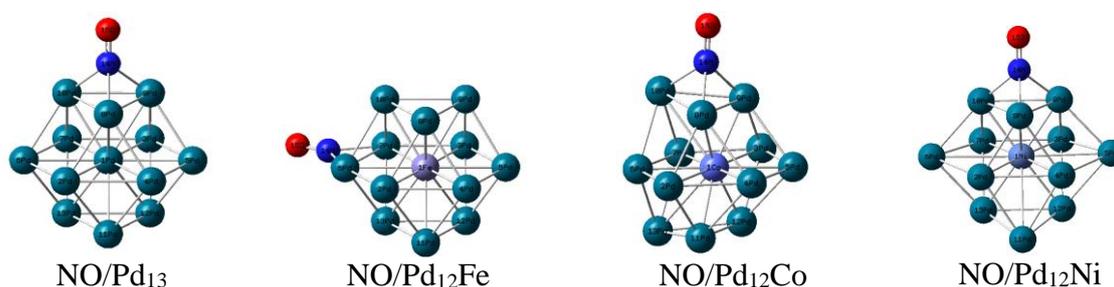
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**Introduction:** The catalysis industries had received great importance since the industrial revolution.<sup>[1]</sup> The clusters of palladium has been widely used to the process of oxidation of CO,<sup>[2-3]</sup> reduction of nitric oxide <sup>[4]</sup> and unburned hydrocarbons in automotive converter.<sup>[1]</sup> Furthermore, palladium is a promising catalyst due to its various applications,<sup>[5-6]</sup> and good thermal stability. <sup>[1]</sup> Due to these factors, the study of palladium catalyst has been substantially increased. <sup>[5-6]</sup> In this work, we performed DFT/BP86/Lanl2dz/6-311+G(d) calculations to study the adsorption of NO in the prototype catalyst Pd<sub>13</sub> and Pd<sub>12</sub>M (M = Fe, Co, Ni) clusters. The scope of this study is to provide information about possible structural and electronic changes in a Pd<sub>13</sub> cuboctahedron cluster when doped with Fe, Co, Ni, face to adsorption of a single NO molecule.

**Key-words:** palladium cluster, DFT, electronic properties, NO adsorption

**Methodology:** In this work, palladium clusters containing 13 atoms in cuboctahedron arrangement (Pd<sub>12</sub>M) were doped at the center position with Fe, Co and Ni. In all Pd<sub>12</sub>M clusters, several electronic spin states were optimized. As a second step, a single NO molecule was optimized in different positions on the Pd<sub>12</sub>M cluster, where Pd–Pd and Pd–M distance were kept fixed in 2.751 Å. <sup>[7]</sup> In all calculations, the lowest energy states were obtained and stability test of wave functions were performed. The calculation of adsorption energy (E<sub>ad</sub>) NO/Pd<sub>12</sub>M (M = Fe,Co,Ni) was performed. The DFT/BP86 methodology was employed using Gaussian 03 program. The electrons of the NO molecule were described by 6-311+G(d) basis sets. For the palladium clusters, the valence and core electrons were described by DV95 and the LANL2DZ pseudopotencial, respectively. All computed energies were corrected by the basis set superposition error (BSSE), calculated by the counterpoise method. The equilibrium geometries were full optimized since no symmetry constraint has been imposed (Fig.1).

**Results and discussion:** The analysis of the adsorption energy of NO on Pd<sub>12</sub>M, when Pd–Pd and Pd–M are kept fixed in 2.751 Å, shows that the NO molecule adsorbs preferentially in *hollow*, followed by the *bridge* and *atop* modes, for both pure and doped Pd<sub>13</sub> cluster (see Tab. 1). When the palladium agglomerate is relaxed, the NO molecule keeps on the *hollow* site preferentially, except on Pd<sub>12</sub>Fe cluster, changing to the *bridge* mode (Fig. 1).



**Figure 1.** Preferential NO adsorption on Pd<sub>12</sub>M clusters optimized with BP86/Lan12dz

**Table 1.** NO Adsorption Energy (kcal.mol<sup>-1</sup>).

| Clusters | NO/Pd <sub>12</sub> M (Pd–Pd = 2.751Å) |               |               | NO/Pd <sub>12</sub> M (opt) |               |               |
|----------|--|---------------|---------------|-----------------------------|---------------|---------------|
|          | <i>atop</i>                            | <i>bridge</i> | <i>hollow</i> | <i>atop</i>                 | <i>bridge</i> | <i>hollow</i> |
| Fe       | -36.85                                 | -49.31        | -54.38        | -40.44                      | -54.32        | -53.32        |
| Co       | -44.59                                 | -52.21        | -58.43        | -36.18                      | (*)           | -46.69        |
| Ni       | -47.03                                 | -55.45        | -61.30        | -44.60                      | -41.02        | -47.54        |
| Pd       | -45.87                                 | -60.74        | -63.02        | -43.34                      | -49.64        | -50.96        |

(\*) changed to *hollow*.

**Conclusion:** By using density functional calculations, we theoretically investigated NO adsorption on Pd<sub>13</sub> and Pd<sub>12</sub>M clusters. The preferential adsorption mode for the NO molecule is *hollow*, regardless whether the clustering is pure or doped by the metals studied. The NBO analysis reveals that the Pd→NO back-donation is stronger than the donation in both Pd<sub>13</sub> and Pd<sub>12</sub>M clusters, in all adsorption modes obtained.

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