MODELING DEHYDRATION AND DEHYDROGENATION IN ZIRCONIA WITH ANION IMPURITY

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Introduction

Earlier we had been constructed quantum-mechanical models diamond [1] and oxid [2] nanoparticles with use of the tight-binding theory [3] and influence of hydrogen on electronic structure has been considered. On the basis of these models within the framework of computer modeling of processes in works [4-6] we estimated influence cation S and D impurity elements on energy of connection of hydrogen with zirconia nanoparticles. The present work is devoted to research of influence anion impurity on binding energy of hydrogen with a surface zirconia.

Results and discussion

Research was made on model of crystal nanoparticle of zirconia. This model has consisted of four planes (111) formed by atoms of oxygen (atoms of oxygen occupied units of four neighbor planes (111) of anion fluorite sub lattice). Atoms of zirconia of two next planes (111) of cation fluorite sub lattice settled down between oxygen planes, as shown in figure.

One of oxygen on a surface of zirconia nanoparticle has the neighbor atom of hydrogen, forming hydroxyl group OH of bridge type. One-electronic wave functions in a particle without anion impurity were searched as decomposition on nuclear functions which can be submitted as

$$\Phi_\alpha = \sum_j^{NZr} (c_s^j \left| 5s^j \right\rangle + \sum_{k=1}^{5} c_{p_k}^j \left| 4d_k^j \right\rangle) +$$
$$+ \sum_j^{NO} \sum_{i=1}^{3} c_{p_i}^j \left| 2p_i^j \right\rangle + \sum_j^{NH} (c_s^j \left| 1s^j \right\rangle$$

where NZr - number of zirconium atoms;

NO - number of oxygen atoms;
NH - number of hydrogen atoms;
i - runs value of three coordinate axes.
$c_{\nu\alpha}$ - the solutions of the one-electronic equations for a cluster:

$$\sum_\nu^n \left(H_{\mu\nu} - \delta_{\mu\nu} E_\alpha \right) c_{\nu\alpha} = 0, \qquad \alpha = 1,2,..n$$

where E_α - one-electronic own energy value of cluster;
$H_{\mu\nu}$ - matrix elements between atomic orbitales.

Anion impurity atom placed in the next unit anion sublattice considered nanoparticle on a place of one of atoms of oxygen. One-electronic wave functions in a particle with anion an impurity were searched as decomposition on nuclear functions which can be submitted as:

$$\Phi_\alpha = \sum_j^{NZr} (c_s^j \left| 5s^j \right\rangle + \sum_{k=1}^{5} c_{p_k}^j \left| 4d_k^j \right\rangle) +$$
$$+ \sum_j^{NO} \sum_{i=1}^{3} c_{p_i}^j \left| 2p_i^j \right\rangle + \sum_{i=1}^{3} c_{p_k}^A \left| n_A p_i \right\rangle + \sum_j^{NH} (c_s^j \left| 1s^j \right\rangle$$

where $\left| n_A p_i \right\rangle$ p- orbital of anion impurity.

The chemical formula of the cluster can be written down as Zr_8AO_{14} (OH), where (A = B, C, N, O, F, Ne).

At research of dehydration it was considered crystal zirconia nanoparticle with a molecule of water also bridge type in place of hydroxyl group. The chemical formula such cluster can be written down as $Zr_8AO_{15}(OH_2)$.

All calculations were conducted with use quantum-mechanical tight-binding theory.

At modelling process of dehydrogenation we started to remove atom of hydrogen.

We have analysed electronic structure of zirconia nanoparticle. We have calculated full of energy of all occupied one-electronic molecular orbitals at various displacement of hydrogen from ideal position.

Measure of the total energy of the system is diven by the sum of the energies of all the occupied one –electron molecular orbitals.

That is,

$$E_{tot} = \sum n_a E_\alpha \ ,$$

when E_α – is the energy and n_α – is the occupancy number of the α-th orbital.

We have calculated energy barriers of process dehydrogenation.

We carried out similar calculations at modelling process dehydration, but instead of hydrogen the molecule of water left.

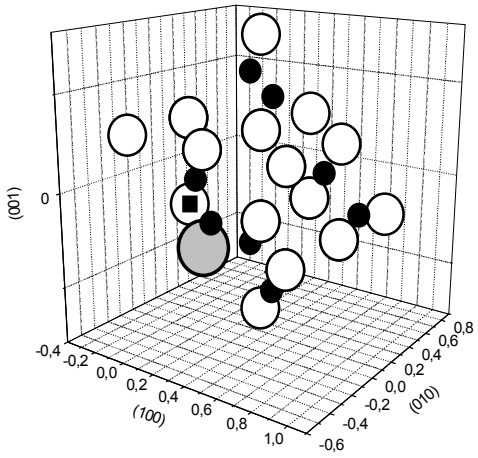

Fig. 1. The structure of three-coordinated (bridge type) hydroxyl group (water) on a surface (111) crystal zirconia nanoparticle.

● - atoms of zirconium,

○ - atoms of oxygen,

◉ - hydroxyl group (or a molecule of water),

◉ - anion impurity atom.

Conclusions

1. The analysis of results quantum-mechanical modelling has shown, that at dehydrogenation hydroxyl group bridge type an anion impurity boron, carbon and nitrogen increase energy of connection of hydrogen with a surface, but impurity of fluorine and a neon reduce energy of connection of hydrogen with a surface zirconia.
2. At dehydration molecule of water of bridge type quantum-mechanical modelling has shown qualitatively opposite influence anion impurity. Impurity boron, carbon and nitrogen reduce an energy barrier of process dehydration from surface zirconia, but impurity fluorine and neon on the contrary increase it. However it is necessary to note, that the value of these changes on the order concedes to changes of energy at dehydrogenation.

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