

Research Article

Structural Stability Study of Nanocluster PD-based Catalyst

Mawan Nugraha^{1*}, Supardianingsih², Susiani³, Tan-Thanh Huynh⁴¹Politeknik Negeri Media Kreatif, Jakarta, Indonesia²Tra Vinh University, Viet Nam

ORCID

Mawan Nugraha: <https://orcid.org/0000-0001-9075-7776>

Abstract.

The rapidly growing population in the world demands an increase in the support of human life by providing massive production of food and medicine. As a result, the catalyst used in the production of the material plays a key role leading to intensive research. Synthesis of nanomaterials is becoming an important way to discover new catalysts by changing sizes and combining two or more metals on the nanoscale. Pd-based catalysts are well-known catalysts such as Pd-Pt, Pd-H, and Pd-Au for many chemical reactions such as the direct synthesis of hydrogen peroxide. Therefore, the provision of nanocluster bimetallic catalysts offers more benefits such as the rearrangement of surfaces to suit characteristics and lower material costs. However, the stability of the catalyst challenges researchers beyond reactivity and selectivity. In this paper, we predict the structural stability of Pd-based catalysts using a density functional theory approach. We use the 38-atom model in the M₆@Pd₃₂ core shell, where M is Hg, Pt, Au, Cu, Ni, Cu, Zn, Ag, Pd, and Cd, Pt. We prepared and investigated a series of structures such as truncated octahedral (TO) and polyhedral (PH) by calculating the excess energy. Based on our calculations and placing the monometallic Pd₃₈ nanocluster as a reference, the TO structure is more stable than that of PH. The Zn₆@Pd₃₂ system showed the most stable followed by Cd₆@Pd₃₂ and Hg₆@Pd₃₂ was the worst.

Keywords: structural stability, core-shell, nanocluster, Pd-based catalyst

1. INTRODUCTION

Since the turn of the 19th century, there have been enormous gains in both world population and affluence, which have been correlated with enormous increases in energy consumption. Natural resources, including coal, oil, and nuclear power, are the main sources of energy. New energy sources are always being explored. Not only are resources becoming more scarce as a result of human activity, but energy use also has an impact on climate change and other environmental changes.[1, 2] As a result, the challenges to human survival include the availability of energy resources and climate change. The proliferation of technological innovations that support prosperity, such as food storage, washing technology, transportation, medical science, and so forth, is what

Corresponding Author: Mawan
Nugraha; email:
mawan@polimedia.ac.id

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has led to an increase in energy consumption. All inventions result in the design and production of new materials, which has negative effects such as cost and waste. The development of technology appears to be significantly aided by nanotechnology.[3] The idea of efficiency has to be connected to every aspect of human activity, including chemical synthesis or production, to be able to control the negative effects of human life achievements, which began with the discovery of nanotechnology. By adopting this way of thinking, we may help ensure a better future for the following generation.

Regarding nanomaterial technology, especially in catalyst finding, the research activity grows quickly with various topics from monometallic to bimetallic or tri-metallic.[4] The combination of metal elements to form nanomaterial can be explored in alloy or core-shell approach. For their distinctive characteristics, which might be significantly differ from pure assemblies of their components, as well as for certain applications, ranging from optics to catalysis, bimetallic nanoclusters have attracted a lot of attention recently. The fact that bimetallic nanoclusters' attributes can vary significantly not just with size, as is the case with pure nanoclusters, but also in their chemical composition, makes them particularly attractive.[5] The first step in preparing the components for custom cluster-assembled materials can be to control their structure and chemical ordering. The identification of magic cluster structures for this application—specifically, those formations exhibiting unique structural, electrical, and thermodynamic stability—is a crucial first step. [6]

One of the structures that need to be considered is poly-icosahedral (*plh*). The core-shell of *plh* structures can be magical. Maximizing the number of closest-neighbour bonds between the atoms is one of the factors that drive high-stability cluster formation. The Ih13, for example, and other compact quasi-spherical structures benefit from this. Internal strain is created, nevertheless, since the interatomic lengths in Ih are different from what they should be in the bulk crystal. In pure systems with pair interactions, the rivalry between the accumulation of strain and the maximizing of the bond number dictates the most beneficial structures. When further atoms are added, a succession of compact poly icosahedral clusters are generated at N19, 23, 26, and 29. LJ 13-atom clusters favor the Ih shape. Beyond N29, the increase in the bond number is insufficient to offset the internal strain, making LJ plh less advantageous. The issue is more complicated for pure clusters of noble and transition metals.

Fine-tuning properties for applications such as catalysis or plasmonics can be realized by synthesizing metal nanocrystals (NCs) of defined shape and size according to individual requirements. Unlike nanocubes that only expose 100 facets, octahedral FCC metallic NCs increase reactivity or selectivity for catalytic reactions tuned on 111

facets.[7] However, these metastable nanostructures constitute stability against their evolution toward equilibrium. For effective function or to avoid functional impairment, the Wulff form is required. Such evolution is typically mediated by sub-coordinated diffusion from the atomic surface onto the NC surface, which is activated by heat. As a result, there is considerable incentive to create reliable atomic-level modeling and possibly even coarse-grained methods to modify octahedral-like NC shapes.[8] This work concentrates on applying a theory of stability cluster affected by shape.

The synthesis of octahedral Pd NCs with a minority of 100 facets at the corners or truncated vertices in addition to the 111 lateral facets has been reported in many previous works. These studies also discuss how they can be used to store hydrogen and for certain catalytic reactions.[9] It is worth mentioning that octahedral NCs have also been produced for many other fcc metals, including Pt, where the existence of truncated vertices revealing 100 facets was again discovered.[10]

Understanding reshaping will revolve around two crucial ideas. First, as previously mentioned, the vertices of the initially produced octahedral NC are likely significantly shortened in comparison to “complete” octahedra. The dynamics of the first reshaping will be managed by this feature. The nucleation and formation of new layers on the “111” side facets are necessary for reshaping octahedra, whether or not they have been truncated. It is understood that these nucleation processes govern how convex NCs with similarly sized facets are reshaped overall to their equilibrium shapes and that the effective barrier to reshaping increases with NC size. However, it will be shown that the effective barrier to initial remodeling of the truncated octahedron is related to the degree of truncation rather than the overall size of the NC.[11]

In this work, we offered to study the Pd-based cluster, especially in core-shell to lead the advanced understanding of the catalyst used for hydrogen peroxide direct synthesis.

2. METHODOLOGY

In this work, the *in silico* computational approach is used with a plane wave and 400 eV of kinetic energy cut-off. A projector-augmented wave (PAW) method is applied with a generalized gradient approximation (GGA-PW91), gamma of k points, together with 1x1x1 grid sampling, energy convergence of less than 0.05 eV/Å. The steps in our computing process are as follows:

Firstly, via realistic many-body atom-atom potential models to represent the clusters, we seek the global energy minimum via evolutionary algorithm optimization for a few

chosen sizes and varied compositions. Secondly, we search for compositions that match the most stable structures at a specific size. Thirdly, to confirm the patterns discovered in 2nd step, we locally optimize the most significant structures using density functional theory (DFT) calculations.

The model was built as a truncated octahedron (TO) and polyhedral (PH) structure with 6 atoms core and 30 or 32 atoms shell and noted as core-shell M₆@Pd₃₂ where the core M is Pd, Ag, Cd, Pt, Au, Hg, Ni, Cu, and Zn, as seen in Figure 1. The core@shell cluster model was chosen to minimize the complexity of the species-surface reaction compared with the Pd-based surface alloy. TO and PH structures consisting of 36 and 38 atoms (core and shell) were employed for the assessment, whereby the excess energy (Δ) is used to compare the relative stability among these structures. It is to be noted that a mismatch caused by different atomic radii would inevitably occur, as the overall geometric structure of these nanoparticles is strictly correlated with the inner core.

The calculation of excess energy is conducted as follow: [12]

$$\frac{E_{GM}^{N_1, N_2} - N_1 \epsilon_1^{coh} - N_2 \epsilon_2^{coh}}{N^{2/3}} = \Delta$$

where N_1 and ϵ_1^{coh} are the number and the bulk cohesive energy of the first chemical species, whereas N_2 and ϵ_2^{coh} refer to the second one. E_{GM} is the global minimum energy at size N, calculated from the total energy which is written in negative value and associated with the most stable structure. The lower the Δ value is, the more stable.

3. RESULT AND DISCUSSIONS

Here, we theoretically demonstrate the existence of a large family of magical Pd-based nanoclusters, all of which share the structural characteristics of being poly-icosahedral (plh) groups and ideal core-shell clusters. Monatomic thick Pd shells in perfect core-shell clusters, containing all Pd atoms on the surface, Ag, Cd, Pt, Au, Hg, Ni, Cu or Zn atoms inside. As seen in Figure 1, plh are clusters created by grouping basic *lh* of 36 and 38 atoms. Core-shell cluster has been demonstrated to have kinetically advantageous (but frequently metastable) forms in the formation of bimetallic clusters. Here, we show that among the core-shell we observed, a new family cluster exists that is remarkably stable from an energy standpoint.

Focusing on N = 36 or 38, we conduct study and search for global energy minima (GM) in different components. Dimension 38 is expected to correlate with pure clusters with good stability, as it is magical for the regular truncated octahedron, a highly symmetrical

component of the FCC bulk lattice. The finding is made when plotting Δ versus a series M for M@Pd, where M is Ag, Cd, Pt, Au, Hg, Ni, Cu, or Zn.

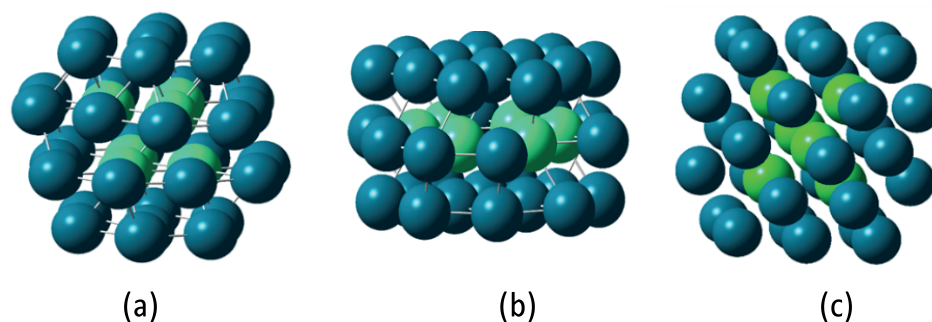


Figure 1: The M@Pd structure proposed as (a) 38-atom truncated octahedral, (b) 38-atom polyhedral, (c) 36-atom polyhedral, where the green core is Ag, Cd, Pt, Au, Hg, Ni, Cu or Zn and the blue shell is Pd.

Based on optimized Figure 1, we calculated the excess energy (Δ) where the comparison among TO M6@Pd32, PH M6@Pd32, and PH M6@Pd30 are to show the structural contribution to the stability. As seen in Table 1, it shows that the Δ tends to be higher due to the lower N, such as it is N=36 versus N=38 for the cores are Au, Ni, Pd, Pt, Hg, Zn, and Cd. However, the core of Cu and Ag leads to the opposite trend. Therefore, we confirmed that the 38-atom structure is more stable compared to the 36-atom polyhedral (PH), except the core is Cu and Ag. The 38-atom cluster based on 111 facets can be arranged in truncated octahedral (TO) and another polyhedral (PH), and it shows that TO structure leads to more stability than PH, except the core Hg. In the case of Hg@Pd, it has the lowest stability among others. The Hg has a specific character compared to other atoms we studied since Hg is full of electrons at $5d^{10} 6s^2$ orbital which leads to strong interaction between the core of Hg and valence. The stronger the interaction atom core-valence, the weaker the interaction among atoms which causes the liquid form of Hg. This is the main reason why the core-shell Hg@Pd has the lowest stability. Based on Table 1, the monometallic such as Pd38, instead of Pd6@Pd32, can be provided as reference to others since there is a lowest strain. However, Zn6@Pd32 or Zn6@Pd30 shows better stability compared to Pd38 or Pd36. It means that Zn-Pd has a stronger interaction than Pd-Pd interaction.

Finding limitation. As a probe, transmission electron microscopy (TEM) can be used to provide an informative experimental description of the remodeling of octahedral NCs with significant vertices truncation. They took into account Pd@PtNi core-shell structures, but the initial remodeling of single-component Pt NC should also be performed to exhibit similar behavior. Reshaping was found to only take place at high temperatures

TABLE 1: Excess energy (eV) of core-shell cluster M6@Pd32 and M6@Pd30.

M	Δ TO M6@Pd32 (1)	Δ PH M6@Pd32 (2)	Δ PH M6@Pd30 (3)
Au	-1.174	-0.945	-0.928
Ni	-1.397	-1.172	-1.242
Pd	-1.912	-1.607	-1.653
Pt	-1.441	-1.181	-1.165
Hg	-0.987	-1.086	-0.756
Zn	-1.917	-1.714	-1.765
Cd	-1.592	-1.426	-1.385
Cu	-1.496	-1.253	-1.274
Ag	-1.239	-0.947	-1.038

(T) above 900 °C. Pd@PtNi core-shell nanocubes and pure Pt nanocubes were easier to reshape when heated over 500 °C. [13]

The realistic stochastic model of the gas atomic lattice provides a logical basis for the fundamental theoretical analysis of surface diffusion-mediated NC restructuring kinetics, as it can accurately capture the evolution at correct temperature and time scale. All atoms are located at the locations of a fcc lattice in this formulation. When viewed in terms of efficient nearest-neighbor (NN) attractive interactions, the energy of the system energetics can simply be yet accurately represented. The calculation of the coordination number of atoms surrounding can support the role of neighbour atoms which we have not yet reported. In the same case, the observation of bond length among the atoms and then comparison among different structures will lead to a more comprehensive understanding

It is more difficult to properly treat surface diffusion kinetics. For temperature T and Boltzmann constant k_B , the rates of hopping of undercoordinated surface atoms have an Arrhenius form, $h = V \exp[-E_{act}/(k_B T)]$, where the activation energy, E_{act} , depends on the local environment. [14]

In this case, V stands for a common prefactor or attempt frequency, and the model's evolution with time (t) depends solely on the combination of t . When describing the local environment-dependent barrier for surface atom hopping, $E_{act} = E_0 - E_{init}$, where E_{init} is the initial system energy before hopping and E_0 is an adjustable parameter, the majority of earlier studies used the so-called initial value approximation (IVA) or bond-breaking. [15] Having more explanation of the unique phenomenon, we are still working and observing on this focus.

4. CONCLUSION

In this study, we employed the DFT approach to forecast the structural stability of Pd-based in the form of M@Pd core-shell, where M is composed of Ni, Cu, Zn, Ag, Cd, Pt, Au, and Hg. The number of core atoms was six atoms while the shell had 30 or 32 atoms. To determine the stability of the core shell and compare to the core shells we studied by calculating the excess energy. Based on our calculation, the truncated octahedron (TO) structure showed more stability compared to other polyhedron structures. Among the core-shells cluster, the Zn₆@Pd₃₂ system indicated the most stable while Cd₆@Pd₃₂ was the second most stable and Hg₆@Pd₃₂ was the worst.

Our finding was based on a computational approach that needed exploration more in correspondence with bond length and coordination number of the arranged atoms to confirm the trend of the result of excess energy calculation. However, this work proposed the opportunity to invent a new catalyst for direct synthesis of hydrogen peroxide.

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