

APPLICATION OF QUANTUM-CHEMICAL METHODS FOR INVESTIGATION OF GOLD NANOCCLUSERS PROPERTIES

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Abstract. Gold nanoparticles supported on metal oxide are important nanomaterials; their applications as biochemical sensors, in optical industry and catalysis have received much attention. The most of gold clusters properties (at first, catalytic activity) strongly depend on a particle size, shape, and type of support. Different quantum-chemical methods: density functional theory with nonempirical local functional PBE, MP2 perturbation theory, and coupled cluster method with single and double substitutions CCSD are used to study structure and properties of Au_n, to simulate the influence of ZrO₂ support on Au₆ structure. Since the information about the strength and nature of interaction of nanoparticles with reactants is very important to understand the mechanisms of catalytic reaction, theoretical data about the adsorption of molecules (H₂, O₂, hydrocarbons) on gold nanoclusters are presented. A gold atom has a rather large nuclear charge, and therefore relativistic effects should be taken into account. For this reason we used the SBK effective core potential and extended basis functions for describing external electron shells. Possibilities and limitations of each method are also discussed.

1. INTRODUCTION

Haruta found that nanosized gold particles adsorbed on metal-oxides such as Fe₂O₃, Co₂O₄, Al₂O₃, MgO, TiO₂, ZrO₂, CeO₂ facilitate a wide class of reactions under near-ambient conditions and this discovery attracted a worldwide interest [1]. Gold is known to be very inert in a bulk form. It is not oxidized, and the surface of gold cannot adsorb the most molecules from a gas phase. However, gold nanoparticles were found to be active catalysts for many reactions of industrial and environmental interest: selective oxidation of CO and hydrocarbons, hydrogenation and isomerization of hydrocarbons [2].

The origin of the catalytic activity of gold nanoparticles is not well understood so far. The

most of the gold clusters properties (at first catalytic activity) strongly depend on a particle size, shape, and type of support. For that purpose, it would be useful to know whether it is possible to estimate the particle size (the number of gold atoms in a cluster) from vibrational spectra. Our calculations showed a weak correlation between Au_n spectrum and their structure [3]. For Au_n clusters, the calculated vibration frequencies are in the low energy range of 10-200 cm⁻¹. Calculated IR intensities are generally small but they are most significant for selected asymmetric stretching modes.

In a gas phase, interaction between gold clusters and small molecules such as O₂, H₂, CO, CH₄, NH₃, N₂ was intensively studied [4], its knowledge is important to develop new sensors. Chemical

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reaction catalysis by gold nanoparticles has been mainly attributed to oxygen, but it is not well understood how oxygen is bonded with gold atoms. It was found that calculated IR spectra of Au_{20}O and Au_{20}O_2 complexes have strong dependence on their structure and type of O-Au bonds [3]. Thus the vibrational spectra can be useful for the identification of oxygen adsorption type and of the structure of oxidized gold clusters. Adsorption of hydrogen, oxygen and hydrocarbons probably appears to be strongly size-dependent on gold clusters [5]. The first question arises, whether chemisorption on nanometer-sized gold particles has dissociative or molecular type.

The high catalytic activity of gold clusters on oxides has been attributed to structural and electronic effects, as well as to support effects. It was previously mentioned that ZrO_2 is considered to be an important catalytic support medium [6]. Zirconia is a technologically important material due to its high strength and stability at high temperature and its excellent dielectric properties, with average static dielectric constant ϵ of around 20. Thus ZrO_2 has a wide range of industrial applications, including uses in ceramic engineering, as an oxygen sensor in fuel cells. It is that zirconia is one of the most radiation-resistant ceramics currently known, and therefore has a particular importance in nuclear industry.

The evolution of structural and electronic properties of zirconia as a function of factors such as temperature and pressure in the polymorphs of pure ZrO_2 , as well as their mixing with various oxides is therefore the subject of intensive experimental studies. As for theoretical studies, the structural properties and electronic ground state have been examined using Hartree-Fock or density functional theory (DFT). The phase stability has been investigated within Landau theory or lattice dynamical models. Zirconium dioxide is the only thermodynamically stable compound in the system Zr-O. At low pressures, zirconia displays three phases: monoclinic, tetragonal and cubic.

Modern quantum-chemical methods are frequently used to understand the mechanism of interaction between support and nanoparticles. It is supposed to be one of the most appropriate ways to understand the influence of support on catalytic properties of gold nanoparticles. It is possible to predict the type of interaction, the structure of adsorbed molecule, the adsorption heat and the type of adsorption center.

In this report, the isomerization of butene and interaction between neutral Au_n clusters ($n=2-20$)

and O_2 , H_2 , C_2H_4 , $\text{C}_n\text{H}_{2n+2}$ ($n=1-8$) were studied by different quantum-chemical methods (density functional theory with nonempirical local PBE (Perdew-Burke-Ernzerhof) functional, MP2 perturbation theory, coupled cluster theory with single and double substitutions CCSD). Benzene adsorption processes on gold clusters Au_6 , benzene adsorption on ZrO_2 and benzene adsorption on Au_6/ZrO_2 were simulated. The objective was to establish which methods should be used to obtain the satisfactory results concerning structure and properties of gold clusters.

2. CALCULATION DETAILS

Calculating the properties of molecules is possible by using the computational chemistry. It uses the results of theoretical chemistry, incorporated into efficient computer programs. The computation chemistry is based on three whales: methods, basis set and program. Correct choice of whales guarantees right solving of the problem. The methods are thus based on theories which range from highly accurate, but are suitable only for small systems, to very approximate, but suitable for very large systems. The accurate methods used are called ab initio methods, as they are based entirely on a theory from the first principles. The less accurate methods are called empirical or semi-empirical because some experimental results, often from atoms or related molecules, are used along with the theory. There are many self-sufficient software packages used by computational chemists. Some include many methods covering a wide range, while others concentrate on a very specific range or even a single method.

One of the most effective methods of modern quantum chemistry is the density functional theory based on the Hohenberg-Kohn theorem. Computational time being comparatively small, this method as a rule gives results of the same accuracy as those of more time-consuming approaches with the same basis set. In this work, we compare the time of computation of second derivatives matrix for small molecules and Au_{20} cluster using MP2 perturbation theory, CCSD and density functional theory with the nonempirical local PBE functional [7], which we have used earlier in the study of gold complexes [8]; implementations provided by the Gaussian 03, Revision B.01 [9] and Priroda [10] packages. The gold atom possesses a fairly large nucleus charge; therefore, relativistic effects play an important role [11]. Applying pseudopotentials within the framework of a nonrelativistic approach

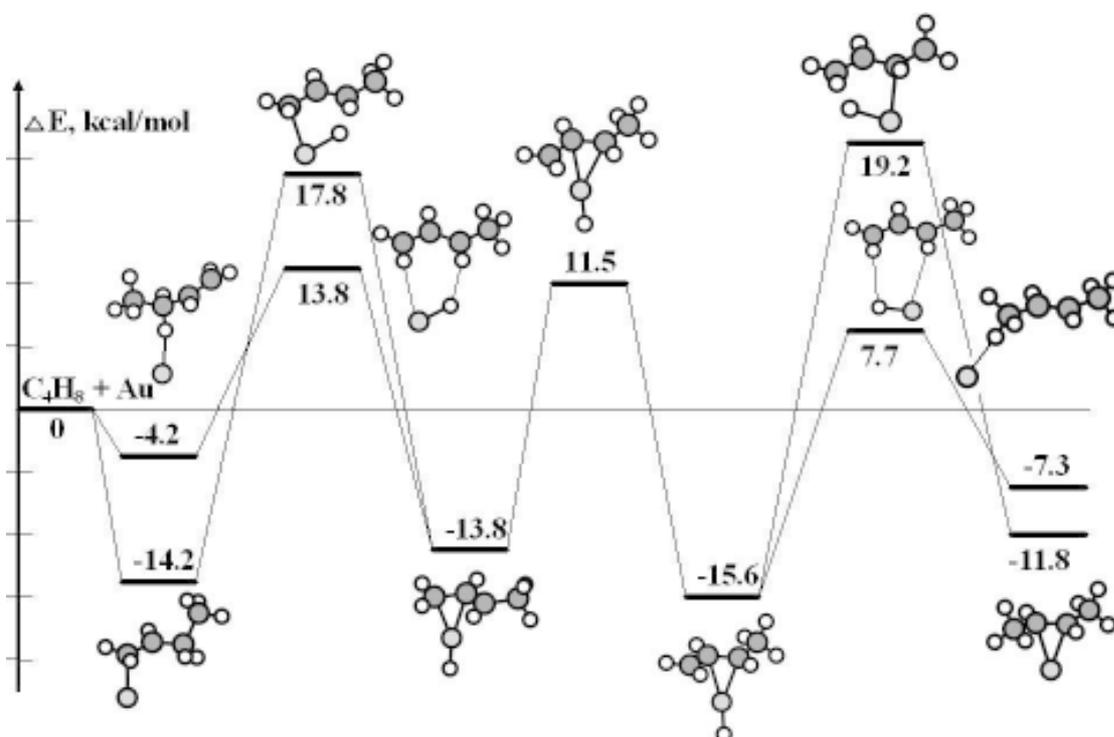


Fig. 1. Energy diagram of butene-1 isomerization by gold atom (grey color).

Table 1. Frequency calculation time by different methods.

Test Molecule	DFT PBE	MP2	CCSD
H ₂	6 sec	7 sec	23 sec
O ₂	11 sec	21 sec	99 sec
Butene-1	20 min	176 min	1552 min
Au ₂	1 min	4 min	240 min
Au ₂₀	1.43 hour	-	-

allows us to effectively include the most important scalar relativistic effects. For this purpose, for gold we used extended basis sets for the SBK and SDD effective core potentials [12,13]. The outer electron shells of O, H, C and Au atoms are described by the basis sets [311/311/11] and [51111/51111/5111] respectively. The types of stationary points on the potential energy surfaces were determined from analysis of Hessians; and the second derivatives were calculated analytically (DFT, MP2) or

numerically (CCSD). The zero-point energy was calculated in a harmonic approximation.

3. RESULTS AND DISCUSSION

Table 1 shows that high accurate quantum-chemical methods based on MP2 perturbation theory suit for calculation of small molecules with no more than 10 light atoms with short basis set (H₂, O₂). More heavy molecules as gold ones require consider-

able dimension of wavefunction basis, so the time for the second derivatives calculation of Au_2 by CCSD method is much longer – 240 min (4 hour), while the same procedure requires only 1 minute by DFT methods. Only density functional theory is suited for calculation of Au_{20} .

Quantum-chemical simulation of butene-1 isomerization into (cis/trans)-butene-2 using DFT, MP2 and CCSD methods shows that there is a high energy barrier (more than 40 kcal/mol) for this process. All the methods used give the same results. If gold atom is present, the situation is changed. To reveal the most probable mechanism, we calculated the energies and the structures of the initial compounds, products and transition states. The results of quantum-chemical simulation of butene isomerization are presented in the energy diagram (Fig. 1). The sum of the energies of C_4H_6 and Au was taken as the zero level.

Fig. 1 shows that this catalytic reaction has three stages and is accompanied by π -complex $\text{Au}-\text{C}_4\text{H}_8$ formation at the first step. In our opinion, the studies of butene isomerization by gold help to understand the mechanism of allylbenzene ($\text{Ph}-\text{C}_3\text{H}_5$) isomerization in the presence of gold nanoparticles [14], and thus opens new prospects for the gold catalysis. According to data from Table 1, density functional theory should be used for calculation of Au_n ($n > 2$) systems. So for investigation of catalytic and adsorptional site of gold nanoparticle DFT PBE/SBK method was used. Au_{20} cluster is considered to be a most appropriate model of a nanoparticle. Its size is about 1 nm, it has all of three types of atoms (apex, edge, and facet), and its structure is experimentally verified [15]. The optimization of Au_{20} cluster structure reveals that the most stable structure is a pyramid composed of Au_4 tetrahedrons with different Au-Au short distances (Fig. 2a). All obtained bond distances, angles and frequencies well agree with the experimental data [15]. A simple defect in Au_{20} structure can be produced by the transition of one atom from an apex to the opposite facet (Fig. 2a) and requires the additional energy (17 kcal/mol). Removal of one gold atom from the apex of Au_{20} cluster is accompanied by energy loss of 70 kcal/mol, while the addition of one atom to Au_{20} cluster is gainful on 38 kcal/mol (Fig. 2c).

The relative energies of surface complexes of O, O_2 , H, and H_2 involved in the chemisorption process on Au_{20} cluster were calculated using density functional theory (Table 2). The binding energy of any molecule M is defined as

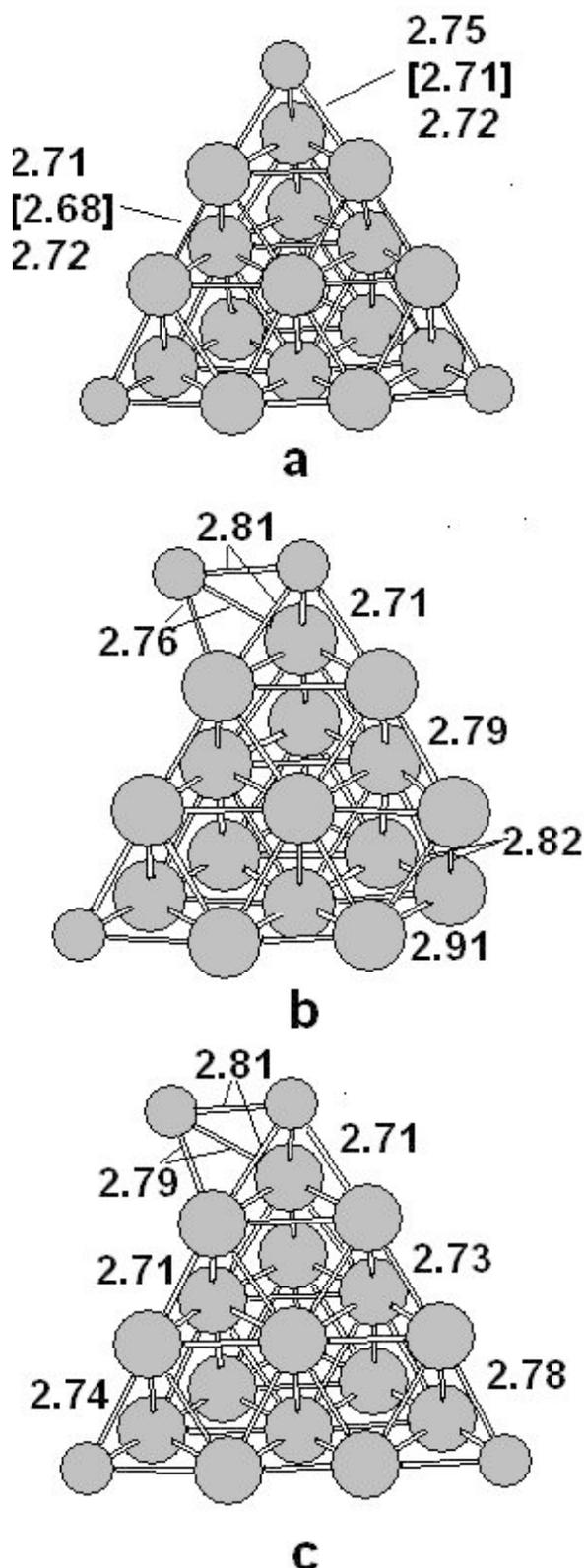
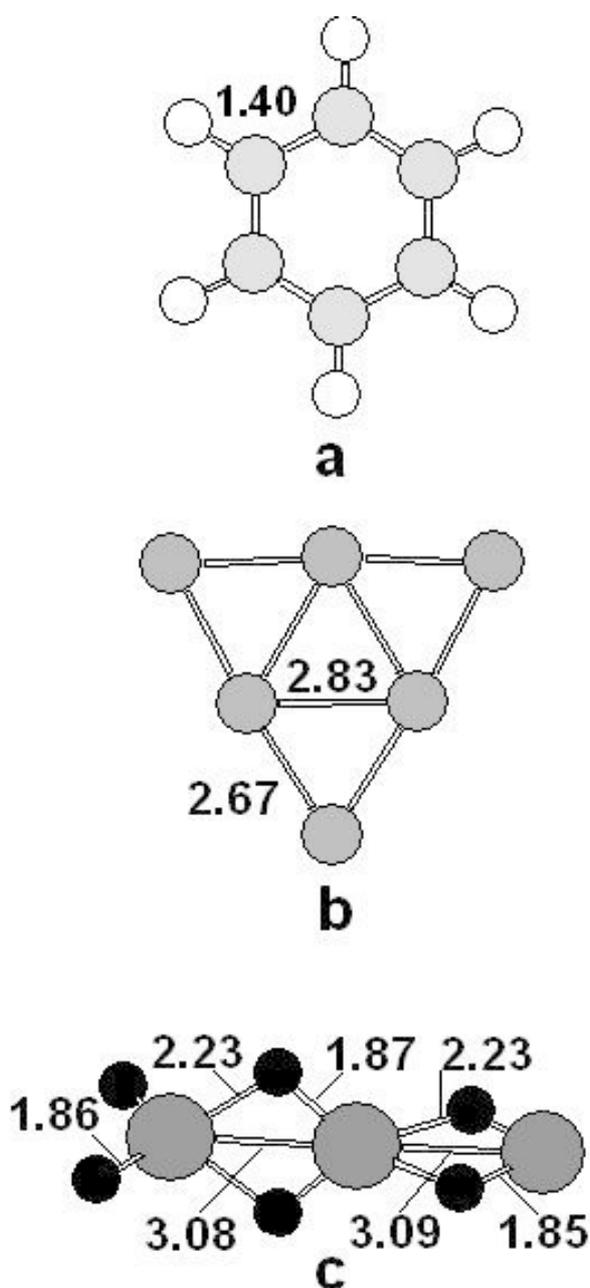


Fig. 2. Optimized structures of Au_{20} clusters: (a) is the lowest-energy configuration, (b) is one of possible distorted isomers, (c) is Au_{21} ; and the calculated bond lengths (Å). Experimental data are given in square brackets, the calculation data [15] are given in italic. Different types of gold atoms in Au_{20} cluster are numbered.

Table 2. Binding energies of test molecules (*M*) with a tetrahedral gold cluster Au₂₀ (kcal/mol).

Au	O	O ₂	H	H ₂	C ₅ H ₁₂	C ₂ H ₄	PhC ₃ H ₅
Au (apex)	-33.7	-15.5	-34.9	-1.0	-3.8	-13.4	-15.3
Au (facet)	-15.6	-9.7	-26.8	-0.1	-1.8	-4.8	-6.0
Au (edge)	-62.7	-19.3	-35.3	-	-2.9	-3.2	-5.0

**Fig. 3.** Structures of isolated benzene (a), cluster Au₆ (b), and model of support (ZrO₂)₃ (c).

$$E_{bind} = E(M - Au_{20}) - E(M) - E(Au_{20}).$$

We have found that the chemisorption energy of atomic and molecular oxygen on Au₂₀ cluster had the value varying from 3 to 35 kcal/mol. From all possible structures of the oxygen atom coordination on Au₂₀ nanocluster only four are realized: monodentate coordination on the apex, Au₁-O (with bond energy of 34 kcal/mol), on the facet, Au₄-O (16 kcal/mol), and two kinds of bidentate coordination on the edge on the ending, Au₁-O-Au₂ (with bond energy of 47 kcal/mol) and in the center of edge, Au₂-O-Au₃ (with bond energy of 63 kcal/mol).

We considered both molecular chemisorption, where the O-O molecular bond is preserved, and dissociative chemisorption, where the two O atoms do not form a direct bond. We searched through a large number of structures to determine a low-energy configuration. In the most stable configurations for dissociative chemisorption, two oxygen atoms act as Au-O-Au bridges (Au₂-O-Au₃ and Au₆-O-Au₇, 35 kcal/mol). For H atom binding on Au₂₀ cluster, the bridge site is the most favorable adsorption site. However, H atom could be coordinated on apex gold atom with the same bonding energy, 35 kcal/mol. For molecular hydrogen chemisorption, dissociative type was only considered. The optimized HAu₂₀H structures have large variations in energy, and the most stable one is the complex, in which two bridged H atoms are located on the neighbor edges of the cluster with common gold atom in the apex of tetrahedron. The formation of this complex from Au₂₀ and molecular hydrogen is accompanied by the energy release (2 kcal/mol). The obtained data were used for elucidation of the mechanism for synthesis of H₂O₂ from hydrogen and oxygen in the presence of Au catalyst.

The investigation of chemisorption of small alkanes (CH₄, C₄H₁₀) and alkenes (C₂H₄, Ph-C₃H₅) on gold nanoclusters shows that saturated hydro-

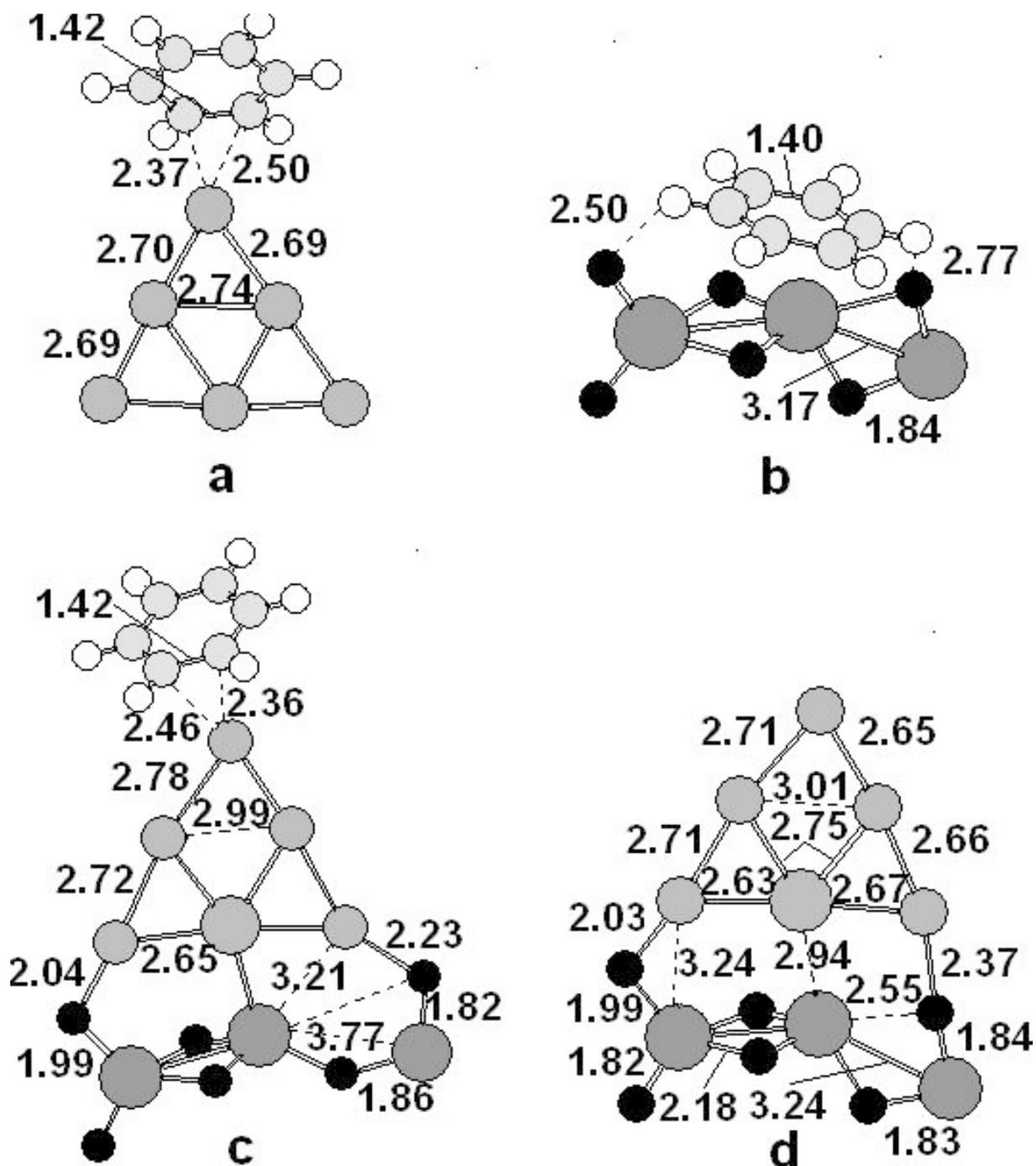


Fig. 4. Optimized structures of benzene with Au_6 (a), $(ZrO_2)_3$ (b), $Au_6(ZrO_2)_3$ (c), and $Au_6(ZrO_2)_3$ (d).

carbons form weakly bonded complexes with Au_{20} cluster, while alkenes are adsorbed on Au_{20} cluster with π -complex formation. We found that the energy of C_2H_4 chemisorption on Au_{20} cluster has the value varying from 3 to 13 kcal/mol. From all

possible structures of C_2H_4 coordination on the nanocluster only three are realized: on the apex with bond energy of 15 kcal/mol, on the facet (3 kcal/mol), and on the edge with bond energy of 5 kcal/mol. Thus gold atoms in the apex of cluster

play the important role in the adsorption process. Similar situation is observed for the allylbenzene absorption. The adsorption of Ph-C₃H₅ on the apex gold atom in the cluster is characterized with the largest value of calculated binding energy (15.3 kcal/mol), experimental heat of adsorption of Ph-C₃H₅ is equal to 17 kcal/mol [16].

For simulation of benzene adsorption on a bare gold cluster and a supported gold cluster Au₆, optimization of isolated structures such as C₆H₆, Au₆, (ZrO₂)₃ (Fig. 3) and adsorbed complexes such as C₆H₆-Au₆, C₆H₆-(ZrO₂)₃, C₆H₆-Au₆-(ZrO₂)₃ (Fig. 4) was carried out.

The upright conformation of Au₆ was found to be more stable than the others. There is likely to be a specific center on the top of cluster. It was shown that the interaction between benzene and (ZrO₂)₃ had led to distortion of the support (Fig. 4). However the structure of C₆H₆ was hardly changed. Adsorption energies of benzene are 13.4 kJ/mol, 11.7 kJ/mol and 17.7 kJ/mol on (ZrO₂)₃, Au₆, Au₆/(ZrO₂)₃ correspondently. Thus adsorption energy of benzene on the supported Au₆ is higher than on a pure one.

4. CONCLUSION

The study provides the impetus for further experimental investigations on structure of gold nanoparticles, the interaction between oxygen, hydrogen and hydrocarbons and gold clusters and their catalytic reactivity. Adsorption energies of benzene calculated by quantum-chemical method are 13.4 kJ/mol, 11.7 kJ/mol, and 17.7 kJ/mol on (ZrO₂)₃, Au₆, Au₆/(ZrO₂)₃ correspondently.

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REFERENCES

- [1] G.J. Hutchings // *Gold Bulletin* **37** (2204) 3.
- [2] A.S.K. Hashmi and G.J. Hutchings // *Angew. Chem. Int. Ed.* **45** (2006) 7896.
- [3] D.A. Pichugina, A.F. Shestakov and N.E. Kuz'menko // *Proceedings of SPIE* **6580** (2006) 658003.
- [4] N.S. Phala, G. Klatt and E. Steen // *Chem. Phys. Lett.* **395** (2004) 33.
- [5] B. Palpant, B. Prével, J. Lermé, E. Cottancin, M. Pellarin, M. Treilleux, A. Perez, J. L. Vialle and M. Broyer // *Phys. Rev. B* **57** (1998) 1963.
- [6] L.K. Dash, N. Vast and P. Baranek // *Phys. Rev. B* **70** (2004) 245116.
- [7] J. P. Perdew, K. Burke and M. Ernzerhof // *Phys. Rev. Lett.* **77** (1996) 3865.
- [8] D.A. Pichugina, A.F. Shestakov and N.E. Kuz'menko // *Gold Bulletin* **40** (2007) 115.
- [9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria *et al.*, *Gaussian, Inc.* (Pittsburgh PA, 2003).
- [10] D. N. Laikov // *Chem. Phys. Lett.* **281** (1997) 151.
- [11] P. Pyykkö // *Inorg. Chem. Acta* **358** (2005) 4113.
- [12] H. Basch and P. G. Jasien // *Can. J. Chem.* **70** (1992) 612.
- [13] A. Nicklass, M. Dolg, H. Stoll and H. Preuss // *J. Chem. Phys.* **102** (1995) 8942.
- [14] V.V. Smirnov, S.A. Nikolaev, G.P. Murav'eva, L.A. Turina and A.U. Vasilkov // *Russ. J. Kinetics and Catalysis* **48** (2007) 271.
- [15] J. Li, X. Li, H.-J. Zhai and L.-S. Wang // *Science* **299** (2003) 864.
- [16] V.V. Smirnov, S.N. Lanin, A. Yu. Vasil'kov and S.A. Nikolaev // *Russ. Chem. Bull. Int. Ed.*, **54** (2005) 2215.