

Supporting Information

First principles insights into relative stability, electronic and catalytic properties of Core-shell, Janus and Mixed structural patterns for bimetallic Pd-X nano-alloys (X = Co, Ni, Cu, Rh, Ag, Ir, Pt, Au)

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S1 : Analyzing sizes of the optimized structures for the studied nano-alloys

Though, the overall symmetry of the optimized structure for each cluster, retains icosahedral symmetry, the variation of morphologies for a Pd-X system and variation of one constituting X atomic species, will affect the effective size of the Pd-X cluster for a fixed composition. We have analyzed it for the optimized structure of each Pd-X nano-alloy. The cluster size is defined as the average distance between the center and the outermost surface atoms. We find that the cluster size for an optimized pristine Pd₁₄₇ cluster, is 0.703 nm. The initial structures of the three patterns for each binary Pd-X cluster, was prepared from the optimized structure of the Pd₁₄₇ cluster. Our estimated cluster size of the three morphologies for each binary Pd-X nano-cluster is given in the following Table 1 for both the compositions limits. It is seen that the cluster sizes varies within a range of 0.65 – 0.73 nm.

Table 1 : Our estimated cluster sizes for the optimized structure of the three patterns of each binary Pd-X clusters in their either compositions limits.

Binary Pd-X clusters	Size for binary Pd ₅₅ X ₉₂ cluster (nm)			Size for binary Pd ₉₂ X ₅₅ cluster (nm)		
	Coreshell	Janus	Mixed	Coreshell	Janus	Mixed
Pd-Co	0.673	0.662	0.657	0.666	0.674	0.676
Pd-Ni	0.676	0.654	0.657	0.666	0.673	0.676
Pd-Cu	0.683	0.667	0.669	0.673	0.682	0.682
Pd-Rh	0.691	0.689	0.689	0.693	0.694	0.696
Pd-Ag	0.723	0.727	0.725	0.717	0.717	0.717
Pd-Ir	0.687	0.692	0.691	0.687	0.694	0.697
Pd-Pt	0.699	0.706	0.703	0.707	0.702	0.703
Pd-Au	0.721	0.732	0.726	0.723	0.722	0.718

S2 : Formation Energy of the nano-alloys

In order to investigate the formation trend for the three morphologies of a bimetallic Pd-X nanoalloy (X = Co, Ni, Cu, Rh, Ag, Ir, Pt, Au), we have analyzed the alloy formation energy (E_{form}) for each binary Pd_mX_n nano-alloy (m+n = 147) of either compositions. The alloy formation energy is defined as $E_{form} = [E(Pd_mX_n) - m/147 E(Pd_{147}) - n/147 E(X_{147})]$, where $E(Pd_mX_n)$ is the total energy of the binary Pd_mX_n nano-alloy and $E(Pd_{147})$, $E(X_{147})$ are the total

energies of the elemental Pd₁₄₇ and X₁₄₇ clusters respectively. A -ve value of E_{form} implies that the alloy formation is favorable, while its +ve implies a phase segregated trend.

Our calculated E_{form} for each bimetallic Pd-X nano-alloy, is shown in the **Figure S1** for both compositions. First, it is to be noted that the most stable structure among the three structural patterns as seen in the analysis of “energy difference”, for each binary Pd-X nanoalloy, is associated with the most -ve formation energy.

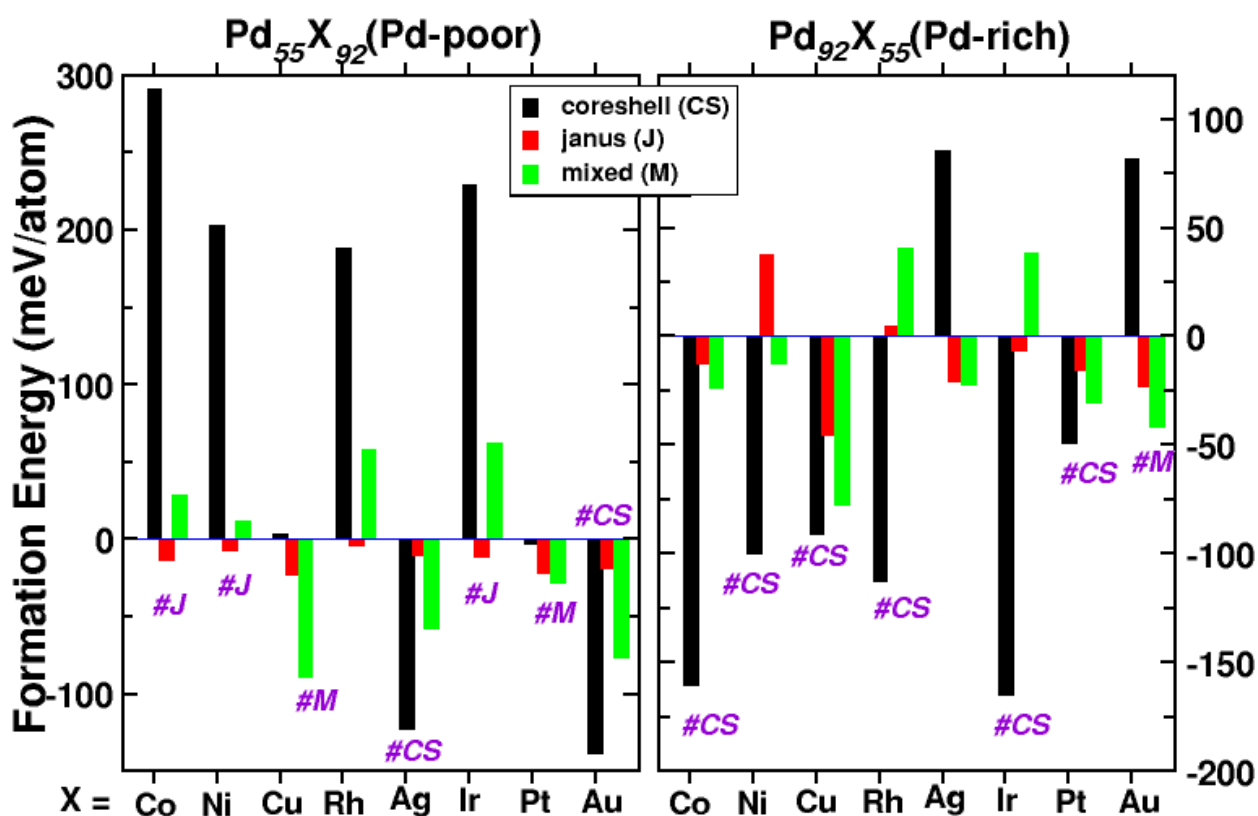


Figure S1 : Plot of our calculated formation energy for the optimized structure of three patterns for every bimetallic Pd-X nano-cluster in either compositions – Pd-poor (left) and Pd-rich (right). The most stable pattern from the analysis of

energy difference, is also marked here with “#” symbol for each bimetallic Pd-X cluster.

This plot also gives some insights about the relative preference among the three patterns for each Pd-X nano-alloy with respect to the variation of compositions as discussed below. For example, focussing on the formation energy for the coreshell structure of the Pd-poor Pd-X nano-alloys (i.e. the Pd atoms at core), it is seen that the binary Pd-Co, Pd-Ni, Pd-Rh, Pd-Ir nano-alloys have large +ve values which implies that their coreshell structures with the Pd-atoms at the core, are energetically very unfavorable. However, the formation energies for the coreshell structure of the Pd-poor Pd-Ag, Pd-Au nano-alloys, are large -ve i.e. the coreshell pattern for them, are now favorable as the the Ag or Au atoms at the surface, has lower surface energy than that of Pd. That is, the surface segregation of Ag or Au, favors the core-shell pattern most. Likewise, the coreshell pattern for the Pd-rich composition (i.e. Pd-atoms at the surface) becomes favorable for the binary Pd-Co, Pd-Ni, Pd-Rh, Pd-Ir nano-alloys for which the core-shell pattern was unfavorable in the Pd-poor composition. Likewise, the core-shell pattern for the Pd-rich Pd-Ag, Pd-Au nano-alloys with the Pd-atoms at the surface, becomes less favorable.

Focussing on the mixed structural pattern, it is seen from the Figure S1, that the mixed pattern for the bimetallic Pd-Rh and Pd-Ir nano-alloys remains unfavorable in the both composition limits. It may be driven by the large cohesive energy difference between the two constituting species.

Finally, focussing on the janus pattern, it is seen that the janus pattern has always some degree of formability for either composition of the binary Pd-X nano-alloys except the Pd-rich binary Pd-Ni nano-alloy (which is characterized by a positive formation energy).