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Structural formation of binary PtCu clusters: A density functional theory investigation

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ABSTRACT

Binary transition-metal clusters have attracted great attention and a large number of studies have been reported, however, our atomistic understanding of the structural formation mechanisms of those clusters is still far from satisfactory. In this paper, we report a systematic study of the Pt_nCu_{m-n} clusters ($m = 2, 3, \ldots, 14, n = 0, 1, \ldots, m$) employing *Ab-Initio* density functional theory calculations within the Perdew–Burke–Ernzerhof functional. Using a set of structural design principles, we obtained a hierarchical set of atomic configurations from which the structural formation mechanisms are discussed in details. We found a negative excess energy for $m > 2$, providing strong evidence favouring the formation of binary PtCu clusters. In general, the Cu atoms tend to form agglomerates located near the center of gravity of the clusters while the Pt atoms tend to lie further away from the center of gravity and separated from each other. Therefore, this behaviour tends to reduce the number of Pt–Pt bonds whereas the number of Cu–Cu and Pt–Cu bonds tends to be maximized. These mechanisms help to release strain energy by means of relaxation of the gas-phase clusters, and the locations of the Cu and Pt atoms suggest that the formation of core–shell like structures starts already in this small size regime. Furthermore, the formation of the PtCu alloy does not lead to changes in the magnetic properties of the clusters in comparison with the parent Pt and Cu clusters. The systematic work presented here provides a basis to understand and tailor the properties of binary cluster.

1. Introduction

For the past decades binary transition-metal (TM) clusters have attracted great interest [1] due to their unique structural, electronic, magnetic, and reactivity properties [2,3], which can be tuned by changing the number of atoms, composition, and charge states [4–6]. This fact opens the possibility for a wide range of technological applications, such as magnetic storage [7–10], and heterogeneous catalysis [2,11–14]. This possibility, along with the novel and interesting properties found on those systems, motivated a large number of experimental and theoretical studies [15–17] focusing on binary TM clusters, such as PtPd [18,19], PdIr [20], PtNi [21], PtRh [22], FeRh [10,23], and PtCu [24–28], with the aim to understand the behaviour of their physical and chemical properties as a function of the number of atoms, compositions, structure, and charge states.

Among those binary TM systems, Pt-based binary clusters and nanoparticles (NPs) have been the focus of intense research, in particular due to the expectations that the mixture of Pt atoms with different TM can improve the reactivity of specific reactions while reducing production costs due to the use of lower Pt loads in comparison with pure Pt systems [29–31]. For example, PtRu core–shell NPs present high activity for preferential oxidation of carbon monoxide in hydrogen [32,33], while Pt clusters deposited on AuPd core–shell NPs show unusually high activity for electro-oxidation of formic acid [34]. Recent studies of dealloyed core–shell PtCu NPs electrocatalysts have revealed an enhanced activity for oxygen reduction reaction compared with pure Pt NPs [35–40]. It has been suggested that the enhancement in the reactivity is due to the charge transfer between Pt and Cu atoms, which can be attributed to the difference in the Pauling electronegativity (2.28 for Pt and 1.90 for Cu) [41,42], and the shortening in the Pt–Pt bond lengths [37]. Both effects contribute to change the *d*-states electronic population, and hence affects the oxygen binding energy,

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as suggested by X-ray absorption spectroscopy analysis on PtCu NPs supported on high surface area carbon [43].

The atomistic understanding of the structural formation mechanism is, therefore, crucial to improve the design of binary TM clusters with specific properties. In order to lay the path to this understanding, several mechanisms have been suggested to address the problem, in particular, segregation, mixing, and atomic ordering in the alloys [2,44]. We can highlight, as an example, the relative strength of the hetero- and homo-atomic chemical bonds can affect the mixing or segregation, and the charge transfer between the chemical species with different electronegativity favours mixing. Moreover, elements with greater bulk surface/cohesive energy tend to lie in the core region of the particles, as well as elements with smaller atomic radius, thus contributing to release the strain energy. There are also electronic effects in play, such as electronic shell-closure for particular sizes and compositions which can contribute to enhanced stability [45]. It is clear, therefore, that presence of such competing effects increase the complexity of the problem, making systematic and careful investigations imperative.

Although several mechanisms have been suggested, the atomistic understanding of the formation of small Pt-based binary clusters is still far from complete, mainly due to the difficulties in identifying the dominant effects. In particular, it can be pointed out that there are very few studies concerning small gas-phase PtCu clusters, for example [24–28]. Furthermore, several key questions remain unsolved. (i) What are the structural mechanisms that lead to the formation of the lowest energy (LOW) configurations? (ii) What are the main factors leading to the stabilization of PtCu clusters? (iii) What is the role of the large difference in atomic size ($R^{\mathrm{Cu}} = 1.28$ Å and $R^{\mathrm{Pt}} = 1.39$ Å) [46] with respect to the formation of the atomic structures? (iv) Is the formation of binary PtCu clusters favoured for every composition or only for particular compositions? (v) What is the relation between the properties of the binary PtCu clusters and their unary parent compounds?

Aiming at contributing to answer those questions, we built a hierarchical set of local minimum configurations using a set of structural design principles employing the unary parent compounds with a wide range of shapes. Using the configurations of that hierarchical set we performed a systematic density functional theory (DFT) investigation of the structural, stability, electronic, and magnetic properties for the $\mathrm{Pt}_n\mathrm{Cu}_{m-n}$ clusters, where m indicates the total number of atoms in the binary PtCu cluster, $m = 2, 3, \ldots, 14$, and $n = 0, 1, \ldots, m$. We found that PtCu cluster formation is favourable in most cases, and we identified clear signs of the initial formation of core–shell like configurations, e.g., the Cu atoms tend to lie closer to the center of gravity of the systems. Furthermore, the curves of the properties of the binary clusters display an almost linear behaviour, and are located in between the respective curves of the unary parent compounds, indicating that even at the subnano-sized particles the parent compounds already play a crucial role.

2. Theoretical approach and computational details

2.1. Total energy calculations

Our calculations are based on spin-polarized DFT [47,48] within the generalized gradient approximation [49] (GGA) formulated by Perdew–Burke–Ernzerhof (PBE) [50]. To validate our choice for the PBE functional, we performed hybrid-functional calculations using the Heyd–Scuseria–Ernzerhof [51,52] (HSE06) formulation. The PBE and HSE06 comparison shows that both functionals yield similar properties for most of the cases, however, there are clear differences in the magnitude of the energy gap, which is expected due to the dependence on the magnitude of the exchange functional.

To solve the DFT equations we employed the all-electron full-potential Fritz-Haber Institute *Ab-Initio* Molecular Simulations (FHI-aims) package [53,54], in which the electrons are described by the scalar-relativistic framework within the zeroth-order relativistic approximation (ZORA) [55]. Furthermore, test calculations were also performed using the *scaled* ZORA approach, however, the results differ only slightly. The Kohn–Sham molecular orbitals are expanded in numerical atom-centered orbitals (NAOs) [56,57], which were hierarchically constructed from the minimal basis on up to meV-level total energy convergence [53]. Thus, it provides great flexibility to perform from low-cost pre-relaxation up to high-accuracy total energy calculations.

To minimize the computational cost for binary systems, our calculations were performed using a two-steps approach: (i) Pre-relaxation of the atomic configurations using the NAO basis set called *light-tier1*, which is the first improvement from the minimal basis adding further radial functions with an overall cutoff radius of 5 Å. A broadening parameter of 0.10 eV was used for the smearing of the electronic states, while the total energy convergence was set up to 10^{-4} eV, and the equilibrium configuration was found once the atomic forces are smaller than 0.10 eV/Å on every atom. This step was crucial as most of the initial PtCu configurations are far away from equilibrium, and hence, their electronic convergence is hard to achieve. (ii) Once the initial optimization was finished, a final optimization was performed on the LOW configurations using a larger basis set (i.e., *tight-tier2*), now with a cutoff radius of 6 Å. Moreover, a smaller broadening parameter of 0.01 eV was used for the smearing of the electronic states, a total energy convergence of 10^{-6} eV, and the equilibrium configuration was reached once all forces are smaller than 0.01 eV/Å.

2.2. Atomic configurations

A basic understanding of the atomistic mechanisms that leads to the formation of binary PtCu clusters requires a set of reliable atomic configurations that should contain, for a given size and composition, the putative global minimum and high energy isomers, the latter being important for prospective comparison with experimental results [58]. It has been known that the number of local minimum configurations for a given unary cluster increases almost exponentially with the number of atoms [58], and hence, the selection of a reliable set of structures is a challenge. This problem is further complicated for binary clusters due to the compositional and permutational isomerisms. Several global optimization algorithms such as the Basin Hopping Monte Carlo (BHMC) [59], Revised BHMC (RBHMC) [60], and Genetic Algorithm [61,62] (GA) have been developed and improved along of the years to address this problem, however, those algorithms have been designed and tailored to obtain putative lowest energy structures and not higher energy isomers.

In this work we employed a set of structural design principles based on physical insights to obtain a hierarchical set of atomic models for the $\mathrm{Pt}_n\mathrm{Cu}_{m-n}$ clusters, where m indicates the total number of atoms in the binary PtCu cluster, $m = 2, 3, \ldots, 14$, and $n = 0, 1, \ldots, m$, i.e., different compositions were studied for the same number of atoms, such as $\mathrm{Pt}_4\mathrm{Cu}_9$ and $\mathrm{Pt}_8\mathrm{Cu}_5$. Our strategy is based on the observation that the atomic structure of an alloy cluster may be derived from the parent unary compounds [63], given that the structural properties of binary systems follow an intermediate behaviour in relation to the unary ones [64]. The following steps were performed: (i) A set of lowest and high energy configurations were obtained from total energy calculations and literature [6,65] for the Pt_m and Cu_m clusters ($m = 2 - 14$), which are composed by a diversified set of 2D and 3D structures. The