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ACTIVATION OF CATALYTIC PROPERTIES OF METAL NANOCLUSTERS

Within the methods of electron density functional and ab initio pseudopotential, we have obtained the spatial distributions of the density of valence electrons and the electron energy spectra for metallic and oxidized small clusters from the atoms of Cu, Ni, and Co with the aim to determine the mechanisms of their high catalytic activity. We have determined a certain organization of the electronic structure of the isolated metallic (Cu, Ni, Co) atoms in the ground and excited states, which is conserved at the association of these atoms in two atomic clusters. This has allowed us to draw conclusion about the easier excitation of d-electrons of copper as compared with the electrons of nickel and cobalt. This provides a possible freeing of d-orbitals that is fundamentally important for the catalytic activity of copper centers.

Keywords: electron density functiona, pseudopotential, nanocatalysts, metallic clusters, activation.

1. Introduction and Statement of Problem

A considerable expansion of the reactionary properties of nanoparticle (NP) catalysts in comparison with their massive analogues is lately shown. In order to use the possibilities of nanocatalysis, it is necessary to have a detailed understanding of the origin of their enhanced performance. While the size of particles is an important factor for their high catalytic activity, many other factors such as the geometry of nanoparticles, their composition, oxidation state, rebuilding of electronic orbitals, in particular, *d*-orbitals which are inherent to the transition metals, and the chemical/physical environment can play a role in determining the NP reactivity. In particular, we will consider the influence of these factors on the reactivity of chemically neutral gold and other metals.

Though bulk gold is known as one of the most inert metals, the oxides of gold are formed in the oxygen atmosphere on polycrystal thin films [1] and, even, on the single-crystals of gold [2] and gold nanoparticles on a substrate [3]. However, the determination of a chemical composition and a topological orientation of active places on structures from gold (and other noble metals) is not reliable till now. There is the ambiguous situation in the estimations of a relative importance of the mechanisms of inclusion of oxygen (chemosorbed oxygen, surface oxides, subsurface oxygen, or volume oxides), which can be realized on NP catalysts under the various working conditions of reactions. Calculations by Okumura et al. [4] suggested that although the O_2 activation occurs on anionic Au, cationic Au atoms bind CO stronger. The authors proposed a model of dynamic charge polarization, in which a strong heterojunction between Au clusters and their support is indispensable for the activation of oxygen species. The presence of negatively charged atoms in the perimeter region of Au NPs was attributed to localized Coulomb blockade effects. Furthermore, this surface negative charge was found to increase with decreasing the cluster size [4], in agreement with the known enhanced catalytic activity observed for small Au clusters.

A number of experimental studies have been published on the chemical reactivity of gold surfaces precovered with atomic oxygen. So, Min et al. [5] reported the existence of three types of oxygen species on Au (111): chemisorbed oxygen, oxygen in surface oxide (well-ordered two-dimensional phase), and subsurface oxygen or bulk oxide (three-dimensional phase). Based on CO oxidation studies, the authors [5] found that chemisorbed oxygen and surface gold oxide species were more reactive than bulk gold oxide.

Lately, the experiments were conducted on bimetallic nanocatalysts. In order to take advantage of bimetallic systems in the design of new catalysts, the structural, chemical, and electronic modifications induced by the addition of a second metal should be fully understood. So, in works [6–8], the catalytic properties of thin layers of palladium and its composition with copper were investigated in details (Figs. 1 and 2). There are complicated adsorption processes in such bimetallic nanocatalysts. The results given in Figs. 1 and 2 illustrate an increase of the surface charging effect at the adsorption of gaseous H_2S due to its catalytic decomposition (Fig. 2). The data were obtained from measuring the capacity of spatial charge (Fig. 1, curves *1* and *2*) and the direct branch of the current-voltage characteristic of a Schottky barrier structure with porous intermediate layer and structures with Pd–Cu nanoparticles. Dissociation of H_2S takes place on the Pd surface, and then the H atoms are carried on copper clusters in the pores of silicon.

The influence of a geometry of nanoparticles on their activity was illustrated by the spatial distributions of the density of valence electrons [9] for copper nanoclusters of the cubic form, which contain, accordingly, 5 and 7 atomic layers or 62 and 172 atoms (Fig. 3). These fragments differ by their surface layers: 62-atom fragment does not contain an atom in a top, whereas such atom is present in the 172-atom fragment. Namely it has the weakest connection with a fragment and is most active.

In work [9], the estimations of a relative importance of the various adsorptive precipitations of surface atomic oxygen, which can be realized on the NP copper catalysts, were executed. From Fig. 4 in [9], the information can be extracted about possible posi-

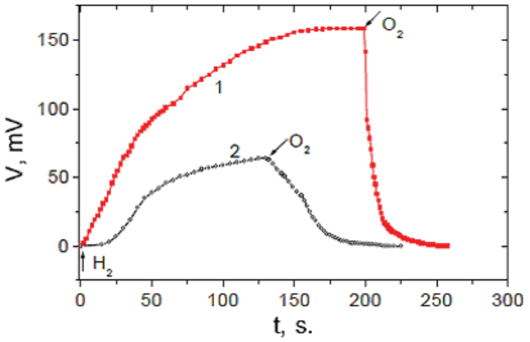

Fig. 1. Kinetic dependences of metal-oxide-semiconductor capacities with thin (∼50 nm) electrode layers from Cu|Pd (curve *1*) and Pd (curve *2*). Measurements took place at room temperature at once after the production of structures. Arrows indicate the start of the filling of corresponding gases

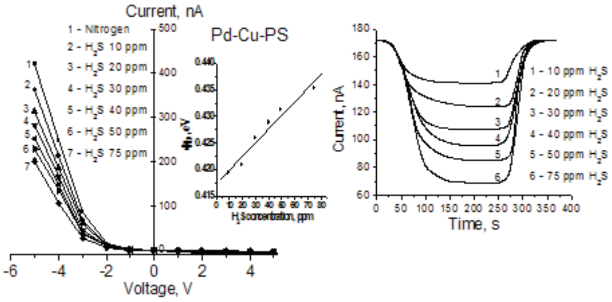

Fig. 2. Current-voltage characteristics of structures of Pd–Cu-porous silicon in the H_2S atmosphere (on the left) and the kinetics of change of the current (on the right). The insertion demonstrates the calculated heights of the Schottky barrier depending on the concentration of H_2S

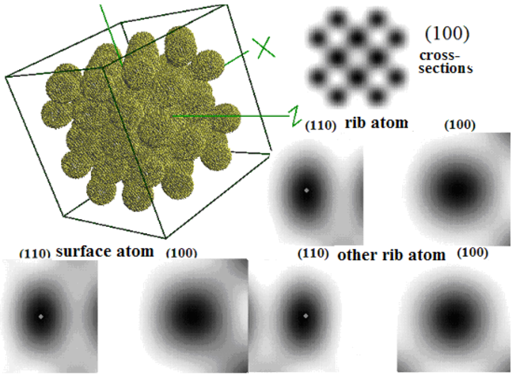

Fig. 3. Distributions of the density of valence electrons in the 62-atomic Cu fragment: spatial distributions within the interval of 0.3–0.4 of the maximum value and the cross-sections of the spatial distributions in the whole fragment in planes (100) and (110) and in a vicinity of surface atoms

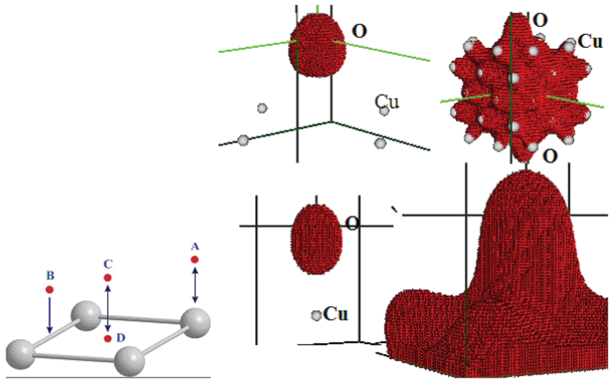

Fig. 4. Positions of the placement of molecules above the surface of a catalyst: A – "top", B – "bridge", C – "hollow", D – "in" (on the left); an oxygen atom above the surface of a catalyst in position B (on the right, top), an oxygen atom above the surface of a catalyst in position A (on the right, bottom). Spatial distributions of the density of valence electrons are brought within the interval of 0.9–1.0 of the maximum value and within the interval of 0.7–0.8

tions of adsorbents in relation to the surface atoms of a Cu cluster, and it is possible to trace a change of the electronic density at the adsorption of oxygen atoms by the catalyst surface. The formation of a common electronic cloud is seen. In Fig. 4, the adsorptions are illustrated only in positions A and B. As for position C, we can say that it looks like B by the electron distribution and the energy. Position D is characterized by a decrease of the energy of the whole atomic system, while others positions have identical energies. On the basis of work [9], the conclusion was drawn that the adsorptions of oxygen in positions A, B, and C are physical. The adsorption in position D is stronger (chemical). Therefore, the atom of oxygen precipitated in position D can be considered lost for the further interaction with an organic or other molecule on the next steps of reactions in a presence of a catalyst.

Question about the freeing of *d*-orbitals it is important for the activity of metallic centers in general and, in particular, for catalysis. By possible mechanisms that stimulate the formation of unfilled *d*-orbitals, there can be 1) a high probability of electronic transitions and the formation of the free *d*-states (it is determined by features of the electronic spectrum structure) and 2) the oxidization of transition metals that, due to the large difference of electro-negativities between a metal and oxygen and a considerable polarity of connections in a metal-oxygen molecule, increases the probability of electronic transitions [10].

In the given work, we will consider the electronic properties of copper metallic (or oxidized) nanoclusters that are investigated by calculations from the first principles by the methods of electronic density functional and pseudopotential.

2. Calculation Methods and Objects

All calculations have been made with the software developed in [11].

The basic states of the electron-nuclear system were found by means of the self-consistent solution of the Kohn–Sham equations, because the electronic variables only were determined with the atomic cores fixed. Following Kohn and Sham, the electronic density was written down in terms of the occupied orthonormal one–particle wavefunctions:

$$n(r) = \sum_i |\psi_i(r)|^2 . \qquad (1)$$

The point on the surface of a potential energy in the Born–Oppenheimer approximation was determined as a minimum of the energy functional with regard to the wavefunctions:

$$E\left[\{\psi_i\}, \{\mathbf{R}_j\}, \{\alpha_\nu\}\right] = \sum_i \int\limits_\Omega d^3r \psi_i^*(r) \times$$
$$\times \left[-\frac{\hbar^2}{2m}\nabla^2\right] \psi_i(\mathbf{r}) + U\left[\{n(\mathbf{r})\}, \{\mathbf{R}_j\}, \{\alpha_\nu\}\right]. \qquad (2)$$

Here, $\{\mathbf{R_j}\}$ are the coordinates of atomic cores; $\{\alpha_\nu\}$ are any external influences on the system.

In the generally accepted formulation, the minimization of the energy functional (2) with respect to one-particle orbitals with additional orthonormal constraint on the one-particle orbitals $\psi_i(\vec{r})$ results in the Kohn–Sham one-particle equations:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + \frac{\partial U}{\partial n(\mathbf{r})}\right\} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \qquad (3)$$

As the calculation algorithm envisages the translational symmetry in the explored atomic system, the tetragonal-type artificial supercell was initially created. The parameters of the supercell and the atomic base were determined by the object under study. The parameters and the coordinates of atoms in the base were such that the interaction between atomic clusters was absent. Clusters were considered isolated.

3. Calculation Results and Their Discussion

Distributions of the energy states of valence electrons of copper (copper has the fully filled 3*d*-shell, $3d^{10}4s^1$), nickel, and cobalt (nickel and cobalt have the not fully filled 3*d*-shell) are calculated during the formation of small clusters:

1) from 1 atom of Cu (Ni, Co) → to 2 atoms of Cu (Ni, Co);

2) clusters with inclusion of an oxygen atom (O: $2s^22p^4$): Cu (Ni, Co) +O → 2Cu (Ni, Co) +O.

In order to determine the nearest unfilled energy states, on which the excitations of electrons are realized, three distributions are presented for each investigated structure. The first distribution corresponds to the states occupied at $T = 0$ K. The right border of this energy distribution determines the last occupied state and is marked by value 0. The second (third) distribution corresponds to the occupied states and one (two) following allowed free state at $T = 0$ K. These free states do not move away from the previous occupied states or become separated by a noticeable interval of forbidden energies (within the limits of the resolution of a plot).

The high-energy states of the 3*d* electrons from the fully filled shell of copper and the 4*s* electrons of copper have a close energies. This is seen from the organization of the electronic states for isolated atoms near a right energy border (Fig. 5, the upper distribution of ground states). This situation provides the close probabilities of excitation of electrons from the mentioned states. For the atoms of nickel and cobalt that have the not fully filled *d*-shells, the high-energy states for 3*d* electrons and 4*s* are separated by a considerable energy interval. The analysis of the location of excited states for each of the atoms indicates that the excited states for the atoms of copper lie very close to the ground states. So, the first excited state practically coincides with the last high-energy ground state at the accepted resolution of plots, and the second excited state is not considerably separated (Fig. 5). On the other hand, the nearest excited states for the atoms of nickel and cobalt are dissociated from the ground ones by an

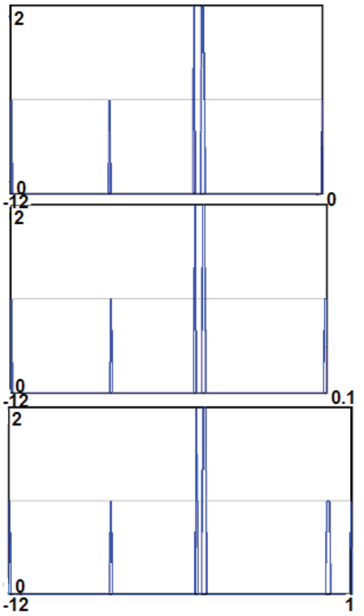

Fig. 5. Distributions of the states of valence electrons for an isolated atom of Cu. The energy in atomic units is reckoned along the abscissa axis, and the number of states is shown on the ordinate axis. In the group of distributions, the upper one corresponds to the occupied (ground) states, two lower – the occupied states and one following allowed free state at $T = 0$ K (and two next allowed free states)

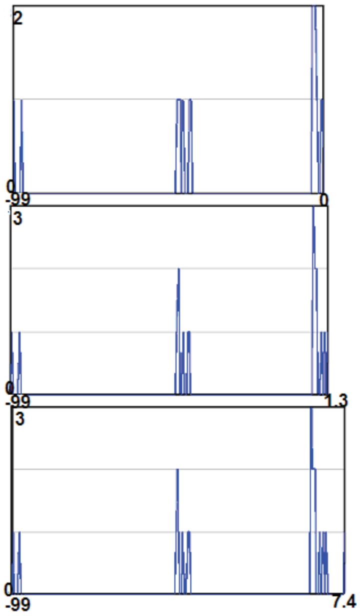

Fig. 6. Distributions of the states of valence electrons for the isolated linear clusters of Cu–O. The energy in atomic units is reckoned along the abscissa axis, and the number of states is shown on the ordinate axis. In the group of distributions, the upper one corresponds to the occupied (ground) states, two lower – the occupied states and one following allowed free state at $T = 0$ K (and two following allowed free states)

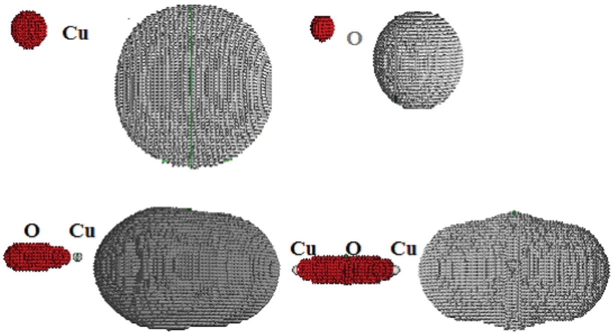

Fig. 7. Spatial distributions of the density of valence electrons for compositions from the atoms of Cu and O. The partial distributions are demonstrated for the maximal value of density and the minimum value, which limits the space of the considered atoms and clusters

energy interval which is less for Co (the first excited state is located relatively close on an energy scale, whereas the second excited state is already notedly remote) and more for Ni. Such organization of the nearest excited states relative to the ground states allows us to draw conclusion about the easier excitation of *d*-electrons of copper and the freeing of *d*-orbitals, that it is important for the activity of copper centers, in comparing to the *d*-electrons of nickel and cobalt.

Then we observe the next variations in the electronic states. Changes of the high-energy states for 3*d* and of 4*s* electrons of copper, nickel, and cobalt have occurred, when the isolated atoms of copper, nickel and cobalt are united in two-atom clusters. As for copper, the isolated atoms and the atoms united in a cluster keep a characteristic organization of the distribution of the ground and excited states for their electrons. Whereas for a cobalt and nickel, this organization changes. For a cluster of Ni, the nearest excited states approach the ground state very close, whereas they go away from it for Co.

We have also studied the influence of atoms of oxygen on the electronic states at its entering in the linear clusters of Cu–O (Fig. 6) and Cu–O–Cu, Ni–O and Ni–O–Ni, and Co–O and Co–O–Co. In these clusters, the different cation positions of $\mathrm{Cu}^{\delta+}$, $\mathrm{Ni}^{\delta+}$, $\mathrm{Co}^{\delta+}$ with the different shares of positive charge are realized. The degree of oxidation was greater for clusters of the metal-oxygen type. Such organization of the electronic states is characteristic of them: first, their structure became similar for all combinations of a metal (Cu, Ni, Co) and oxygen; second, it is evident that the high-energy ground states of *s*- and *d*-electrons are drawn together on a energy scale, and they are separated by an insignificant energy interval from the nearest excited states. The metallic centers in clusters of the metal-oxygen-metal type are characterized by a less loss of electronic charge, i.e., a less degree of oxidation. This was reflected in the organization of the electronic structure of these clusters. High-energy *s*- and *d*- ground states were divided and removed from the nearest excited states by a greater energy interval for clusters from the atoms of Cu and Ni. Whereas, for clusters from the atoms of Co, the situation became better from the point of view of the easiness of excitation of electrons, i.e., the nearest excited states approach, on the contrary, the ground states.

In Fig. 7, the spatial density of valence electrons is presented for atomic compositions from Cu and O atoms. There, the partial distributions are demonstrated for the maximal value of density and the minimum value, which limits the space of the considered atoms and clusters. Evidently, there is a redistribution even in a simple molecular structure. The charge on the atom of Cu is reduced. Thus, a part of electronic orbitals of Cu can be unfilled; it can be one of the *d*-orbitals.

4. Conclusions

Within the framework of the methods of electron density functional and *ab initio* pseudopotential, we have obtained the spatial distributions of the density of valence electrons and the electron energy spectra for metallic and oxidized small clusters from the atoms of Cu, Ni, Co with the aim to determine the mechanisms for increasing their catalytic activity.

We have determined a certain organization of the electronic structure of the ground and excited states for the isolated metallic (Cu, Ni, Co) atoms, which is kept at their association in two-atom clusters. This has allowed us to draw conclusion about the easier excitation of the *d*-electrons of copper, as compared with the electrons of nickel and cobalt. This provides the possible freeing of *d*-orbitals, which is fundamentally important for the catalytic activity of copper centers.

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АКТИВАЦІЯ КАТАЛІТИЧНИХ ВЛАСТИВОСТЕЙ НАНОКЛАСТЕРІВ МЕТАЛІВ

Резюме

Методами функціонала електронної густини та псевдопотенціалу із перших принципів отримані розподіли густини валентних електронів та електронні енергетичні спектри металічних та окислених малих кластерів із атомів Cu, Ni, Co з метою визначення механізмів їх підвищеної каталітичної активності. Визначена організація електронної структури основних та збуджених станів для ізольованих атомів, що зберігається при об'єднанні атомів у 2-х атомні кластери. Зроблено висновок про легше збудження *d*-електронів міді у порівнянні з електронами нікелю та кобальту, що забезпечує можливе вивільнення *d*-орбіталей та є принциповим моментом для каталітичної активності мідних центрів.