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Activation and transformations of phenylethanol on a tetrahedral gold cluster

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Abstract

Quantum chemical simulation of the adsorption of phenylethanol on a tetrahedral Au₂₀ cluster was carried out using the density functional theory, DFT/B3LYP/LANL2DZ. It has been shown that gold atoms located at the top of the cluster have the highest activity in the adsorption of alcohol. Possible reactions of phenylethanol on Au₂₀ cluster to form phenylacetaldehyde were studied. Based on the calculated thermodynamic and kinetic values, it is concluded that the transformation proceeds predominantly through the metal hydride mechanism.

Keywords: mechanism, active centre, nanocluster, catalysis, gold, phenylethanol

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INTRODUCTION

One of the essential industrial processes from the viewpoint of green chemistry is the oxidation of alcohols [1]. The traditional methods of their synthesis involve the use of toxic oxidisers (for example, chromium oxides and salts, 2-iodoxybenzoic acid, sodium hypochlorite) or hazardous organic solvents (dimethylsulphoxide – in the case of the Swern oxidation, carbodiimides – for the Pfitzner–Moffatt oxidation) and often require rigid reaction conditions [2–6]. As a consequence, the search of catalysts is carried out to provide efficient implementation of the environmentally friendly process of alcohol oxidation under soft

and safe conditions using oxygen or peroxides as the oxidising agent.

One of the promising catalysts of low-temperature oxidation is gold nanoparticles deposited on various oxide supports [7]. The catalytic properties of gold nanoparticles in the oxidation of CO, aromatic and aliphatic alcohols, carbonyl compounds, alkenes are known [8–10]. In particular, the catalytic properties of gold nanoparticles have been studied in the oxidation of phenylethanol [11] with the formation of phenylacetaldehyde, the compound used in cosmetics and in food chemistry.

The catalytic oxidation of phenylethanol on gold nanoparticles was considered in a number of works [11–18]. For instance, the relationship be-

tween the activity of a catalyst and the size of metal particles has been detected [12]: spherical gold nanoparticles less than 3 nm in size can oxidise various alcohols in high yields into the corresponding carbonyl compounds and exhibit high selectivity in this process. The effect of the electron properties of gold on the process mechanism is under discussion. In the opinion of some researchers, fine gold without changed centres is responsible for activity [13–15], however, there are also the followers of the cation or anion nature of active gold centres in this process [16–18].

Modern quantum chemical methods are a powerful research tool in catalysis. These methods allow not only simulation of the catalytic process at the molecular level but also investigation of the structure of active centres and prediction of reaction mechanism.

In the present work, simulation of phenylethanol activation and its subsequent transformation into phenylaldehyde at the tetrahedral Au₂₀ cluster has been carried out to reveal the nature of active centres and the mechanism of this reaction.

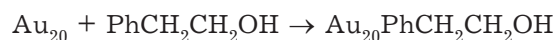
CALCULATION

Objects of investigation

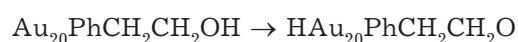
A gold nanoparticle was simulated by the tetrahedral Au₂₀ cluster. Its stable structure is a regular tetrahedron, which has been confirmed by numerous experimental and theoretical studies [19–22]. The cluster contains atoms having different coordination numbers: at the top, at the edge, and on the face. Each face of the Au₂₀ cluster can be considered as a fragment of Au(111) surface.

Investigation procedure

The main stages of phenylethanol oxidation on gold cluster can be represented as follows. At first, adsorption of the alcohol and its activation occur (stage 1):



Then the rupture of O–H bond in the adsorbed alcohol takes place (stage 2):



followed by dehydrogenation with the formation of phenylacetaldehyde (stage 3):



Energy changes were calculated for these three stages of the process under consideration. The transition states were determined to calculate activation energies and reaction rate constants.

Method of investigation

The structures of Au₂₀ cluster, its complex with phenylethanol and all reaction participants were completely optimised by the density functional theory DFT using a three-parameter hybrid Becke–Lee–Yang–Parr functional (B3LYP) [23]. Calculations were carried out on the basis set LANL2DZ with effective pseudo-potential LANL2DZ-ECP, which is employed to describe the relativistic effects of gold [24]. Optimisation of local and global minima on the potential energy surface was carried out according to the BFGS algorithm [25]. Calculation of vibration frequencies, performed for all reaction participants for the purpose of testing the absence of imaginary frequencies in initial substances and in the products of each stage, and the presence of the imaginary frequency corresponding to the reaction coordinate, was carried out in the harmonic approximation. Identification of the transition state was performed by IRC. Calculations were carried out using the ORCA 5.0.3 software package [26, 27].

RESULTS AND DISCUSSION

Adsorption and activation of phenylethanol on Au₂₀ (stage 1)

We performed quantum chemical simulation of the interaction of phenylethanol with Au₂₀ cluster (stage 1). Coordination of the alcohol to different gold atoms located at the top, on the edge, and on the face of the cluster was considered. Three isomeric structures obtained as a result of optimisation are presented in Fig. 1. The formation of IM₁ complex in which phenylethanol is coordinated at the gold atom at the top of the cluster is most favourable: energy change at stage 1 is –45 kJ/mol in this case. Activation of OH-bond at the cluster edge involves the formation of IM₂ cluster, and the corresponding energy change is –28 kJ/mol. The IM₃ structure in which the alcohol is located along the edge of Au₂₀ is found. The calculated energy change accompanying the formation of IM₃ is equal to –27 kJ/mol. For a more thorough investigation of the interac-

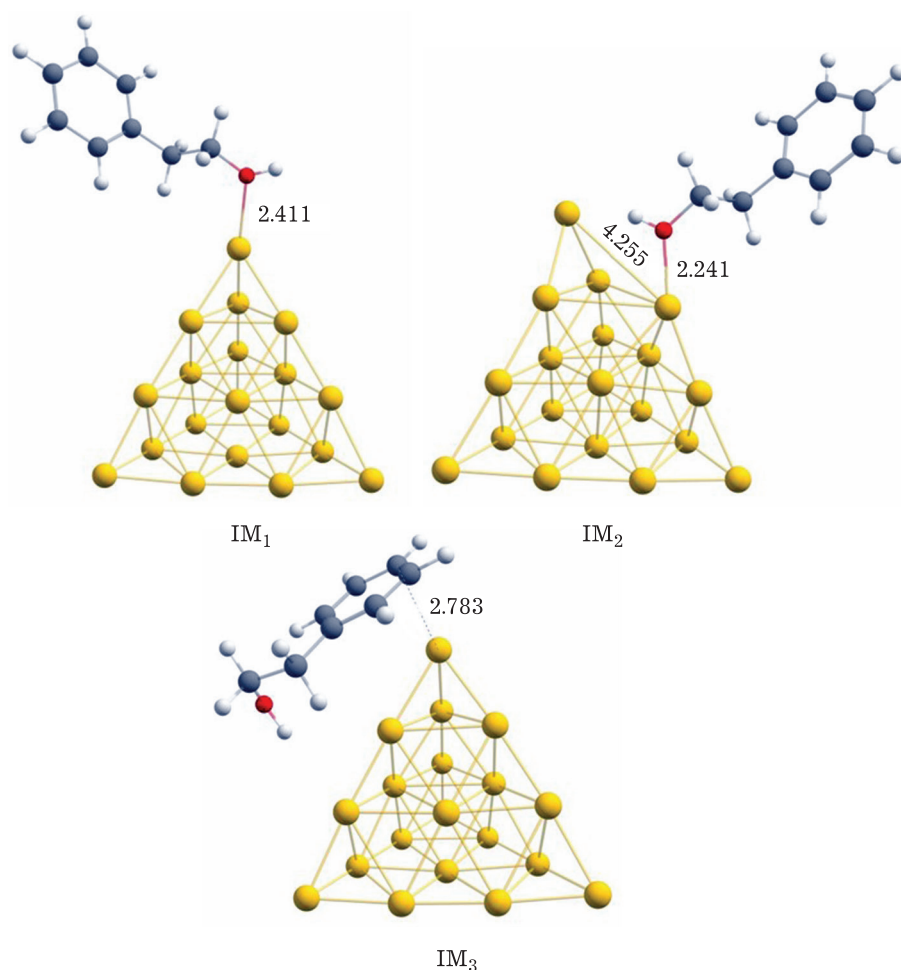


Fig. 1. Optimised structures of the complexes of phenylethanol and gold cluster Au_{20} . Interatomic distances are indicated in Angstroms (Å). Here and in Fig. 2, 3: the gold cluster is marked with yellow colour, the complex of phenylethanol is grey, and the oxygen atom of phenylethanol is red.

tion, we analysed molecular orbitals localised in the IM_3 structure, which revealed the absence of a covalent bond between the carbon atom in the benzene ring and Au atom in the cluster. Therefore, the aromatic system does not participate directly in the interaction with the cluster. Stability of the complex corresponding to phenylethanol position at the cluster face was not detected. So, gold atoms located at the top and edge of the cluster play a significant part in the activation of alcohol.

Rupture of O–H bond in phenylethanol on Au_{20} (stages 2 and 3)

The possibility of O–H bond rupture in the alcohol under investigation at the formation of adsorbed complexes IM_1 , IM_2 and IM_3 will be now considered. The result of quantum chemical modelling is shown in Fig. 2 in the form of energy

diagrams as energy changes in three processes: A – rupture of the O–H bond with the participation of the gold atom at the top of the cluster; B – rupture of the O–H bond with the participation of the gold atom at the edge of the cluster; C – rupture of the C–H band at the carbon atom bound with the hydroxyl group, participated by the gold atom at the top of the cluster. According to computational data, the rupture of O–H in process A requires overcoming a substantial activation barrier and leads to the formation of a stable hydride complex IM_4 , in which the formed structure $\text{HAu}_{20}\text{--PhCH}_2\text{CH}_2\text{O}$ is coordinated at the cluster edge. A decrease in activation energy is possible if the O–H is broken at the cluster edge. The formed hydride complex IM_5 is stable, too; it is an isomer of IM_4 with a similar structure.

Possible subsequent transformations of the complexes $\text{HAu}_{20}\text{--PhCH}_2\text{CH}_2\text{O}$ formed in pro-

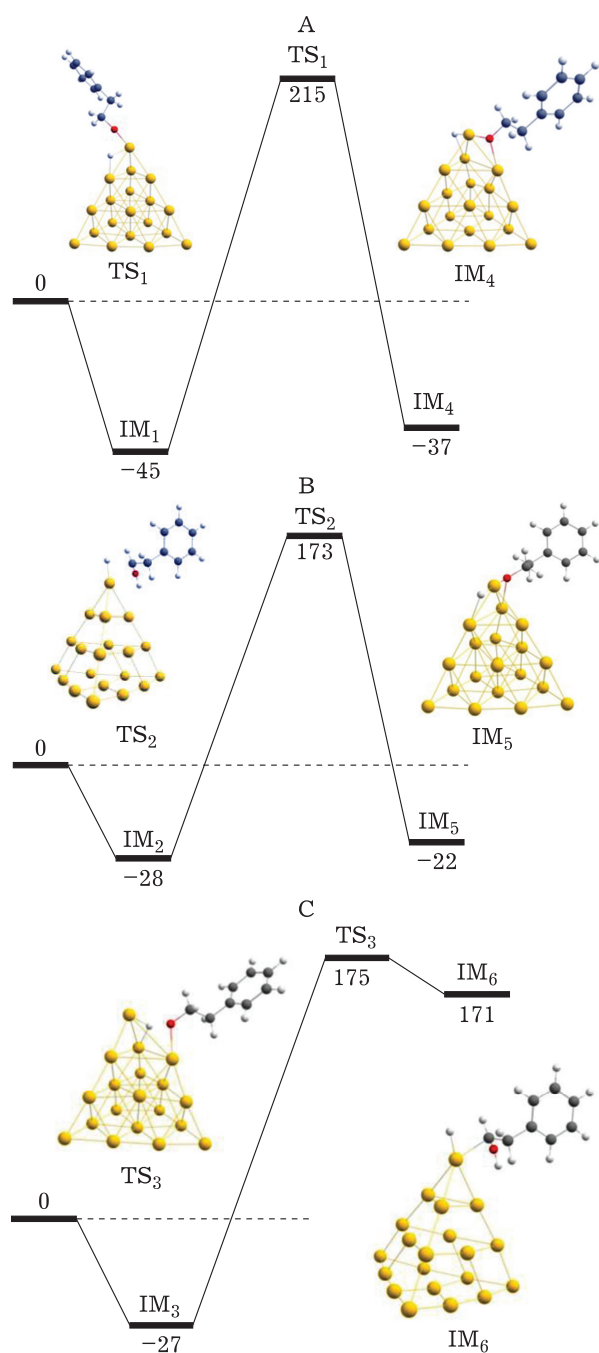
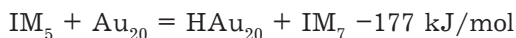
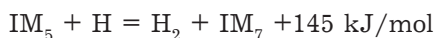


Fig. 2. Energy diagrams illustrating energy changes (kJ/mol) during phenylethanol transformations on Au_{20} (relative to the total energy of phenylethanol and Au_{20}): rupture of OH-bond with the participation of the gold atom at the top (A) and on the edge (B) of the cluster; C – rupture of C–H-bond at the carbon atom bound with the hydroxyl group, with the participation of the gold atom at the top of the cluster. The key interatomic distances in the structures are: TS_1 $R(\text{Au}-\text{O}) = 2.172 \text{ \AA}$, $R(\text{Au}-\text{H}) = 1.180 \text{ \AA}$; IM_4 $R(\text{Au}-\text{O}) = 2.123 \text{ \AA}$, $R(\text{Au}-\text{H}) = 1.640 \text{ \AA}$; TS_2 $R(\text{Au}-\text{O}) = 2.241 \text{ \AA}$; IM_5 $R(\text{Au}-\text{O}) = 2.117 \text{ \AA}$, $R(\text{Au}-\text{H}) = 1.652 \text{ \AA}$; TS_3 $R(\text{Au}-\text{O}) = 2.387 \text{ \AA}$, $R(\text{Au}-\text{H}) = 1.639 \text{ \AA}$; IM_6 $R(\text{Au}-\text{O}) = 2.252 \text{ \AA}$, $R(\text{Au}-\text{H}) = 1.622 \text{ \AA}$. For designations, see Fig. 1.

cesses A and B are to be considered now. Possible reactions participated by hydrogen, for example, for IM_5 :



lead to the formation of complex IM_7 (Fig. 3), in which the structure $\text{PhCH}_2\text{CH}_2\text{O}$ is coordinated by oxygen to the gold atom at the top of the cluster. Then dehydrogenation proceeds through the transition state TS_4 (see Fig. 3) with activation energy 103 kJ/mol, leading to the formation of the final product, phenylacetaldehyde, and Au_{20}H :



From the complex IM_3 , the route $\text{IM}_3 \rightarrow \text{TS}_3 \rightarrow \text{IM}_6$ proceeding through hydrogen detachment from the carbon atom at the hydroxyl group (see Fig. 2) was found. The complex IM_6 is unstable and transforms almost without any barrier through the transition state TS_5 (see Fig. 3) into the major product phenylacetaldehyde, H_2 and initial cluster:



So, this route is preferable.

CONCLUSION

To refine the detailed mechanism of the catalytic oxidation of phenylethanol on gold nanoparticles and to assess the effect of atoms with low coordination number, quantum chemical simulation of phenylethanol and its subsequent transformation into phenylacetaldehyde on the tetrahedral cluster Au_{20} has been carried out by the density functional method. According to calculation results, the alcohol is adsorbed on gold atoms with low coordination numbers, at the tops or edges of the cluster. Further dissociation of the O–H bond requires surpassing the high activation barrier, which becomes lower if the process takes place at the cluster edge. An alternative mechanism leading to the formation of phenylacetaldehyde through sequential dehydrogenation of the carbon atom at the carboxyl group has been found. It is noteworthy that this route also requires passing over the high activation barrier. Possible decrease in activation energy can be achieved using bimetallic catalysts or forming cation or anion centres on gold clusters. Future quantum chemical studies are planned to determine the effect of charge and heteroatom on the

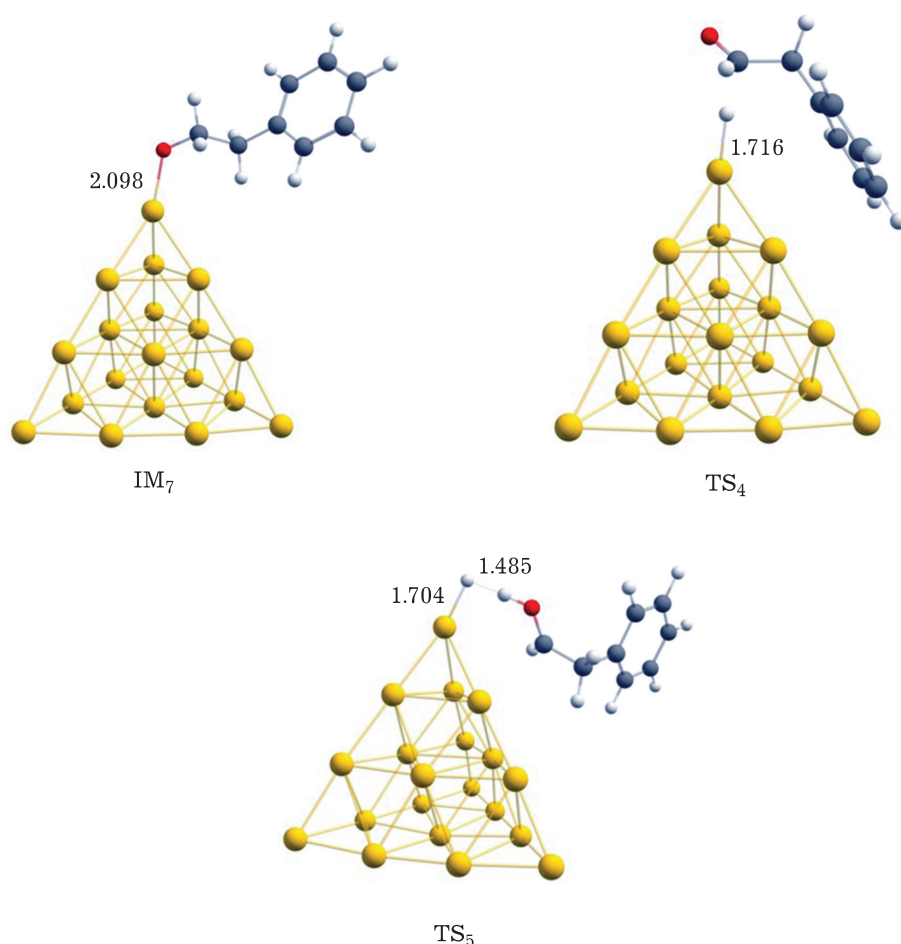


Fig. 3. Optimised structures of the complex $\text{Au}_{20}\text{-PhCH}_2\text{CH}_2\text{O}$ (IM_7), the transition state of its dehydrogenation (TS_4) and dehydrogenation of the intermediate complex IM_6 . For designations, see Fig. 1.

catalytic activity of gold nanoparticles in the oxidation of phenylethanol.

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