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## Influence Atoms of Co, Ni, Cu on the Catalytic Activity of Small Pt Clusters: First Principles Calculations

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Based on the calculations from the first principles, we obtained the distributions of valence electron densities and electronic energy spectra for small Pt<sub>n</sub> clusters (where n = 1 - 5 atoms). According to the results of calculations, it is determined that the inclusion of oxygen atoms or atoms of other kinds in small Pt<sub>n</sub> clusters, as a rule, affect the catalytic activity of research systems. It is established that during doping of small platinum clusters by atoms of 3-d transition metals (Cu, Ni, Co), the electronic structure of the cluster and the band gap change. This in turn helps to increase the catalytic activity of platinum.

**Keywords:** oxide transition metals, nanostructures, electron density functional theory method, pseudopotential, state density, electronic structure, energy band gap, small clusters, fuel cells, nanoparticles.

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### Introduction

The main problem in the development of energy efficiency technologies is the reduction of waste and by-products, reduction of consumables. In this regard, the main attention is paid to the sources of alternative energy. One of the alternative energy sources is fuel cells (FC). On the basis of FC, chemical energy is converted into electrical energy. The development of these technologies is associated, first of all, with the possibility of implementing environmentally friendly and more efficient power generation systems.

The most widely studied low-temperature fuel cells. The development and implementation of efficient low-cost catalysts due to the absence or low content of Pt is a priority in the development of such catalytic systems. Regarding the implementation of this task, the most favorable approach in this direction is the doping of Pt with other metals (Ni, Co, Cu, Fe, Y, Pd, Ti, Cr, etc.) [1]. The increase in the catalytic activity of such systems is due to a change (decrease) in the interatomic distance Pt-Pt due to the inclusion of atoms with a smaller crystal lattice constant; reducing the size and structure of catalytic systems [2]; by changing the structure of the

PtM orbit3, which is due to the electron occupation of the orbitals between dz<sup>2</sup> and d<sub>xy</sub>-d<sub>yz</sub> [3]. Hammer and Nyorskov developed a computational model based on the theory of excitations to predict the adsorption of molecules on the surface of transition metals. To do this, they applied the theory of electron density functionality and showed that molecular chemisorption energies can be predicted only by considering the interaction of the HOMO and LUMO molecules with the center of the common d-band density of states (DOS) of the metal [4].

No less important in increasing catalytic activity and durability for fuel cells is given to the electrode. To do this, take into account the content, type of catalyst and method of its manufacture. For example, Dedi Rohendi and his team found that the reduction process of H<sub>2</sub>PtC<sub>6</sub>.6H<sub>2</sub>O and CoCl<sub>2</sub>.6H<sub>2</sub>O in a carbon matrix using NaBH<sub>4</sub> as a reducing agent was successful using a Pt-Co/C catalyst. This good catalytic activity is achieved in the ratio Pt:Co = 20:80, as evidenced by the analysis curves of cyclic volt-ampere characteristic (CV) and electrochemical active surface area (EAS) [5].

One of the way to improve the final characteristics of fuel cells is the development and research of active, reliable, and inexpensive catalysts for the reaction of

oxygen reduction. In order to improve the electrocatalytic activity of Pt-based alloys for the hydrogen oxidation reaction and the ORR oxygen reduction reaction in fuel cells, the Todi group conducted a study to study bimetallic systems based on PtCo, PtFe and PtNi for fuel cells (PEM). They found that the maximum activity was observed when included in pure platinum Ni, Co and Fe approximately 30, 40 and 50%, respectively. The inclusion of these elements in Pt increased the kinetic current density by 10, 15 and 20 times than in pure Pt. The mechanism of ORR amplification was due to the increase of d-electron vacancies of the thin surface layer Pt caused by the base alloy PtM [6].

Of great importance in solving a number of applied problems in industrial catalysis and other areas of scientific and technical activities is the study of small clusters. These studies have helped to understand and explain many experimental findings in cluster physics: the distribution of mass spectrometry, ionization potentials, electron affinity, and polarization.

One of the directions of studying the increase of catalytic properties of transition metals in the composition of fuel cells is the study of small clusters of platinum. The morphology of such small platinum clusters has been studied by many scientists [7]. Thus, Yoshihide Watanabe and his group studied the morphology of Pt<sub>n</sub> clusters (n = 5 - 13) on the surface of CeO<sub>2</sub> (111)/Ru (0001) using a scanning tunneling microscope (STM) at room temperature. They found that the formation of Pt<sub>5</sub> clusters on the CeO<sub>2</sub> surface is most likely in two-dimensional planar morphology, while Pt<sub>n</sub> (n ≥ 6) clusters were regrouped into three-dimensional morphology. In addition, at n ≥ 10 the advantage in morphology was in favor of a three-layer three-dimensional structure [8].

Understanding the stability of transition metal clusters (TMs) requires a detailed study of each specific cluster size, a combination of experiment with theoretical calculations. The stability of small cationic platinum clusters Pt<sub>n</sub><sup>+</sup> (N = 3 - 8) was studied by the Piero Ferrari group combining an experiment based on photo-fragmentation and theoretical calculations based on the method of electron density functional theory (DFT). The distribution for small clusters at N = 3 - 20, obtained using photo-fragmented mass spectra, showed a decrease in intensity only for clusters at N = 5. Which indicates the lack of dependence of the stability of the clusters on the size of the structure (except for strengthening the relative stability of Pt<sub>4</sub><sup>+</sup>). For clusters at N = 3 - 8, the maximum in the second order of the energy difference is obtained at N = 4, and the minimum of the dissociation energy of the monomer at N = 5 [9].

Thus, at present, theoretical and computer modeling to understand the atomistic properties of fcc transition metals in different conditions is becoming increasingly important. Such calculations help to simplify the manufacturing process and the use of transition materials as catalytic components of fuel cells. Therefore, the study of mechanical and electromagnetic properties of small platinum clusters, as well as their relationship to size and shape, will contribute to our understanding of the use of these nanoparticles in the chemical industry

and the design of new materials.

## I. Methods and objects of computing

Theoretical description of experiments to study the increase in the catalytic properties of transition metals in fuel cells requires a full quantum description of the entire system, including the electronic component and the electromagnetic field. Therefore, in our description of the above-mentioned systems, we use the calculations of the first principles. The calculated results were obtained using the author's program code that implements the algorithm of quantum dynamics [10]. In this case, with the simultaneous optimization of variables of electronic and nuclear subsystems of polyatomic structure, or the algorithm of self-consistent solution of Kona-Schem equations in the local approximation, only electronic variables were determined for fixed atomic backbones [11].

According to Kona-Schem's theory, the electron density is found by the equation:

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2, \quad (1)$$

which forms a system of corresponding equations. In equation (1)  $|\varphi_i(\mathbf{r})|^2$  - the probability of finding an electron in the position  $\mathbf{R}_i = \mathbf{r}_i$ .

The motion of electrons in the external potential  $V(\mathbf{r})$ , taking into account their interaction, must be described by the same one-particle equations that are true for the model of none interacting electrons in the potential  $V_{\text{eff}}$ :

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right)\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}), \quad i = 1, \dots, N. \quad (2)$$

Where  $\varphi_i(\mathbf{r})$  are one-particle Kohn-Schem wave functions,  $\varepsilon_i$  are the eigenvalues of equation (2). The effective potential  $V_{\text{eff}}(\mathbf{r})$ , which is located from the charge density distribution, is the sum of the external potential, the Coulomb part of the electron-electron interaction and the exchange-correlation part.

Given the frequency of the crystal lattice:

$$U_{ik}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{\text{cell}}}} \sum_m C_{im}(\mathbf{k}) \exp(i(\mathbf{G}_m \cdot \mathbf{r})), \quad (3)$$

where  $\Omega = N_{\text{cell}}\Omega_{\text{cell}}$  for  $N_{\text{cell}}$  the number of cells ( $\Omega$  - volume of single cells that make up the periodic crystal or artificial super lattice),  $\mathbf{G}_m$  is the inverse lattice vector,  $\mathbf{k}$  is the wave vector.

The total energy per unit determined from the equation:

$$E = \sum_i \int_{\text{BZ}} \frac{dk}{\Omega_{\text{BZ}}} f_{ik} \varepsilon_{ik} - E_{\text{H}} - \int d\mathbf{r} V_{\text{xc}}(\mathbf{r})n(\mathbf{r}) + E_{\text{xc}}. \quad (4)$$

The density of states is taken as:

$$\rho(E) = \frac{1}{\Omega_{\text{BZ}}} \sum_i \int_{\text{BZ}} \delta(E - \varepsilon_{ik}) d\mathbf{k}. \quad (5)$$

What satisfies the attitude:

**Table 1**

The band gap and interatomic distances in diatomic clusters of platinum with the inclusion of 3-d transition metals in the system.

| Diatomic systems | d-bond distances, Å | Energy band gap, eV |
|------------------|---------------------|---------------------|
| Pt-Pt            | 2.78                | 0.99                |
| Pt-Co            | 2.63                | 0.02                |
| Pt-Cu            | 2.67                | 0.07                |

**Table 2**

Dependence of the band gap for binary and ternary platinum oxide clusters on the interatomic distance.

| Binary systems | d-bond distance, Å | Energy band gap, eV | Ternary atomic systems | Energy band gap, eV |
|----------------|--------------------|---------------------|------------------------|---------------------|
| Pt-O           | 1.99               | 1.84                | Pt-O-Pt                | 0.99                |
| Ni-O           | 1.84               | 3.20                | Ni-O-Ni                | 2.47                |
| Co-O           | 1.85               | 0.83                | Co-O-Co                | 1.14                |
| Cu-O           | 1.88               | 1.08                | Cu-O-Cu                | 1.30                |

$$N = \int_{-\infty}^{E_f} \rho(E) dE, \quad (6)$$

where  $N$  is the number of electrons.

The distribution of electrons by energies was obtained by numerically calculating the derivative  $\lim_{\Delta E \rightarrow 0} \Delta N / \Delta E$ , where  $\Delta N$  is the number of allowed states belonging to the energy interval  $\Delta E$  obtained from the diagonalization of the Kohn–Scheme matrix of a single-particle energy spectrum, the number of values in which is controlled by the size of the decay of the wave function. According to the ideology of the electron density functional, occupied states were found at  $T = 0$  K, the number of which was determined by half the number of electrons in the cluster (due to the electron spin disregard) [12].

In these calculations, according to the calculation algorithm, an artificial supercell of the tetragonal type was first created. Its parameters and atomic basis were determined by the object of study. The parameters of the cell and the atomic basis were chosen so that the interaction between atomic clusters did not occur. The program implements a model of plates, the distance between which was about 12 Å.

## II. Results of calculation

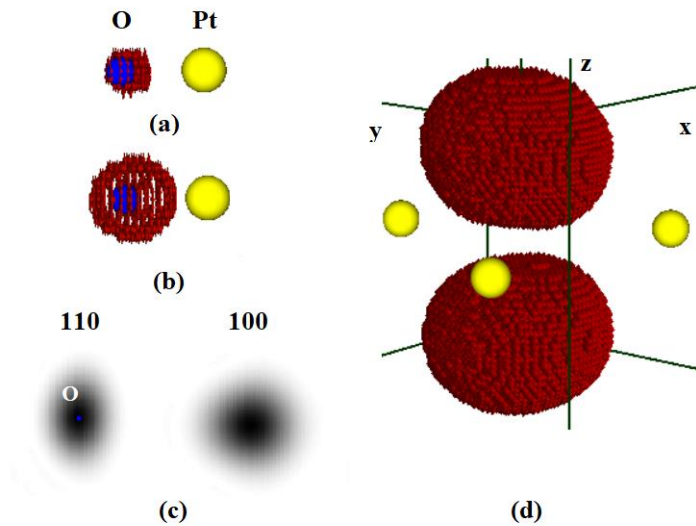
For a detailed understanding of the local mechanisms that occur on the surface of transition metals in the composition of platinum fuel elements during catalytic reactions, we calculated distributions of valence electron densities and electronic energy spectra for the following electronic configurations: Pt-[Xe]  $4f^{14}5d^96s^1$ ; Co-[Ar]  $3d^74s^2$ ; Ni-[Ar]  $3d^84s^2$ ; Cu-[Ar]  $3d^{10}4s^1$ ; Al-[Ne]  $3s^23p^1$ ; O-[He]  $2s^22p^4$ . Models of small clusters (Pt, Cu, Ni, Co) are formed, and itself: 1) monoatomic, linear and triangular platinum clusters; 2) small platinum clusters (at  $n = 4 - 6$  atoms) with the addition of transition metals

(Cu, Ni, Co), which are formed into bulk clusters; 3) bulk clusters for Cu, Ni, Co where  $n = 4 - 6$  atoms. The above-mentioned systems with the addition of atomic oxygen are also calculated. The distance between the atoms in the calculations is given as the sum of the radii of the atoms. No further optimization was performed.

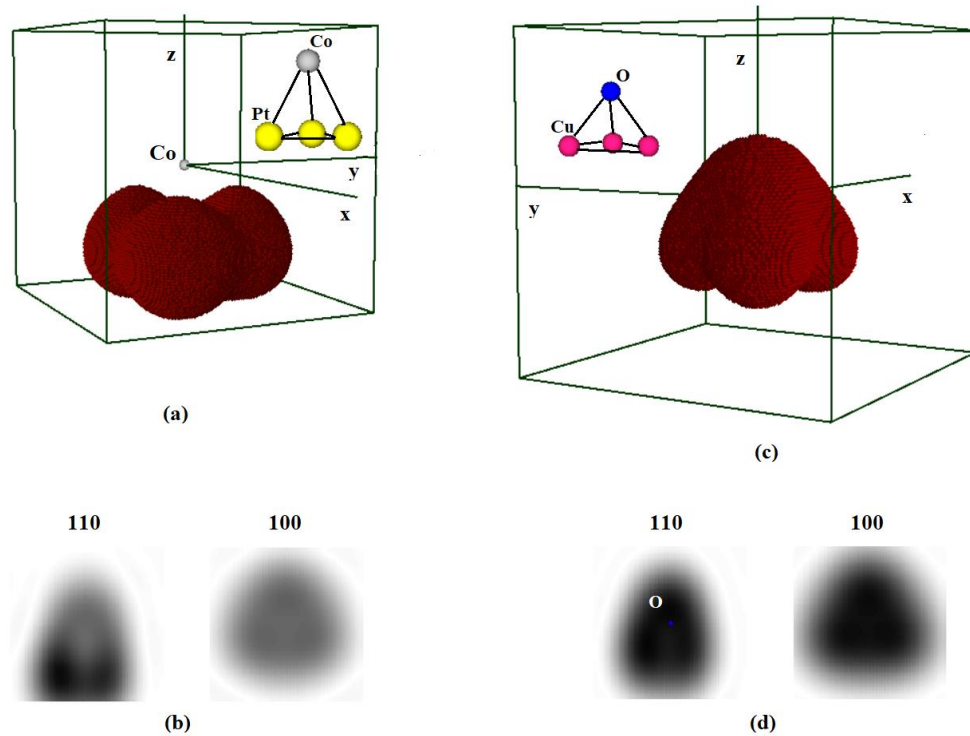
Alloying small platinum clusters with other transition metals can cause a change in the width of the d-band, which shifts the d-band center to maintain the degree of filling of the d-band. It is known that a monotonic decrease in lattice constants or interatomic distances occurs in each alloy system with an increase in the alloying element. The change in the interatomic distance is the largest in the system of Pt-Co alloys with decreases by an order of  $\text{Co} > \text{Cu} > \text{Pt}$  with the same content in the alloys (Table 1). In Table 1, we see how the band gap decreases with decreasing distance between the atoms of a diatomic cluster.

Therefore, when studying oxide transition metals based on PtO, CoO, CuO, NiO, we found that in the ternary system Pt-O-Pt (0.99 eV) the band gap decreases compared to Pt-O (1.84 eV). The same trend is observed for Ni-O-Ni (2.47 eV) compared to Ni-O (3.20 eV) (table 2). Another situation for Co-O and Cu-O systems. When an additional Co or Cu atom is added to a binary system, the band gap increases. It can be assumed that the addition of the second metal to the binary systems Pt-O and Ni-O increases the catalytic activity than for the systems Co-O and Cu-O.

Figure 1 shows the spatial distributions of the electron density and the cross sections of the spatial distribution of valence electrons in mutually perpendicular planes for Pt-O and Pt<sub>3</sub>O<sub>2</sub>. These systems show that when oxygen atoms are added to platinum, spatial regions appear with a locally elevated charge in the vicinity of oxygen atoms. That is, oxygen atoms take on electron density. Analyzing the spectra of valence electrons for the systems described above, we found that the distribution of electrons by energy is regrouped to a distribution with a dominant maximum near the Fermi



**Fig.1.** Spatial distributions of electron density for two and five atomic clusters: Pt-O at 0.9 - 1.0 (a) and 0.7 - 0.8 (b) from the maximum and for Pt<sub>3</sub>O<sub>2</sub> at 0.7 - 0.8 of the maximum (d). Intersections of the spatial distribution of valence electrons in mutually perpendicular planes in the vicinity of oxygen atoms for a diatomic cluster Pt-O (c).



**Fig.2.** Spatial distributions of electron density for four-atom clusters Pt<sub>3</sub>Co (a) and Cu<sub>3</sub>O (c) 0.7 - 0.8 from the maximum. Intersections of the spatial distribution of valence electrons in mutually perpendicular planes in the vicinity of atoms: Co for a quadriatomic cluster Pt<sub>3</sub>Co (b); oxygen for Cu<sub>3</sub>O (d).

energy.

Figure 2 shows the spatial distributions of the electron density and the cross sections of the spatial distribution of valence electrons in mutually perpendicular planes for four-atom Pt<sub>3</sub>Co and Cu<sub>3</sub>O clusters. In these calculations, a small Pt<sub>3</sub>Co cluster is derived from Pt<sub>4</sub> cluster by replacing one platinum atom with Co atom. The distance between Pt atoms was 2.78 Å, and between Pt and Co atoms 2.64 Å. In this case, the charge is transferred from Co atoms to Pt atoms. This reduces the bond for both Pt-Pt and Pt-Co

[10]. Modification of the electronic structure by adding a Co atom increases the catalytic activity of platinum. Analyzing the quadratic Cu<sub>3</sub>O cluster changes the electronic structure inherent in oxide metals, namely, there are spatial regions with a locally increased charge in the vicinity of oxygen atoms.

## Conclusions

The valence electron densities and electron energy

spectra for small Pt<sub>n</sub> clusters (where n = 1 - 5 atoms) were obtained from the first principles by the methods of the electron density functional and the pseudopotential. According to the results of the calculations, we determined that the inclusion in small Pt<sub>n</sub> clusters of oxygen atoms or atoms of another kind, as a rule, affect the catalytic activity of research systems. Alloying small platinum clusters with other transition metals can cause a change in the width of the d-band, which shifts the d-band center to maintain the degree of filling of the d-band. It is established that during doping of small platinum clusters by atoms of 3-d transition metals (Cu,

Ni, Co), the electronic structure of the cluster and the band gap change. In this case, the modified small platinum clusters show greater catalytic activity than platinum clusters without the addition of atoms of another kind.

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## Вплив атомів Со, Ні, Сu на каталітичну активність малих кластерів Pt: розрахунки з перших принципів

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На основі розрахунків з перших принципів нами отримано розподіли густини валентних електронів та електронні енергетичні спектри для малих кластерів Pt<sub>n</sub> (де n = 1 - 5 атомів). Згідно результатів розрахунків визначено, що включення в малі кластери Pt<sub>n</sub> атомів кисню або атомів іншого роду, як правило, впливають на каталітичну активність досліджуваних систем. Встановлено, що при легуванні малих кластерів платини атомами 3-d перехідних металів (Cu, Ni, Co), змінюється електронна структура кластеру та ширина забороненої зони. Це в свою чергу сприяє збільшенню каталітичної активності платини.

**Ключові слова:** оксидні перехідні метали, наноструктури, метод теорії функціоналу електронної густини, псевдопотенціал, густина станів, електронна структура, ширина забороненої зони, малі кластери, паливні елементи, наночастинки.