Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: 'On the Structure and Reactivity of Pt_nCu_n ($n = 1 - 7$) Alloy Clusters'

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1 Formulas and Definitions for the Energetic Parameters

1.1 Binding energy and fragmentation energy

The stability of Pt_nCu_n clusters (with $n = 1-7$) is investigated by calculating the binding energy per atom (E_B), fragmentation or dissociation energy (E_f), defined as

$$E_B[Pt_nCu_n] = \{nE[Cu] + nE[Pt] - E[Pt_nCu_n]\}/2n, \tag{1}$$

$$E_f[Pt_nCu_n] = E[Pt_{n-1}Cu_{n-1}] + \{E[Pt] + E[Cu]\} - E[Pt_nCu_n], \tag{2}$$

where E[Cu], E[Pt], and E[Pt_nCu_n] are the total energies of the bare Cu atom, the Pt atom, the Pt_nCu_n alloy cluster, while n denotes the number of both Cu and Pt atoms in the cluster, respectively.

1.2 Ionization potential and electron affinity

The vertical ionization potential (vIP) and vertical electron affinity (vEA) are calculated as follows:

$$vIP = E[Pt_nCu_n]^+ - E[Pt_nCu_n]^0, \tag{3}$$

$$vEA = E[Pt_nCu_n]^0 - E[Pt_nCu_n]^-, \tag{4}$$

in which the geometries of the neutral and charged clusters remain unchanged.

1.3 Chemical Hardness

The chemical hardness is approximated as

$$\eta \approx \frac{1}{2}(vIP - vEA). \tag{5}$$

1.4 The d-band center

The position of the d-band center ε_d is calculated by the following expression:

$$\varepsilon_d = \frac{\sum_i \varepsilon_i * d(\varepsilon_i)}{\sum_i d(\varepsilon_i)}, \tag{6}$$

since the clusters studied in this work have a magnetic character, we have included the d-band center (ε_d) of the clusters for the majority ($\varepsilon_d \uparrow$) and minority spin states ($\varepsilon_d \downarrow$), respectively.