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Palladium and platinum based solid and hollow nanoparticles: An ab-initio study of structural and electronic properties

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ABSTRACT

Nanoparticles composed of palladium and platinum are particularly interesting for catalytic purposes, for instance, selective hydrogenation and alcohol oxidation. The reactivity and selectivity of nanostructures are mostly based on the size and shape of the nanocrystals in catalytic reactions. In this work, we studied the structural stabilities of Pd and Pt based nanocubes and nanocages and adsorption strength of chemisorbed species on these nanostructures to investigate their structure dependent catalytic activities. Solid cubic and hollow cage like nanostructures of different sizes were designed with Pd and Pt atoms. The volume of the crystal cavity in nanocage structures was tuned by removing of atoms from solid cubic structure. The effect of size and shape on the formation energies and HOMO-LUMO energy gap of nanostructures were elucidated and correlated to structural stabilities, hardness-softness, electronegativity and electrophilicity index. The relationship between size and chemical reactivity clearly showed that increasing the number of atoms participating in a catalyst enhances the activity. For further understanding of the catalytic activity we employed 4-nitro thiophenol, as an S-donor representative molecule, to evaluate the adsorption characteristics of the nanostructures.

1. Introduction

Nowadays, nanotechnology is the most interesting area for many scientific and technologic studies because of distinct properties of nanoscale materials which are formed by various sizes, shapes, and compositions [1–3]. Thus, designing or modeling nanomaterials (NMs) in proper compositions and characterization of their structures are vital for the researchers to obtain desired properties. Metallic NMs having some superior properties, such as high mechanical strength and good expansibility, are attracting for promising fields of catalysis, magnetic recording, biosensors and medical diagnosis [4–7].

For nanomaterials the size and shape of a nanocrystal are crucial parameters, which are utilized to explore the chemical and physical potentials of a nanostructure. The size and shape dependent electron distribution at the surfaces, corners, edges and interior of a nanostructure can express the distinct chemical activity and selectivity of the nanoparticles in catalytic reactions [8–12]. Thus, for a successful application of a nanocatalyst, optimization of the size and shape of a nanocrystal is substantial in any research area [13].

The noble metal based cage like nanostructures such as gold (Au), Pt and Pd nanocages were developed and used in many catalytic reactions as nanocatalysts as well as nanoreactors [4]. The hollow interior with various volume of the cavities increases the active surface area in nanocages by double sides of the walls. Besides, nanocages can increase the rate of the reaction by allowing the reactants to be accumulated in the interior body and decreasing the activation energy. This is known as the “cage effect” [14].

Recently, materials scientists are seeking new approaches of computational modeling to understand the surface dependent activity of nanostructures to design new nanocatalysts. The density functional theory (DFT) approach, one of the most favorable computational methods that can yield results with sufficiently high accuracy, affords the treating a wide variety of nanostructure systems [15]. When the DFT is adequately applied to the molecular geometries, it can reveal the vibrational frequencies, atomic charges, dipole moment and thermodynamic properties of the desired systems [16]. Those properties could be used to understand the global properties of a molecule such as hardness, softness, electronegativity and electrophilicity index.

In this work, we conducted an analysis for the structural and electronic properties of the Pd and Pt based solid nanocubes and

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Table 1
Nanostructures with volumes and number of atoms.

Nanostructure	Pd_s^{63}	Pd_s^{171}	Pd_s^{365}	Pt_s^{63}	Pt_s^{171}	Pd_h^{50}	Pd_h^{108}	Pd_h^{194}	Pt_h^{108}
Number of atoms	63	171	365	63	171	50	108	194	108
Volume (nm^3)	0.39	1.41	3.48	0.41	1.46	0.38	1.22	2.41	1.27

hollow nanocages. We performed ab-initio calculations, through the DFT, using the software package Atomistix ToolKit (ATK) [17]. Concentrating on the structural and electronic properties, we obtained highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), formation energy, hardness, electronegativity and other relevant properties. The calculation results revealed that the size and shape, determined by hollowness, of the nanoparticles played an essential role in both structural and electronic behavior.

2. Computational method

Pd and Pt based nanocubes and nanocages were constructed from perfect Pd and Pt fcc crystals. The number of atoms (n) determines the size of these structures. The cubic structures with the n values of: 50, 63, 108, 171, 194 and 365 were modeled using the ATK software. The modeled nanoparticles in solid (s) nanocubes are denoted by Pd_s^{63}, Pt_s^{63}, Pd_s^{171}, Pt_s^{171} and Pd_s^{365} on the other hand, hollow (h) nanocages are denoted as Pd_h^{50}, Pd_h^{108} Pt_h^{108} and Pd_h^{194} (Table 1). The nanocages were produced by removing atoms inside and keeping the atoms on the surface of the nanocubes (Fig. 1). Such particular structures can easily be modeled by the ATK software through its functional parameters. To this end, without following a particular pattern, only those atoms which were inside the cube were removed. After removing these atoms, the structures having only surface atoms were relaxed. The difference in volume for identical dimensions originate from the relaxation of nanocages upon removing the interior atoms of the nanocubes. In order to expose the structural and electronic properties of Pd and Pt nanoparticles, ab-initio calculations and analysis were carried out employing the ATK.

When both the nanocubes and nanocages were optimized (or relaxed) the relaxation led to optimized atomic distance between the atoms in nanocrystals. Fig. 2, for instance, illustrates the atomic distances for Pd_h^{50} and Pd_s^{63} after the optimization. During the relaxation of these structures, the force tolerance was set to 0.05eV/Å without constraining the systems. The relaxed Pd nanocages (Pd_h^n) and Pd nanocubes (Pd_s^n) with various sizes are illustrated in Fig. 1, as representative systems. In calculations, the exchange–correlation potential was approximated within the Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional (GGA.PBE) [18], for the exchange and correlation effects of the electrons. The software ATK employs the Troullier–Martins pseudopotentials [19] for the ion cores in the systems. A mesh cutoff energy of 150 Ry was utilized. In order to enhance the accuracy of the calculations, the double-zeta polarized basis set of local numerical orbitals was employed.

3. Results and discussion

Conceptual DFT based descriptors have helped at many points to understand the structure of the Pd and Pt nanocubes and nanocages. We examined the structural stability of nanostructures by performing formation energy (FE) calculations and electronic properties by HOMO

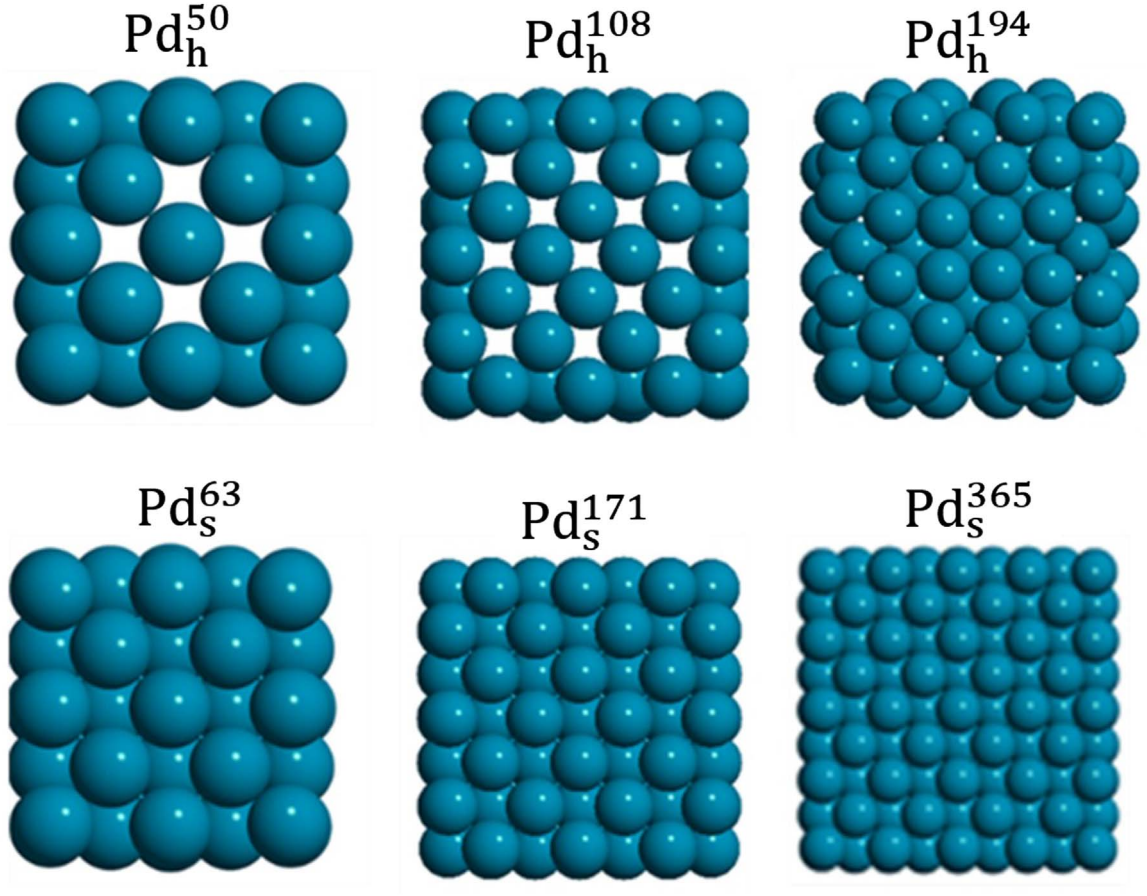

Fig. 1. Pd nanocages (Pd_h^n) and Pd nanocubes (Pd_s^n) with various n values.