

Tuning of Electron States of Transition Metal's Catalysts Using Acceptor's Atoms: *ab initio* Calculation

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Within the methods of density functional theory and *ab initio* pseudopotential, we have obtained the spatial distributions of the density of valence electron and the electronic energy spectrum for the small clusters from the atoms of Cu, Ni, Co, O, Si with the aim to determine the mechanisms of their high catalytic activity. Electron's levels of catalyst guide course of chemical reaction. We explored, that the organization of electronic states of nanocatalysts on the basis of transition metals possible control by changing the spatial organization of clusters and adding electronegative atoms.

Keywords: Transition metal's catalysts, Silicide of transition metal, Oxides of transition metals, *Ab initio* calculation.

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1. INTRODUCTION

As known, transition metals (TM) exceed other elements by chemisorptions and catalytic properties because of the specific symmetry of *d*-orbital, the features of angular and radial distribution of their wave functions [1-3]. The *d*-orbital energetic organization of the objects with TM determines the way of the transformation of molecules in catalytic reactions. The transition metals peculiar coordinating interaction with reagents. They are characterized by ability to change the oxidation state (anion or cation charge) during catalysis. Thereby the TM shows the catalytic action in reactions [4]. One of the tasks of modern kinematics and dynamics of heterogeneous catalysis is the switchover from atomic-molecular kinematics to electron state kinematics. It means to explore the role of electron levels during reaction.

The occupancy of the *d*-orbitals by electrons, the coordinating saturation state, and the impact of the internal crystal field has analyzed in the work [5]. The authors of this article have proposed the model of the increased catalytic activity of the composites based on porous silicon with the incorporated nanoclusters of the TM (Cu, Ni, and Co). Nevertheless, a role of above specified factor was not analyzed in details, the mechanism of the action of the acceptors (O and Si), which create clusters of the TM oxides on the surface of catalyst and change the occupancy of *d*-orbitals has not been realized. These factors are capable to increase the catalytic activity of metal.

For to explanation of the electronic properties of the TM composites the theory of ligands have used [4] as from work John Hasbrouck van Vleck. This theory based on the method of molecular orbital. Here the ligands

have been considered like a charges, which have own structure. A molecular orbital of the complex of the TM atom and ligands is formed by the linear combination of the central atom orbitals and the atom orbitals of ligand. In order to determine the combination the group orbitals of the ligands should be found by the rules the group theory. To find energy of the group orbitals the single-particle Schrödinger equation with taken into account electronic interaction, should be solved.

In this work the organization of energy levels of the atomic complexes with the different symmetry from atoms of TM, oxygen and silicon were evaluated by methods of the electron density functional and *ab initio* pseudopotential. All calculations have been made with the proprietary source code.

2. METHODS

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

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

The point on the surface of potential energy in the Born-Oppenheimer approximation was determined as a minimum energy functional with regard to the wavefunctions, where $\{R_j\}$ are coordinates of atomic cores; $\{\alpha_\nu\}$ are any external influences on the system:

$$E[\{\psi_i\}, \{R_j\}, \{\alpha_\nu\}] = \sum_i \int_{\Omega} d^3\mathbf{r} \psi_i^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \psi_i(\mathbf{r}) + U[\{n(\mathbf{r})\}, \{R_j\}, \{\alpha_\nu\}], \quad (2)$$

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

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

Distribution of electrons along the energy zones for Γ -state of catalyst structures was found by means of numerical calculation of derivative $\lim_{\Delta E \rightarrow 0} \Delta N / \Delta E$ (where ΔN is a number of the allowed states for the ΔE interval of energy). The one-particle energy spectrum was obtained from calculation of the eigenvalues of the Kohn-Sham matrix. In accordance with ideology of the electronic density functional, the occupied states at absolute zero temperature were defined. It allowed to define position of the last occupied state, their number being half the number of electrons (due to ignoring the spin of the electron), and position of the first free states. Attention should be paid to the fact that the Γ -point for superlattice calculations has the value of the Baldereschi mean-value point, which represents all vectors in the Brillouin zone.

The partial electron density have been carried according to the formula:

$$n(\mathbf{G}) = \sum_{i=k1}^{k2} \sum_{\alpha} \psi_i(\mathbf{k} + \mathbf{G}) \psi_i^*(\mathbf{k} + \alpha \mathbf{G}'), \quad (4)$$

where $\psi_i(\mathbf{k} + \mathbf{G})$ are the plane waves expansion coefficients of the one-particle wave function, which derived from band-structure calculations; α is operator of symmetric transformation of the point group symmetry of the atomic basis; $k1$ and $k2$ are numbers of certain electron states.

3. RESULTS AND DISCUSSION

The spatial distributions of density of valence electrons and the electron energy spectra were obtained for nanoclusters, which based on atoms Cu ($3d^{10}4s^1$), Ni ($3d^84s^2$) and Co ($3d^74s^2$). The flat and volumetric models of clusters have been formed. The linear, triangular and square flat clusters contained one, two, three, four atoms of Cu, Ni, Co only or Cu, Ni, Co, O ($2s^22p^4$) and Si ($3s^23p^2$). The pyramidlike volumetric clusters contained atoms of Cu, Ni or Co with O and Si. They illustrated on Fig. 1a. The distance between atoms in clusters was the sym of the atomic radiuses. The coordinate optimization has not been performed.

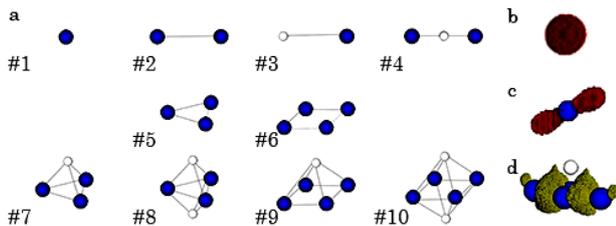


Fig. 1 – Models of nanoclusters (a) with different chemical composition and configuration. Atoms of TM are black; atoms

of O or Si are white. Spatial distribution of the total electron density (b) and the partial electron density (c) of the isolate Ni atom within the interval of 0.8-0.7 of the maximum value. Spatial distribution of the partial electron density (d) of cluster of the silicide copper (model #9, Fig. 1a) within the interval of 0.4-0.3 of the maximum value

Attention should be paid to the fact that the calculated one-particle wave functions, which expanded in plane waves, do not allow us to estimate the contribution of atomic orbitals of a certain type (s -, p -, d -, f -) to the full distribution of the electron density and to belong to the certain chemical element too (without additional effort). Similarly, the calculated spectrums of valence electron states do not provide information about the identity of these states as s -orbital or d -orbital of certain atom. To have a possibility these problems make clear, firstly, systematic analysis of the spectrum of valence electrons of free atoms (Ni, Co, Cu, O, Si) have been carried out, secondly, the partial electron density has been calculated according to the formula (4). It looks spatial shape of the electron cloud we determined state belonging to a particular orbital configuration. Really, the spatial distribution of the density of all valence electrons of the isolated nickel atom has a spherical shape (Fig. 1b), but the spatial distribution of the partial electron density is resemblance to a typical d -orbitals surface (Fig. 1c). According to such algorithm, the electronic states of model clusters with different chemical composition have been identified. For example, we published the electron state spectrum and the spatial distribution of the partial electron density of the model cluster of silicide cooper (configuration #9 on Fig. 1a) on Fig. 2.

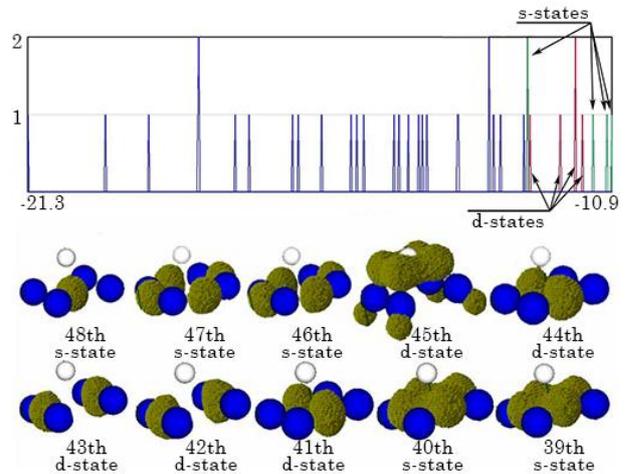


Fig. 2 – Electron states in the cooper with Si cluster (at the top). The abscissa is Hartree energy; the ordinate is a number of states. The spatial distribution of the electron density within the interval of 0.4-0.3 that is calculated on wave function only separate single states of the model cluster of cooper with Si from the 39th to the 48th state from the energy spectrum (at the bottom)

The results of our calculations collected on Fig. 3-5. The restructuring of the high-energy occupied d - and s -states (full markers) and the first free level at $T = 0$ K (empty markers) when change the mutual location atoms in the clusters and their chemical composition have been illustrated.

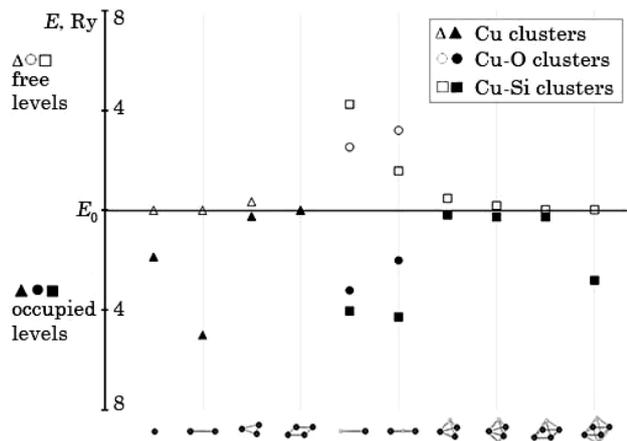


Fig. 3 – Energies of the high *d*-levels of cooper (full markers) and the first free level of cooper (empty markers) with regard to energy of the last occupied level ($E_0 - 4s^1$ Cu) for different atomic configurations

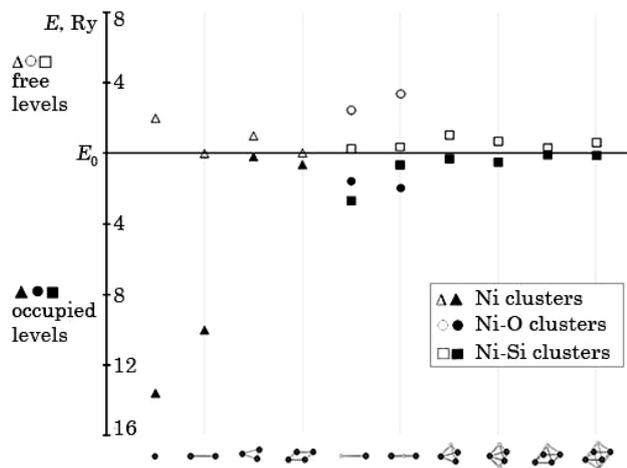


Fig. 4 – Energies of the high *d*-levels of nickel (full markers) and the first free level of nickel (empty markers) with regard to energy of the last occupied level ($E_0 - 4s^2$ Ni) for different atomic configurations

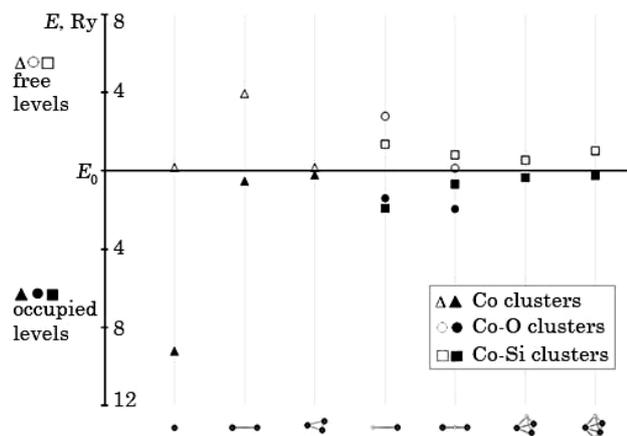


Fig. 5 – Energies of the high *d*-levels of cobalt (full markers) and the first free level of cobalt (empty markers) with regard to energy of the last occupied level ($E_0 - 4s^2$ Co) for different atomic configurations

It was noticed, that the energy values of the high-energy *3d*-states from the completely filled shell of the

free cooper atom and *4s*-states are similar. This equality provides high probability of the excitation of electrons from these states. Then, the energy values of high-energy states of *4s*-electrons and *3d*-electrons from the partially filled shell of single nickel and cobalt atoms separated by the significant energy gap. From following analysis of the location of the excited states for the each single atom, we have done such conclusions. The nearest excited states of copper atoms lie very close to the last occupied (Fig. 3); the nearest excited states of the nickel atom and cobalt atom are separated by energy gap which less for Co, more for Ni (Fig. 4, 5). Such an organization of states allowed concluding that the copper *d*-electrons are easy able to become excited then nickel and cobalt *d*-electrons. *D*-orbital frees oneself that is important for activity of copper centers.

Next, we dissected the restructuring of the electronic states due to the transition from the one atomic cluster to the many atomic clusters (Fig. 3-5). Here we observed that the one atomic cluster and the two atomic clusters save characteristic distribution of the electronic states. But for the many atomic clusters of the configurations #5, #6 the first free energy level approach to the last occupied. That is to say, for excitation electron from external shell of the many atomic clusters is required energy less, in contrast with the single atomic clusters.

We explored also influence oxygen’s atom on electronic states when oxygen’s atom fell into linear clusters (Cu-O and Cu-O-Cu, Ni-O and Ni-O-Ni, Co-O and Co-O-Co). The different cationic positions of $Cu\delta^+$, $Ni\delta^+$, $Co\delta^+$ with different parts of the positive charge δ^+ are formed in these clusters. The degree of oxidation and linearity of configurations are reflected on organization of the electronic structure of these clusters. The degree of acidity is greatest for clusters of “metal-oxygen” type, for these clusters mentioned below organization of the electronic states is representative. In the first, their structure became to be alike for all combination of “metal (Cu, Ni, Co)-oxygen”, in the second, the high-energy basic states of *s*- and *d*-electrons approached on energy scale to one another and they were separated from nearest excited states on small gap. Smaller loss electronic charge (smaller degree of oxidation) is a typical for metallic centre in clusters of the “metal-oxygen-metal” type; this was shown in organization of the electronic structure of these clusters. The energy gap between the high-energy basic occupied levels and the nearest free energy levels increased for Cu clusters. The situation has improved from the standpoint of the electron excitation for the clusters, which consist of Co or Ni atoms. As follows, the nearest free levels approached to the last occupied levels.

Besides, the calculation of the linear clusters with Si demonstrated a similar behavior of the electron states as the linear clusters with O, but the energy gaps are less here. In summary, combination of atoms Cu, Co, Ni with Si and O atoms in the manner of linear configuration increases the energy of the excited state. At that, the energy gap between the first free level and the last occupied level smaller for clusters with Si than clusters with O.

With increase amount atom in clusters before four-six atoms, which united in three-dimensional

formation, there is a significant approaching the high d-states of Cu, Co, Ni to their 4s-states. There is also the approach of the first excited state to the basic state.

4. CONCLUSION

It is known [1-4] that the catalysts provide to reagents the additional energy levels that facilitate the transition of electrons of reagent to high-energy level, and thus accelerate the reaction. This energy levels of reagents must be located between the catalyst levels and be on the optimal energy distance from them for easy flowing of process. We explored the opportunity to lead the organization of electronic states of nanocatalysts on the basis of transition metals by changing the spatial organization of clusters and adding electronegative atoms.

The specific properties of radial and angular distribution of d-orbitals determine the increased

chemical, adsorption and catalytic properties of TM composites too. These distributions are more spatially delocalized, more directed, more diffuse [2]. Really, fig.1d shows that the electron density is squeezed out of the cluster. The electron density becomes directed forms; it makes more active this catalyst system.

In order to define mechanisms of high catalytic activity, it was obtained and analyzed full and partial valence electron density distributions and energy spectra of model TM clusters of different configurations and chemical composition. All data have been obtained by methods of electron density functional and ab initio pseudopotential.

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Налагодження електронних станів каталізаторів перехідних металів з використанням акцепторних атомів: розрахунок із перших принципів

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Методами теорії функціоналу електронної густини і псевдопотенціалу із перших принципів ми отримали просторовий розподіл густини валентних електронів і електронного енергетичного спектру для малих кластерів із атомів Cu, Ni, Co, O, Si, з метою визначити механізми їх високої каталітичної активності. Електронні рівні каталізатора визначають напрям хімічної реакції. Ми дослідили, що організацію електронних станів нанокаталізаторів на основі перехідних металів можливо контролювати шляхом зміни просторової організації кластерів і додавання електронегативних атомів.

Ключові слова: Каталізатори перехідних металів, Силіциди перехідних металів, Оксиди перехідних металів, Розрахунки із перших принципів.

Тюнинг электронных состояний катализаторов переходных металлов с использованием акцепторных атомов: расчет из первых принципов

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Методами теории функционала электронной плотности и псевдопотенциала из первых принципов мы получили пространственное распределение плотности валентных электронов и электронного энергетического спектра для малых кластеров с атомов Cu, Ni, Co, O, Si, с целью определить механизмы их высокой каталитической активности. Электронные уровни катализатора определяют направление химической реакции. Мы обнаружили, что организацию электронных состояний нанокатализаторов на основе переходных металлов возможно контролировать путем изменения пространственной организации кластеров и добавления электроотрицательных атомов.

Ключевые слова: Катализаторы переходных металлов, Силіциди перехідних металлов, оксиды переходных металлов, Расчеты из первых принципов.

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