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纳米团簇 Au_{19}Pd 和 Au_{19}Pt 催化解离 N_2O 俞炜铃¹ 左会文¹ 陆春海^{2,*} 李 奕¹ 章永凡¹ 陈文凯^{1,*}¹福州大学化学系, 福州 350116; ²成都理工大学核技术与自动化工程学院, 成都 610059

摘要: 采用密度泛函理论研究 Au-Pd 和 Au-Pt 纳米团簇催化解离 N_2O . 首先根据计算得到 Au_{19}Pd 和 Au_{19}Pt 团簇的最优构型(杂原子均位于团簇的表面). 以 Au_{19}Pd 催化解离 N_2O 为例研究催化解离的反应机理. 对此主要考虑两个反应机理, 分别是 Eley-Rideal (ER) 和 Langmuir-Hinshelwood (LH). 第一个机理中 N_2O 解离的能垒是 1.118 eV, 并且放热 0.371 eV. N_2 分子脱附后, 表面剩余的氧原子沿着 ER 路径消除需要克服的能垒是 1.920 eV, 这比反应沿着 LH 路径的能垒高 0.251 eV. 此外根据 LH 机理, 氧原子在表面的吸附能是 -3.203 eV, 而氧原子在表面转移所需的能垒是 0.113 eV, 这表明氧原子十分容易在团簇表面转移, 从而促进氧气分子的生成. 因此, LH 为最优反应路径. 为了比较 Au_{19}Pd 和 Au_{19}Pt 对 N_2O 解离的活性, 根据最优的反应路径来研究 Au_{19}Pt 催化解离 N_2O , 得到作为铂族元素的铂和钯对 N_2O 的解离有催化活性, 尤其是钯. 同时, 将团簇与文献中的 Au-Pd 合金相比较, 得到这两种团簇对 N_2O 解离有较高的活性, 尤其是 Au_{19}Pd 团簇. 再者, O_2 的脱附不再是影响反应的主要原因, 这可以进一步提高团簇解离 N_2O 的活性.

关键词: 纳米团簇; 催化活性; N_2O 解离; 反应机理

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Nitrous Oxide Decomposition Catalyzed by Au_{19}Pd and Au_{19}Pt ClustersYU Wei-Ling¹ ZUO Hui-Wen¹ LU Chun-Hai^{2,*} LI Yi¹
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Abstract: The catalytic decomposition of N_2O using Au_{19}Pd and Au_{19}Pt clusters as catalysts with optimized geometries was studied using density functional theory (DFT). The optimized geometries of the Au_{19}Pd and Au_{19}Pt clusters were obtained as a function of structural and thermodynamic analyses, in which the heteroatoms are on the surfaces of the clusters. We selected the Au_{19}Pd cluster as a model cluster to investigate the reaction mechanism of N_2O decomposition. There are two reaction pathways to be considered: Eley-Rideal (ER) and Langmuir-Hinshelwood (LH). We found that the first N_2O decomposition needs to surmount an energy barrier of 1.118 eV, and is exothermic by 0.371 eV. The elimination of the residual oxygen atom on the surface has an energy barrier of 1.920 eV along the ER pathway after N_2 desorption, which is higher than that along the LH channel (1.669 eV). The adsorption energy of the oxygen atom on the surface is -3.203 eV, and the oxygen atom diffusion on the surface needs to surmount an energy barrier of 0.113 eV along the LH pathway. This indicates that the oxygen atom is prone to transfer on the cluster to promote the generation of the O_2 molecule, and therefore the LH is the optimized reaction pathway. We investigated the catalytic activity of Au_{19}Pt for N_2O decomposition along the LH pathway in comparison with the Au_{19}Pd cluster. Both platinum and palladium have

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catalytic activities for N_2O decomposition, especially the palladium in this study. Comparison between this work and the theoretical study on periodic systems shows that these two clusters can be used as better catalysts for N_2O decomposition, especially the Au_{19}Pd cluster. Furthermore, the O_2 desorption is no longer the main barrier to the reaction, which further enhances the catalytic activities of these two clusters for N_2O decomposition.

Key Words: Nanocluster; Catalytic activity; N_2O decomposition; Reaction mechanism

1 Introduction

Recently, metallic nanocluster with unique shape and size exhibits unusual physical and chemical properties. They have many applications in the fields of magnetic, optical, and electronic materials, catalysts, and drug delivery and so on, which have been of great interest and intensely researched.^{1–24} Therefore morphology of nanocluster can control reactivity and selectivity. Furthermore, multimetallic cluster composed of two or more elements possesses activity, selectivity, and stability, in which there exist structural, ligand, or electronic effects.^{25,26} It is found that bimetallic nanoclusters have been particularly attractive because of the improvement of catalytic properties.^{27–30} And also bimetallic catalysts have been investigated to obtain the relationship between the metal structure and catalytic activity.³¹ Note that it is elusive for catalytic origin of gold or gold-based bimetallic catalysts with nanosize because of the lack of understanding on the nanoscale core–surface property correlation. However, it is interesting to find that the gold-based bimetallic materials of nanoscale exhibit synergistic effect, which are the protection from poisonous species adsorption and change for electronic band structure to alter the adsorption ability of surface.

In the magical world of gold clusters, there is a gold cluster containing 20 gold atoms (Au_{20}), which is enough chemical inert and a highly stable cluster with a tetrahedral pyramidal structure *via ab initio* DFT-based calculation^{32–34} and experimental studies like far-infrared vibrational spectroscopy and photoelectron spectroscopy.³³ There is a large energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Au_{20} cluster, which is superior to that of C_{60} to manifest that Au_{20} cluster should be a chemical inert and stable cluster.³⁵ Meanwhile there are some literature on interaction between a pyridine molecule and surface of Au_{20} cluster³⁶ and catalytic activity of Au_{20} cluster with an anion to CO oxidation,³⁷ which indicate that the Au_{20} cluster is also a good catalyst. Furthermore, multimetallic nanoclusters intimately alloyed are of high interest due to their optical and catalytic properties.^{38–40} In particular, these bimetallic gold clusters have more widely catalytic applications. And also some literature has reported the electronic properties and geometries of gold clusters with the doped transition metal or alkali atoms.^{41–52}

The Au-Pd bimetallic alloys have been widely used as catalysts because of their superior catalytic activities in many reactions,^{24,53–70} like selective oxidation for alcohols,^{62–67} synthesis for vinyl acetate,^{60,61} direct synthesis for H_2O_2 on the surface of the Au-Pd bimetallic alloy,^{53–59} selective oxidation for alkene,⁶⁸ generating benzene *via* coupling acetylene,²⁴ and oxidation for primary carbon-hydrogen

bond.⁶⁹ And also palladium serves as a catalyst for CO oxidation and Suzuki reaction in the form of monometal and bimetal.^{71–73} Moreover, the platinum has many applications including CO/ NO_x oxidation, syngas reformation, and petroleum refinement as an excellent catalysts. The catalytic activities of Au-Pt nanoparticles are superior to those nanoclusters containing gold or platinum alone, which is indicated by recent theoretical studies.⁷⁴ Therefore Pt-doped gold clusters have attracted the special attention because of many potential applications in catalysis.⁷⁵

Furthermore, the catalytic decomposition of nitrous oxide has been attracting much attention to propulsion systems for satellites⁷⁶ and environmental protection.⁷⁷ Meanwhile, Rh-,^{78–88} Ir-,^{76,89–91} and Pd-supported catalysts^{78–88} viewed as platinum group metal catalysts possess effective catalytic activities for this reaction. However, the platinum group metals have the strong adsorption toward oxygen. It is cumbersome for desorption of the oxygen molecule on the metal surface, which is usually viewed as a rate-determining step in the process of N_2O decomposition,^{92–95} while desorption of O_2 on the gold can be more easily.⁹⁶ And also the recent study presents that the presence of gold could have no obvious influence on the catalytic activity of platinum in any significant way.⁹⁷

Therefore the single gold atom on the cluster can be substituted with the palladium or platinum atom in the Au_{20} cluster. To investigate the catalytic activities of the doped gold clusters for N_2O decomposition, we have studied the reaction mechanism of N_2O dissociation on the cluster. Note that the mechanisms of the nitrous oxide dissociation on the surface of metal cluster have been simply indicated as follows:^{98,99}

Here, the step 1 means that nitrous oxide on the active site of the cluster decomposes to generate N_2 molecule leaving from the cluster and oxygen atom on the cluster. Step 2 presents the two adjacent oxygen atoms on the surface close to each other and then are desorbed by oxygen molecule. $\text{O}(\text{a})$ means the oxygen atom on the catalyst. Both of the step 1 and step 2 would be described by the LH mechanism. Meanwhile the step 3 shows the oxygen atom adsorbed on the cluster is removed by the ER mechanism.¹⁰⁰ Dandl and Emig¹⁰¹ presented that the ER mechanism could be more inclined at the lower temperature while the LH mechanism might be more inclined at the higher temperature according to the kinetics simulation.

In the present work, we want to obtain the most optimized geometries *via* structural and thermodynamic analyses in order

to investigate their catalytic activities for N₂O decomposition. There are two reaction pathways for N₂O decomposition on the cluster to be considered: ER and LH, respectively. And we select Au₁₉Pd cluster as a model cluster to investigate the reaction mechanism *via* DFT-based calculation. The catalytic activity of the Au₁₉Pt cluster for N₂O decomposition has been studied in comparison with the Au₁₉Pd as a function of the optimized reaction channel, which indicates how the different heteroatom located at the same site on the cluster influences the activity of the cluster in this reaction. Finally, comparison between this work and the study on the periodic systems presents the influence of the geometry on the catalytic activity of the cluster in this reaction.

2 Computational method

To investigate catalytic activities of Au₁₉Pd and Au₁₉Pt clusters for N₂O molecule decomposition, the program package Dmol³ of Materials Studio of Accelrys Inc has been performed to optimize geometries and search transition states. Generalized gradient approximation (GGA) with exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE) was performed. The DFT semicore pseudopotential was employed for core electrons of gold, palladium, and platinum atoms, but the N and O atoms were treated with all-electron basis set. Meanwhile the double-numerical basis with polarization functions (DNP) has also been employed in the calculation. The Fermi smearing method for a window size was set as 0.005 hartree, and it was 0.45 nm for orbital cutoff range. The energy, maximum displacement, and maximum force for convergence tolerance were 10⁻⁵ hartree, 0.0005 nm, and 0.02 hartree·nm⁻¹, respectively. Every atom of the cluster was relaxed in the calculation. The transition states were determined by the complete linear synchronous transit and quadratic synchronous transit methods. Every transition state struc-

ture has a single imaginary frequency, which corresponds to the reaction pathway.

In order to investigate and compare the stability between Au₁₉Pd and Au₁₉Pt clusters, we have calculated the bind energy (BE) and the interaction energy (IE) of the heteroatom with the Au₁₉ cluster.

The bind energy for Au₁₉Pd or Au₁₉Pt cluster was calculated *via*

$$BE = E(\text{Au}_{19}\text{Pd}/\text{Au}_{19}\text{Pt}) - 19E(\text{Au}) - E(\text{Pd}/\text{Pt}) \quad (4)$$

Meanwhile the interaction energy of the heteroatom with the Au₁₉ cluster was obtained by performing

$$IE = E(\text{Au}_{19}\text{Pd}/\text{Au}_{19}\text{Pt}) - E(\text{Au}_{19}) - E(\text{Pd}/\text{Pt}) \quad (5)$$

Here, $E(\text{Au}_{19}\text{Pd}/\text{Au}_{19}\text{Pt})$, $E(\text{Au})$, $E(\text{Pd}/\text{Pt})$, and $E(\text{Au}_{19})$ mean the energies for Au₁₉Pd or Au₁₉Pt, gold atom, palladium or platinum atom, and Au₁₉ clusters, respectively.

And then we calculated adsorption energy using following equation

$$E_{\text{ads}} = E_{\text{system}} - (E_{\text{cluster}} + E_{\text{adsorbate}}) \quad (6)$$

where E_{ads} is the adsorption energy for the system, E_{system} means the total energy of the substrate and adsorbate, the E_{cluster} and $E_{\text{adsorbate}}$ present the energies of cluster and adsorbate, respectively.

3 Result and discussions

3.1 Investigation for structural properties of the Au₁₉Pd and Au₁₉Pt clusters

The heteroatom can be on the vertex (V), edge (E), or surface (S) of the cluster, as shown in Fig.1. It is noted that the radii of palladium and platinum atoms are 0.137 and 0.139 nm, respectively, which are close to the radius of gold atom, 0.144 nm. Fig.1 presents that there is no obvious deformation for the geometries of Au₁₉Pd and Au₁₉Pt clusters in comparison with the Au₂₀ cluster with a tetrahedral structure after optimization. Furthermore, we have calculated the bond distances between the heteroatom and

Fig.1 Optimized geometries of Au₁₉Pd and Au₁₉Pt clusters with heteroatom located at (a) vertex (V), (b) edge (E), and (c) surface (S)

the nearest adjacent gold atom. And also we have obtained the corresponding bond distances on the Au_{20} cluster. These bond distances are compiled in Table 1. The letter X means the gold atom on the Au_{20} cluster and heteroatom on the clusters shown in Fig.1, respectively. And also the letter in the bracket in the first column indicates the position of atom on the cluster, in which the E1 and E2 present the gold atom on the edge without and with the heteroatom, respectively. It is found that there is no obvious elongated or shorter for these bond distances, which indicate that the both of the palladium and platinum can not make configurations obvious deformations.

Moreover we have studied the thermodynamic stability of these clusters shown in Fig.1 as functions of the bind energy and interaction energy *via* the DFT-based calculation. These results are compiled in the Table 2. It is noted that the more negative value indicates that the system may be more optimized. Therefore both of the palladium and platinum can make cluster stable *via* thermodynamic analysis. Furthermore, the heteroatom locates at the surface of the cluster to obtain the more optimized geometry, especially the platinum atom, which is also demonstrated by the recent study.¹⁰² It is found that the heteroatom is on the surface of the cluster and surrounded by gold atoms, which is similar to the surface of the $\text{Au}_3\text{Pd}(111)$ alloy in the previous study.¹⁰³ The catalytic activity of the Au-Pd alloy for N_2O decomposition has been investigated *via* DFT-based calculation, in which the palladium atom is also isolated by the gold atoms.¹⁰³ We have investigated catalytic activities of these two clusters with the heteroatom on the surface for N_2O decomposition.

3.2 Investigation for N_2O decomposition on the Au_{19}Pd and Au_{19}Pt clusters

It is found that the platinum group metal (PGM) catalysts are effective for N_2O decomposition.^{82,104–108} Therefore both of the palladium and platinum atoms on the clusters are considered as active sites in this study. The adsorption of N_2O on the cluster is

an elementary step. In the previous study, N_2O is weakly and tiltedly on the active site *via* terminal N atom.^{100,103,109} We have obtained the optimized adsorption geometries for N_2O on the clusters *via* DFT-based calculation, as shown in Fig.2, which are the most stable.

The bond distances of N—N and N—O in the N_2O molecule are 0.1142 and 0.1195 nm before adsorption. They are slightly elongated after N_2O adsorption on the clusters, as shown in Fig.2, indicating that N_2O can be activated. And the adsorption energies for N_2O on the Au_{19}Pd and Au_{19}Pt cluster are -0.176 and -0.087 eV, respectively, suggesting that they may be physical adsorption. Furthermore, it is found that the *d* orbital of heteroatom and *p* orbital of N_2O molecule can play major roles for the adsorption of the N_2O on the active site in this study. Therefore the partial density of states (PDOSs) for the N_2O molecule, Pd and Pt before and after adsorption are obtained, as shown in Fig.3, to better understand the interaction between the N_2O molecule and heteroatom on the surface of the cluster. The *p* orbital of N_2O molecule shifts to the lower energy region and there is a wide range near the HOMO, which overlaps with the *d* orbital of the heteroatom, after adsorption, suggesting the charge transfer between heteroatom and the adsorbate so that it can slightly activate N_2O molecule in the reaction. Moreover the different heteroatom has no obvious influence on the adsorption of the N_2O on the cluster in this study.

Fig.4 presents the first N_2O decomposition on the Au_{19}Pd cluster on the basis of the reaction mechanism. It is found that the adsorption energy is -0.176 eV for N_2O on the Au_{19}Pd cluster, but adsorption energies of N_2O on the Pd(111) and $\text{Au}_3\text{Pd}(111)$ are -0.120 and -0.080 eV, respectively. The energy barrier and the value of reaction energy for the first N_2O decomposition on the Au_{19}Pd cluster are 1.118 and -0.371 eV, respectively, which are larger than those on the Pd(111), but less than those on the $\text{Au}_3\text{Pd}(111)$. And also the imaginary frequency of the transition state in the energy profile is -505.62i cm^{-1} . It is noted that the palladium atom is isolated by gold atoms on surface of the Au_{19}Pd cluster, which is similar to the surface of $\text{Au}_3\text{Pd}(111)$. Therefore we have

Table 1 Bond distances between the X atom and its nearest adjacent gold atoms

Atomic pair	Bond distance/nm		
	Au—Au	Au—Pd	Au—Pt
X(V)—Au(E)	0.2742	0.2678	0.2644
X(E)—Au(E1)	0.2970	0.2878	0.2880
X(E)—Au(E2)	0.2697	0.2700	0.2670
X(E)—Au(S)	0.2837	0.2791	0.2736
X(S)—Au(V)	0.4685	0.4728	0.4729
X(S)—Au(E)	0.2837	0.2815	0.2801

Table 2 Binding energy for every atom and the interaction energy for the gold and heteroatoms with the corresponding Au_{19} clusters

Cluster	BE/eV	IE/eV	Cluster	BE/eV	IE/eV
Au_{20}	-2.237	-3.029			
$\text{Au}_{19}\text{Pd}(\text{S})$	-2.249	-3.984	$\text{Au}_{19}\text{Pt}(\text{S})$	-2.297	-4.823
$\text{Au}_{19}\text{Pd}(\text{E})$	-2.231	-3.279	$\text{Au}_{19}\text{Pt}(\text{E})$	-2.292	-4.570
$\text{Au}_{19}\text{Pd}(\text{V})$	-2.225	-2.788	$\text{Au}_{19}\text{Pt}(\text{V})$	-2.275	-3.667

Fig.2 Optimized structures for the N_2O molecule on the (a) Au_{19}Pd and (b) Au_{19}Pt clusters

The values indicate the bond distances, which are given in nanometer.

Fig.3 Partial density of states (PDOSs) for N₂O, Pd, and Pt before and after adsorption, in which the adsorption systems are as a function of the corresponding configurations in Fig.2

The dashed line represents the Fermi level.

obtained that Pd is the active site in this reaction, but the gold can weaken the catalytic activity of substrate for the first N₂O decomposition in this study. However, the structure of the substrate is changed so that it can improve the catalytic activity. Finally, we have obtained that the Au₁₉Pd cluster has better catalytic activity for the first N₂O decomposition.

Furthermore, the palladium has been substituted with the platinum atom on the surface of the cluster. Then we can compare

catalytic activity between the Au₁₉Pd and Au₁₉Pt clusters for N₂O decomposition. Therefore Fig.5 has been obtained. The adsorption energy of N₂O on the platinum atom on the surface of cluster is -0.087 eV, which is more weakly than that on the Au₁₉Pd cluster with the adsorption energy of -0.176 eV. However, the energy barrier of N₂O decomposition on the cluster is 0.989 eV, which is slightly lower than that on the Au₁₉Pd cluster with the energy barrier of 1.118 eV. The reactions on the

Fig.4 Energy profile for the first N₂O decomposition on the Au₁₉Pd cluster

The bond distances are given in nanometer and the angles are given in degree.

Fig.5 Energy profile for the first N₂O decomposition on the Au₁₉Pt cluster

The bond distances are given in nanometer and the angles are given in degree.

Au_{19}Pt and Au_{19}Pd clusters are exothermic by 0.303 and 0.371 eV, respectively. And also the N_2 desorption energies on these two substrates are 0.258 and 0.110 eV, respectively. Therefore platinum atom possesses effective catalytic activity for the first N_2O decomposition as well as palladium atom on the surface of the cluster. However, N_2O adsorption and N_2 desorption on Au_{19}Pt cluster are more difficult than those on the Au_{19}Pd cluster, which can weaken the catalytic activity of cluster. Thus the Au_{19}Pd has a little bit better catalytic activity than Au_{19}Pt cluster for the first N_2O decomposition. Meanwhile, an atom on the cluster can be changed to enhance the catalytic activity.

There are two reaction pathways to clear residual oxygen atom on the cluster after the first N_2O decomposition and N_2 desorption, which are the ER and LH reaction channels, respectively. The Au_{19}Pd cluster is similar to the Au_{19}Pt cluster for the influence on the reaction pathway. Therefore we can select the Au_{19}Pd as a model to investigate the reaction mechanism after the first N_2O decomposition and N_2 desorption. Fig.6 indicates that the second N_2O on the palladium reacts with the residual oxygen atom to generate N_2 and O_2 molecules along the ER pathway, in which the energy barrier is 1.920 eV and the reaction energy is 0.454 eV. However, the second N_2O can continue decomposing to leave oxygen atom on the cluster. Therefore oxygen atoms on the cluster are removed by the LH pathway, as shown in Figs.7 and 8. The adsorption energies of single oxygen atom and two adjacent oxygen atoms on the cluster are -3.203 and -6.173 eV, respectively, indicating that oxygen is very easily on the heteroatom and these two oxygen atoms are prone to be close to each other. There is a low energy barrier of 0.113 eV and it is endothermic by 0.099 eV in the oxygen atom transferring on the cluster after N_2 desorption,

Fig.6 Energy profile for the elimination of residual oxygen atom on the Au_{19}Pd cluster along the ER reaction pathway

The bond distances are given in nanometer and the angles are given in degree.

suggesting that the surface of the cluster benefits the diffusion of the oxygen atom. It is found that the formation of oxygen molecule has an energy barrier of 1.669 eV and is exothermic by 0.324 eV, which are less difficult than the elimination of the residual oxygen atoms along the ER pathway. Therefore the residual oxygen atoms on the cluster can be more prone to be desorbed by the LH pathway.

It is noted that oxygen atom diffusion on the Pd(111) has an

Fig.7 Energy profile for the diffusion of the oxygen atom on the Au_{19}Pd cluster after N_2 desorption

The bond distances are given in nanometer.

Fig.8 Energy profile for the formation of oxygen molecule on the Au_{19}Pd cluster along the LH reaction pathway

The bond distances are given in nanometer.

Table 3 Comparison of the adsorption energy (E_a), energy barrier (E_b), and reaction energy (ΔE_r) of N₂O decomposition on the Au₁₉Pd and Au₁₉Pt cluster with literature values

Process	Substrate	E_a /eV	E_b /eV	ΔE_r /eV
first N ₂ O decomposition	Au ₁₉ Pd	-0.176	1.118	-0.371
	Pd(111) ^a	-0.120	0.590	-1.450
	Au ₃ Pd(111) ^a	-0.080	1.560	0.410
	Au ₁₉ Pt	-0.087	0.989	-0.303
second N ₂ O decomposition	Au ₁₉ Pd	-0.337	1.920	0.454
oxygen atom diffusion	Au ₁₉ Pd	-3.203	0.113	-0.099
	Pd(111) ^a	-1.390	0.540	0.230
		0.440	0.190	0.410
	Au ₃ Pd(111) ^a	0.030	0.060	-0.120
combination of two adjacent oxygen atoms		-0.090	0.780	0.680
	Au ₁₉ Pt	-3.024	0.201	-0.114
	Au ₁₉ Pd	-6.173	1.669	-0.324
	Pd(111) ^a	-1.870	1.960	0.860
	Au ₃ Pd(111) ^a	1.110	0.500	-1.550
	Au ₁₉ Pt	-6.325	1.385	-0.542

^a These results obtained by Wei *et al.*¹⁰³

energy barrier of 0.540 eV and is endothermic by 0.230 eV, as illustrated in the Table 3. Then the elimination of the residual oxygen atoms on the Pd(111) has an energy barrier of 1.960 eV and is endothermic by 0.860 eV along the LH pathway, which illustrates that the formation of the oxygen molecule on the palladium should be more difficult. Furthermore, Table 3 presents the oxygen atom is more easily transferring on the surface of Au₃Pd (111) and elimination of two adjacent oxygen atoms on the surface has a low energy barrier of 0.500 eV. However, the adsorption energy of two adjacent oxygen atoms is 1.110 eV, indicating that the gold benefits the formation of the oxygen molecule, but hinders the adsorption of the oxygen. Moreover it is interesting to find that O₂ desorption, which used to be thought to be a rate-limiting step, becomes more easily in this study, indicating that the existence of the gold can promote desorption of O₂ molecule to improve the catalytic activity of cluster for N₂O decomposition. Therefore Au₁₉Pd cluster also possesses high catalytic activity in this reaction process, which can promote the adsorption of the oxygen, the formation, and desorption of the oxygen molecule. We have found the importance of the structure of the catalyst in the reaction further.

We have compared catalytic activity between the Au₁₉Pt and Au₁₉Pd clusters for the elimination of oxygen atoms along the LH pathway. Here, Fig.9 presents the transfer of oxygen atom on the Au₁₉Pt cluster surface after N₂ desorption. The adsorption energy of oxygen atom on the surface is -3.024 eV, signifying that the Au₁₉Pt cluster is very favourable for oxygen atom adsorption. Then energy barrier and reaction energy are 0.201 and -0.114 eV for the oxygen atom transferring on the surface, respectively, suggesting that this reaction process is prone to proceed. Then the formation of oxygen molecule on the Au₁₉Pt cluster is shown in Fig.10. The energy barrier for formation of oxygen molecule on the Au₁₉Pt cluster is 1.385 eV, which is 0.284 eV lower than 1.669

Fig.9 Energy profile for the diffusion of the oxygen atom on the Au₁₉Pt cluster after N₂ molecule desorption
The bond distances are given in nanometer.

Fig.10 Energy profile for the formation of oxygen molecule on the Au₁₉Pt cluster along the LH reaction pathway
The bond distances are given in nanometer.

eV on the Au₁₉Pd cluster. And also the reaction energy is -0.542 eV, which is 0.218 eV lower than -0.324 eV on the Au₁₉Pd cluster. Therefore Au₁₉Pt cluster has higher activity than Au₁₉Pd cluster in this reaction process. However, O₂ desorption energy on the Au₁₉Pt cluster is 0.603 eV, which is 0.335 eV higher than 0.268 eV on the Au₁₉Pd cluster so that it can weaken the activity of the Au₁₉Pt cluster. Finally, it has obtained that they have similar activity in

this reaction process.

4 Conclusions

In summary, the heteroatom is located at the surface of the cluster to obtain more optimized configuration on the basis of the structural and thermodynamic analyses *via* DFT-based calculation. And also it is found that the LH is a superior reaction pathway for N₂O decomposition on the Au₁₉Pd and Au₁₉Pt clusters. The palladium has effective activity for N₂O decomposition, but hinders the formation and desorption of the oxygen molecule in comparison with the investigation of the N₂O dissociation on the Pd (111) *via* DFT-based calculation, which weakens the catalytic activity. Gold on the Au₃Pd(111) promotes the formation of oxygen molecule on the surface, but makes the adsorption of the oxygen atoms become more difficult, which obviously lowers the activity of the catalyst. In this study, bimetallic clusters with the heteroatoms on the surfaces have high catalytic activities in a complete process of N₂O decomposition and improve the O₂ desorption, which used to be thought to be a rate-limiting step, especially for Au₁₉Pd cluster. Therefore the change of the geometry and the single atom on the cluster can present different activities. Finally, it is hoped that these could provide clue for further explanation on the influence of the geometry for catalytic activity.

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