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Quantum chemical study of the spatial and electronic structure of the active centers of the nano-dispersed anatase surface and it's derivative doped with Ag_2 cluster

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The density functional method with a hybrid exchange-correlation B3LYP functional and the valence basis set sbkjc with an effective core potential was used to perform quantum chemical modelling of Ag dimers' adsorption centers on the anatase surface. Changes in the geometric and electronic structure of the Ag_2 cluster during adsorption were analyzed, and the most stable positions on the TiO_2 surface were determined. The results are in good agreement with the data obtained by X-ray photoelectron spectroscopy.

Keywords: anatase surface, adsorption of Argentum dimers, density functional method, X-ray photoelectron spectroscopy.

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Introduction

Nanomaterials based on titanium dioxide are promising for creating solar cells and photocatalysts active in the visible part of the spectrum due to their high photocatalytic activity, chemical stability, non-toxicity, and relatively low cost. They are widely used to neutralize organic pollutants, disinfect, and create antimicrobial and self-cleaning surfaces [1–4].

It is known that the photocatalytic activity of titanium nanodioxide can be enhanced by adding a small number of noble metals to it [3, 5–8]. They change the electronic band structure caused by adsorption, increasing the photogeneration of electron-hole pairs localized close to the photocatalytic centers, and forming a depleted or enriched electron space charge zone at the metal-oxide interface, which prevents electron-hole recombination. In addition, resulting localized surface plasmon resonance in nanoparticles induces light absorption in the visible region [3, 7].

Although there is a large number of publications in the literature on the experimental study of metal nanoparticle adsorption on the surface of titanium dioxide and their catalytic action, there is little data on the theoretical study of Ag/TiO_2 systems. This especially applies to the silver-doped anatase modification of TiO_2. Mostly, there are theoretical works related to the research of silver adsorption on the surface of rutile [9–14].

Thus, in works [10, 11], the interaction of silver clusters (Ag_n, n = 1, 2, 4, 8) with the surface of titanium dioxide, namely with the surfaces of (110) rutile and (100) anatase, was studied by the method of the density functional in the gradient-corrected approximation with the PBE functional [15] with the imposition of periodic boundary conditions. The authors have shown that there are two main types of binding of silver particles to the TiO_2 surface: the interaction of the frontal molecular orbitals (MO) of the silver cluster with the orbitals of two-coordinated oxygen atoms and the overlap of the highest occupied molecular orbital (HOMO) of the Ag_n cluster with the *d*-orbitals of five-coordinated titanium atoms. A higher binding energy characterizes the first type of interaction and causes the deformation of silver clusters during adsorption. It is also shown that the adsorption of silver clusters occurs mainly in the cavities between the rows of bridging oxygen atoms (two-coordinated) on the surface of rutile (110) since both types of binding are realized in this case. It has been shown that the factors responsible for forming the bond between Ag_n clusters and atoms of the anatase and rutile surfaces are almost identical.

The formation of adsorption complexes of Ag_2 over five-coordinated Ti atoms is much less favorable since silver clusters are stabilized mainly by electrostatic interaction with negatively charged two-coordinated O atoms [12].

Anatase is believed to be the most photocatalytically active modification of titanium (IV) oxide. Compared to other phases of TiO_2, the crystalline phase of anatase is characterized by increased stability and photocatalytic and antibacterial effects due to its high degree of crystallinity and large specific surface area. These parameters are crucial in photocatalytic reactions [16].

The crystalline anatase TiO_2 naturally grows with the formation of a coordination polyhedron of a distorted truncated octahedron, and mainly (101) and (001) faces come to the surface, with the (101) face covering more than 90 % of the surface [16]. The paper presents the results of a quantum chemical study of the interaction of silver dimer with the stoichiometric surface of (001) anatase, since it is characterized by a significantly higher surface energy compared to the surface of (101) anatase and, accordingly, an increased reactivity, which is caused by the fact that all surface atoms of Ti and O are valence unsaturated.

The data available in the literature, both experimental and theoretical, are rather ambiguous and do not provide an accurate answer to the question of the bonding nature in the cluster complexes formed on the surface of anatase, in particular, silver dimer. Therefore, the work aimed to find out how silver dimer adsorbs to the surface of (001) anatase, to study the electronic state of O and Ti atoms on the surface of anatase, as well as to substantiate the reasons for the increased photocatalytic activity of Ag/TiO_2 systems compared to individual nanostructured anatase and colloidal silver.

I. Methodology of calculation

The calculations were carried out by density functional theory using the B3LYP exchange-correlation functional and the sbkjc valence basis set with an effective backbone potential within the US GAMESS software package. To regard the dispersion contributions to the energy of formation of intermolecular complexes, the Grimme dispersion correction D3 was used [17]. To represent the core electrons of atoms after the third period, effective nuclear potentials (ECPs) are used, which significantly reduces the computation time without affecting the results, since core electrons are assumed to have little effect on adsorption [18].

The X-ray photoelectron spectra (XPS) of anatase were measured on a SPECS Surface Nano Analysis Company (Germany) photoelectron spectrometer with a PHOIBOS hemispherical analyser.

The chosen calculation method allows us to obtain results that, as seen from table 1, correspond to the experimental results of the energy gap size of bulk anatase samples. In addition, it has been shown in [19-21] that the use of this method gives results that are in good agreement with the experimental ones when calculating the atomic and electronic structures of several crystalline oxides, including titanium dioxide and systems based on it, such as Ag/TiO_2. The equilibrium spatial structures of all the clusters considered in this work were found by minimizing the norm of the total energy gradient. The stationarity of the points corresponding to the minimum energy of the optimized structures was proved by the absence of negative eigenvalues of the Hesse matrices.

Table 1.

Structural parameters for the $(TiO_2)_x{\cdot}nH_2O$ cluster modelling the (001) anatase surface and corresponding experimental data for the bulk anatase phase

Parameter	$(TiO_2)_{15}{\cdot}11H_2O$	anatase (Exp.)
The elementary lattice parameters, nm	a = 0.37 – 0.38	a = 0.3784 c = 0.9515
d (Ti–O), nm	0.194 – 0.198	0.1937(4) 0.1965(2)
∠ O-Ti-O	77.0° 93.4°	77.7° 92.6°
E_g, eV	3.9	3.2

II. Results and discussion

To study the electronic structure of titanium dioxide (precursor of metatitanic acid), we first used the X-ray diffraction method (Fig. 1 *a*-*c*). The overview spectrum includes the C1*s*, Ti2*p*, O1*s* lines, which mainly indicate the presence of the elements Ti and O in the sample. The O1*s* line of the sample is represented by two peaks of different intensities. The peak with a lower binding energy value of 521.4 eV can be attributed to lattice oxygen in TiO_2, and with a higher binding energy value of -530.05 eV to surface OH groups (consistent with IR and Raman), as well as possible chemisorbed oxygen on the surface. For the studied sample, the binding energy for the Ti2$p_{3/2}$ (458.8) and Ti2$p_{1/2}$ (464.5 eV) multiplets corresponds to the charge state of Ti^{4+} in titanium dioxide. From the observed spectrum in Fig. 1 *a*, Ti and O are characterized by intense Auger transitions, the so-called Koster-Kronig transitions (LMM and KLL). For Ti L3, the index 3 level is $2p_{3/2}$ and M45 – the index 45 may mean that the Auger electron is emitted from one of the spin levels of the orbital doublet $3d_{3/2}$ and $3d_{5/2}$. The M_{23} index is an Auger electron emitted from one of the spin levels of the orbital doublets $3p_{1/2}$ and $3p_{3/2}$. The most intense Auger transitions are those of the KLL and LMM types. In the Koster-Kronig transitions, the vacancy is filled with electrons. Therefore, the spectra in Fig. 1*c* show that the Ti–O bond can be defined as covalently polar, hence the TiO_2 valence band is formed by external oxygen p-electrons (KLL), and the conduction electron wave function is localized on O_2^- ions. In this case, the charge transfer is carried out from Ti^{4+} to O_2^- (the presence of oxygen vacancies and surface hydroxyl groups with Ti^{4+} centers).

In this work, the cluster approximation is used to perform quantum chemical calculations. The X-ray diffraction data on the unit cell of the bulk phase of anatase were used to construct a model of the anatase surface (Fig. 2, *a*) [22]. It is known that the structural unit of the anatase crystal lattice is distorted TiO_6 octahedra connected by common edges. Each octahedron has four common edges with its neighbours, forming zigzag chains. The titanium atom has four valence electrons and is six-coordinated in the bulk phase of anatase, i.e. surrounded by 6 oxygen atoms, four of which are in the equatorial position and two in the axial position. In bulk anatase crystals, there are two types of Ti–O bonds: equatorial – short (1.94 Å) and axial – long (1.97 Å). The Ti–O bonds are the superposition of four covalent and two dative bonds. The two extended dative bonds are axial [22].

The spatial structure of the cluster chosen as a model of the anatase surface is shown in Fig. 2 *b*. It corresponds to the gross formula $Ti_{15}O_{41}H_{22} \equiv (TiO_2)_{15} \cdot 11H_2O$. The broken valences of the oxygen and titanium atoms, which arise during the construction of the cluster, were saturated with hydroxyl groups and hydrogen atoms so that in this model there are two types of oxygen atoms, namely two- and three-coordinated (Fig. 2 *b*) and five-coordinated titanium atoms, which is typical for the (001) anatase surface. The principle of embedded cluster models was applied in this work, i.e., the self-consistency was performed only for Ti and O atoms located in the first surface layer (highlighted in Fig. 2 *b*). In contrast, the surroundings (the second layer and hydroxyl groups on the periphery) remained unchanged during the self-consistency.

The electronic ground state of all clusters studied in this paper is a singlet.

In the study of silver dimer adsorption, various variants of Ag_2 cluster placement relative to the surface

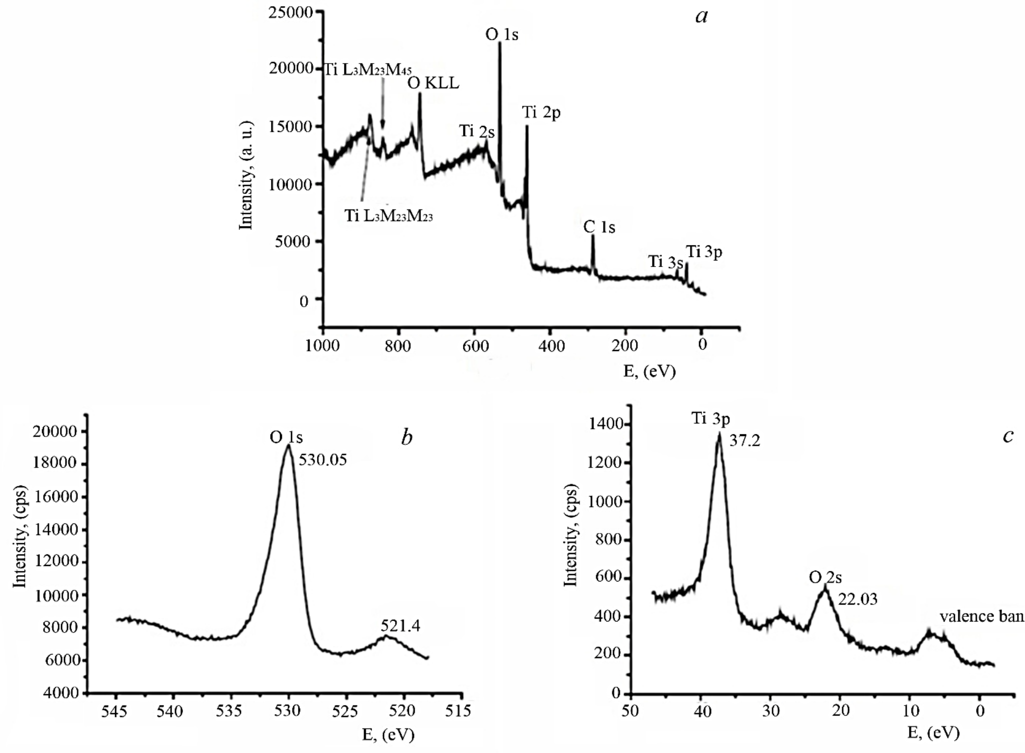

Fig. 1. Photoelectron spectra of TiO_2 sample (metatitanic acid): *a* – overview spectrum, *b* – spectrum of O1*s* photoelectrons, *c* – spectrum of Ti3*p* and O2*s* photoelectrons of the valence band of anatase.

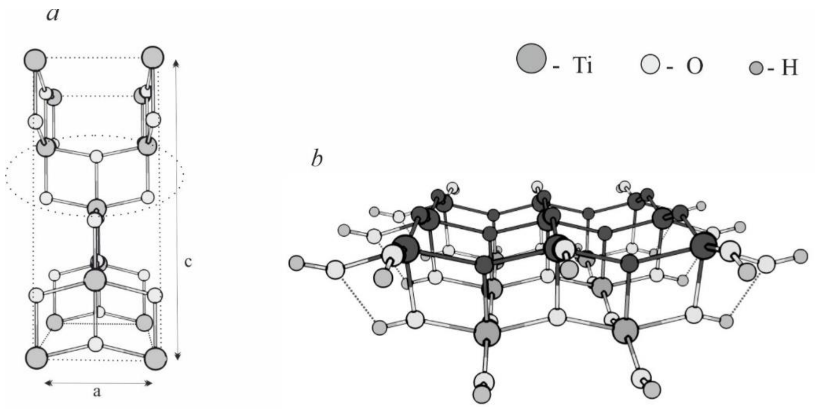

Fig. 2. The anatase unit cell – *a* and the optimised structure of the $(TiO_2)_{15} \cdot 11H_2O$ cluster – *b*.

(001) of anatase were considered (Fig. 3):

Ag–Ag axis was located perpendicular to the (001) face above one of the five-coordinated titanium atoms (Fig. 3 *a*);

the Ag–Ag axis was orientated parallel to the (001) face in the middle between the chains of two-coordinated O atoms (Fig. 3 *b*);

the Ag–Ag axis was placed parallel to the face (001) above the chain of double-coordinated O atoms (Fig. 3 *c*).

All the initial structures as a result of optimization lead to the equilibrium state of the adsorption complex, in which two Ag atoms form 4 Ag–O bonds (whose lengths are 2.43, 2.44, 2.66, and 2.69 Å, respectively) with two-coordinated O atoms of the TiO_2 surface (Figs. 3 *d*, 4 *b*). On the O atoms in the equilibrium state of the $Ti_{15}O_{41}H_{22}$ cluster, the charges averaged -0.2 atomic units (according to Lövdin). The length of the Ag–Ag bond in the formed complex is 2.74 Å, which is 0.12 Å longer than the corresponding calculated value for the Ag_2 cluster in the gas phase (2.62 Å). This indicates the vibrationally excited state of the two-atom fragment in the $Ti_{15}O_{41}H_{22}Ag_2$ adsorption complex and announce an increased reactivity of the argentum atoms compared to their reactivity in the two-atom Ag_2 molecule. The Lövdin charge analysis shows that during the adsorption of the silver dimer, the electron density is transferred from Ag_2 to the surface of the $Ti_{15}O_{41}H_{22}$ cluster, as evidenced by the positive charge (+0.18 atomic units) on the argentum atoms in the formed complex. During the adsorption of the silver dimer, the length of the Ti–O bonds increases (from 1.97 to 2.14 Å) in the adjacent surface area, i.e., the adsorption of Ag_2 causes deformation of the anatase surface (Fig. 4).

The adsorption energy (E_{ads}) of the silver dimer on the anatase surface is -234.8 kJ/mol and was calculated according to the formula

$$E_{ads}=E(Ti_{15}O_{41}H_{22}Ag_2) - [E(Ti_{15}O_{41}H_{22}) + E(Ag_2)],$$

where $E(Ti_{15}O_{41}H_{22}Ag_2)$, $E(Ti_{15}O_{41}H_{22})$ and $E(Ag_2)$ are the total energies of the optimized structures of the adsorption complex of silver dimer with anatase surface, a cluster modelling the anatase surface and silver dimer, respectively. The process of formation of this complex is exothermic. The obtained value of the binding energy of the silver dimer to the anatase surface is in good agreement with the corresponding values reported in [12].

To determine the factors responsible for the binding of the silver dimer to the anatase surface, the density distribution of single-electron states was analyzed. The total density of states was constructed from the discrete energy spectrum of the one-electron levels of the Ag_2 molecule, the $Ti_{15}O_{41}H_{22}$ cluster, and their adsorption complex $Ti_{15}O_{41}H_{22}Ag_2$. Each of these levels was blurred by a Gaussian function with a half-width at a half-height

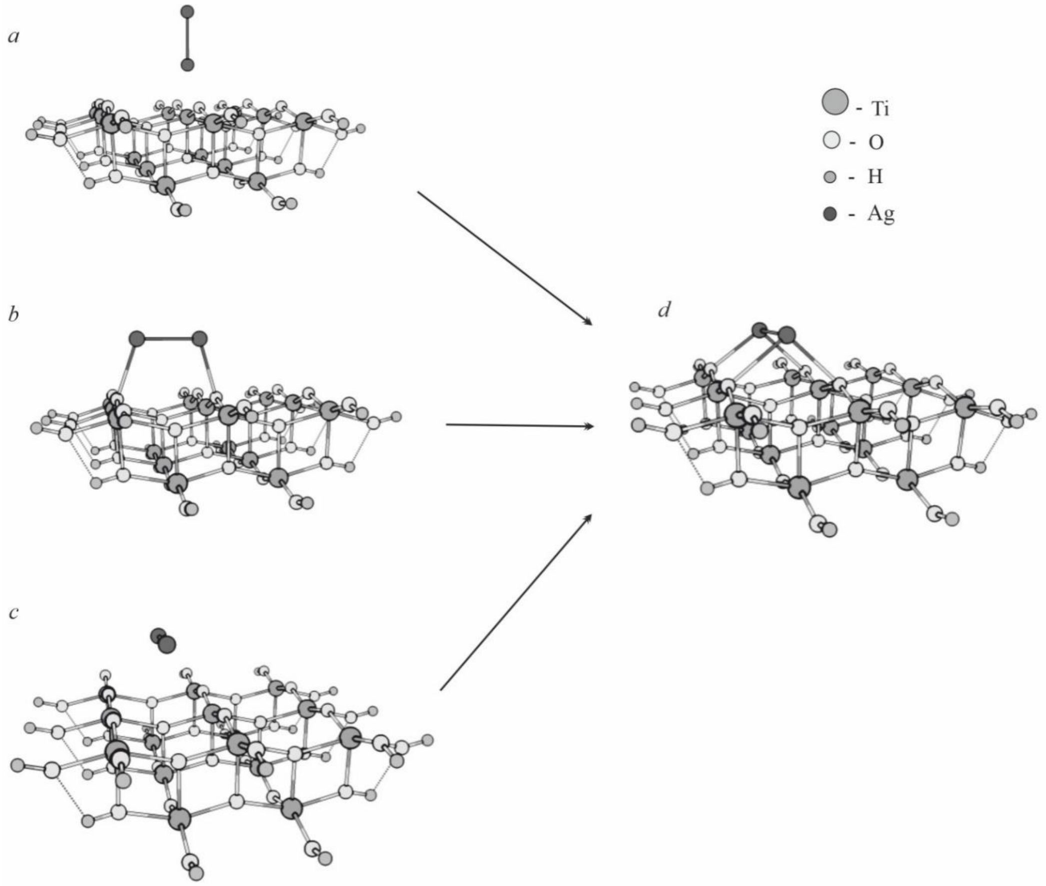

Fig. 3. Initial (*a*, *b*, *c*) and equilibrium (*d*) structures of adsorption complexes of the $(TiO_2)_{15}{\cdot}11H_2O$ cluster and Ag_2 dimer.

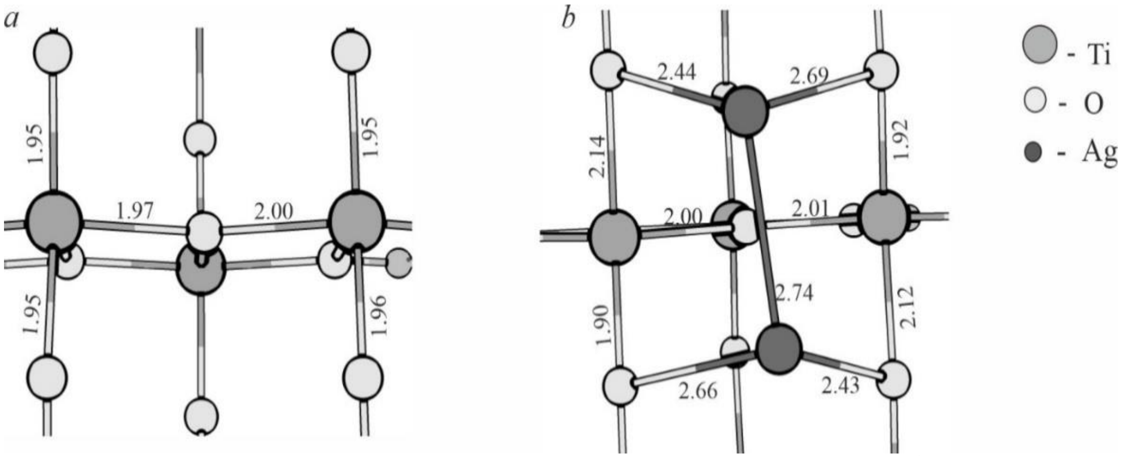

Fig. 4. The structure of the adsorption centre of the anatase surface (001) (bond lengths in Å) and the complex with Ag_2.

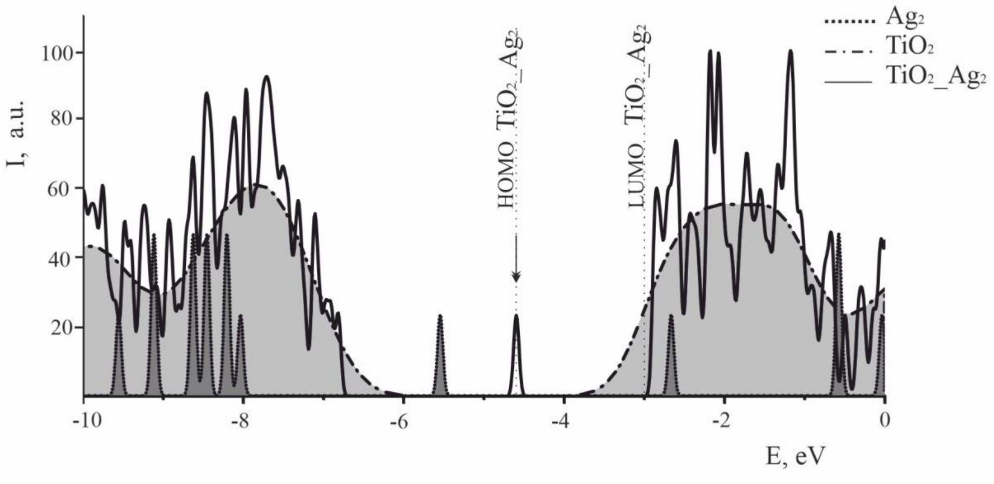

Fig. 5. Spectra of one-electron states of $Ti_{15}O_{41}H_{22}$, $Ti_{15}O_{41}H_{22}Ag_2$ clusters and two-atom Ag_2 molecule.

of 0.4 eV, and the total intensity of the density of states was normalized to 1.

The calculated single-electron density spectra of the $Ti_{15}O_{41}H_{22}$, $Ti_{15}O_{41}H_{22}Ag_2$ clusters and the two-atom Ag_2 molecule without the introduction of a correction factor that takes into account all the shifts on the energy scale due to the approximate nature of quantum chemical calculations are shown in Fig. 5.

The distributions of the total densities of the one-electron states of the systems under consideration have certain peculiarities. Namely, the transition from Ag_2 and $Ti_{15}O_{41}H_{22}$ components to their complex $Ti_{15}O_{41}H_{22}Ag_2$ changes the energy gap width and the valence band profile. The valence band of the $Ti_{15}O_{41}H_{22}$ cluster consists of 2*p*-orbitals of two- and three coordinated oxygen atoms, which do not significantly contribute to the conduction band, while the conduction band is mainly composed of 3*d*-orbitals of titanium atoms (Fig. 6). From the spectra of one-electron states in the range from -10 to 4 eV, it is clear that the one-electron level (-4.6 eV), localized on the two-atom Ag_2 fragment of the $Ti_{15}O_{41}H_{22}Ag_2$ adsorption complex, falls into the band gap of the $Ti_{15}O_{41}H_{22}$ cluster. That is, during the formation of the complex, the HOMO is localized mainly on the argentum atoms (Fig. 6). The result of this arrangement of single-electron levels is a decrease in the width of the band gap and, consequently, an increase in the efficiency of solar radiation absorption.

Consequently, the holes and electrons formed during the absorption of solar radiation can occupy these additional levels, which will finally lead to an increase in the photocatalytic efficiency of systems based on silver-doped titanium dioxide samples [6].

The connection between the Ag_2 dimer and the cluster modelling the anatase surface occurs mainly due to the overlap of filled Ag_2 MOs with vacant surface eigenstates, which are concentrated generally on five-coordinated Ti atoms. During the formation of the $Ti_{15}O_{41}H_{22}Ag_2$ complex, the density of states peaks (Fig. 7) corresponding to the bulk Ti 3*s*, Ti 3*p*, and O 2*s* levels are split, which is due to the deformation of the $Ti_{15}O_{41}H_{22}$ cluster surface during the adsorption of the silver dimer and the appearance of non-equivalent titanium and oxygen atoms in the cluster.

Conclusions

The optimization of the spatial structure of the complex modelling the anatase surface with the adsorbed silver dimer $Ti_{15}O_{41}H_{22}Ag_2$ showed that the two-atom Ag_2 fragment is bound by four Ag–O bonds in pairs for each

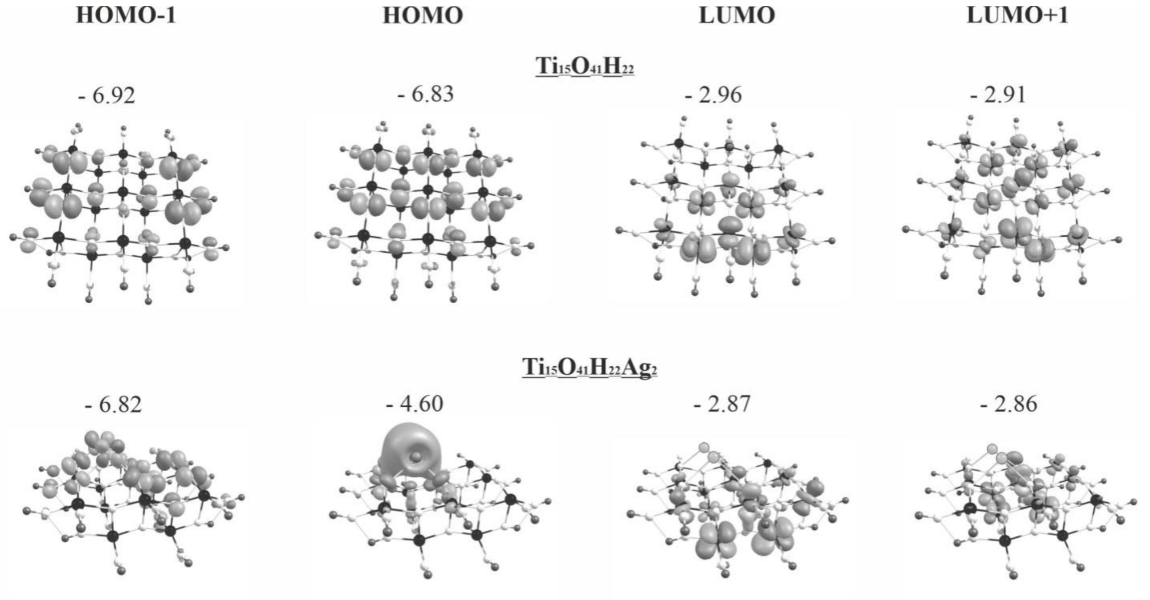

Fig. 6. Energy (eV) and localization of the HOMO and LUMO of $Ti_{15}O_{41}H_{22}$ and $Ti_{15}O_{41}H_{22}Ag_2$ clusters.

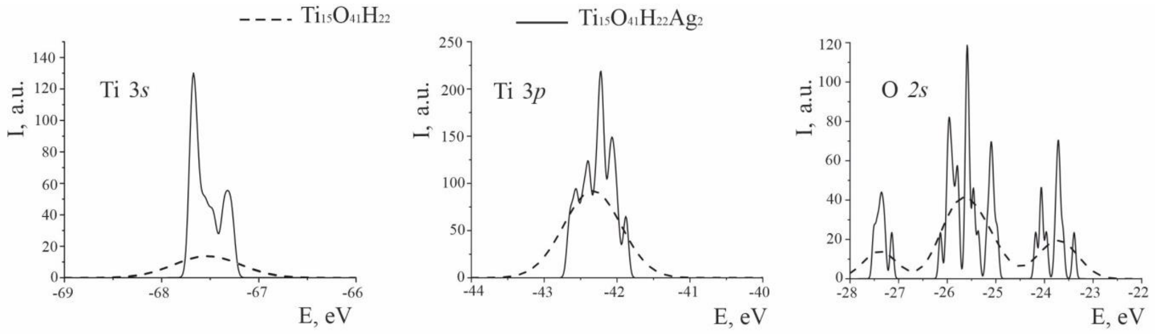

Fig. 7. Partial densities of states of Ti and O atoms of $Ti_{15}O_{41}H_{22}$ and $Ti_{15}O_{41}H_{22}Ag_2$ clusters.

Ag atom. The equilibrium Ag–Ag distance in it is 2.74 Å, which is slightly higher than in the isolated two-atom Ag_2 molecule (2.62 Å). That indicates the vibrationally excited state of the two-atom fragment of Ag_2 in the $Ti_{15}O_{41}H_{22}Ag_2$ adsorption complex and indicates an increased reactivity of argentum atoms compared to their reactivity in the two-atom Ag_2 molecule. In addition, the increase in the reactivity of Ag atoms in the adsorbed state is indicated by a decrease in the ionization potential for the $Ti_{15}O_{41}H_{22}Ag_2$ complex (5.72 eV) compared to the corresponding value for the silver dimer (7.67 eV). That is, the adsorption complex $Ti_{15}O_{41}H_{22}Ag_2$ is characterized by increased electron donor properties compared to the Ag_2 dimer. At the same time, it should be taken into account that the HOMO of the $Ti_{15}O_{41}H_{22}Ag_2$ adsorption complex is localized exclusively on the two-atomic fragment of silver.

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Квантовохімічне дослідження просторової будови і електронної структури активних центрів поверхні нанодисперсного анатазу та допованого кластером Ag_2 його похідного

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Методом функціоналу густини з гібридним обмінно-кореляційним функціоналом B3LYP та валентним базисним набором sbkjc з ефективним остовним потенціалом проведено квантовохімічне моделювання центрів адсорбції димерів Ag на поверхні анатазу. Проаналізовано зміни геометричної та електронної структури кластера Ag_2 при адсорбції, визначені найбільш стабільні його положення на поверхні TiO_2. Отримані результати добре узгоджуються із даними отриманими методом рентгенівської фотоелектронної спектроскопії.

Ключові слова: поверхня анатазу, адсорбція димерів Аргентуму, метод функціоналу густини, рентгенівська фотоелектронна спектроскопія.