

## THEORETICAL STUDY ON THE CATALYTIC REDUCTION MECHANISM OF NO BY CO ON Ag7Au6 CLUSTER



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## A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE MAJOR IN CHEMISTRY FACULTY OF SCIENCE UBON RATCHATHANI UNIVERSITY ACADEMIC YEAR 2016 COPYRIGHT OF UBON RATCHATHANI UNIVERSITY



## UBON RATCHATHANI UNIVERSITY THESIS APPROVAL MASTER OF SCIENCE MAJOR IN CHEMISTRY FACULTY OF SCIENCE

## TITLE THEORETICAL STUDY ON THE CATALYTIC REDUCTION MECHANISM OF NO BY CO ON Ag7Au6 CLUSTER

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Yuithana riongnongwa Yutthana Wongnongwa Researcher

#### บทคัดย่อ

 เรื่อง : การศึกษาเชิงทฤษฎีเกี่ยวกับกลไกการเกิดปฏิกิริยารีดักขั้นของในตริกออกไซด์ (NO) โดยใช้ คาร์บอนมอนนอกไซด์ (CO) บนตัวเร่งปฏิกิริยาคลัสเตอร์ชนิด Ag<sub>7</sub>Au<sub>6</sub>
 ผู้วิจัย : ยุทธนา วงษ์หนองหว้า

ชื่อปริญญา : วิทยาศาสตรมหาบัณฑิต

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คำสำคัญ

 คลัสเตอร์ชนิด Ag<sub>7</sub>Au<sub>6</sub>, ปฏิกิริยารีดักซันของไนตริกออกไซด์โดยใช้คาร์บอน มอนนอกไซด์, ทฤษฎีเด็นซิตี้ฟังก์ชันแนล

การศึกษาเชิงทฤษฎีของการใช้คลัสเตอร์ชนิด Ag<sub>7</sub>Au<sub>6</sub> เป็นตัวเร่งปฏิกิริยาสำหรับปฏิกิริยารีดักขัน ของ NO โดยใช้ CO ปฏิกิริยานี้ถูกแบ่งออกเป็นสองขั้นตอน ขั้นตอนแรกคือการเกิดดีออกซิจีเนชันของ NO เพื่อสร้างโมเลกุล N<sub>2</sub>O และขั้นตอนที่สองคือการเกิดดีออกซิจีเนชันของ N<sub>2</sub>O โดยใช้ CO เพื่อสร้าง โมเลกุล N<sub>2</sub> และ CO<sub>2</sub> โมเลกุลผลิตภัณฑ์ N<sub>2</sub> และ CO<sub>2</sub> สามารถหลุดออกจากคลัสเตอร์ชนิด Ag<sub>7</sub>Au<sub>6</sub> ได้อย่างง่ายดายดังนั้นจึงสามารถนำคลัสเตอร์ชนิด Ag<sub>7</sub>Au<sub>6</sub> กลับมาใช้ไหม่ได้ พลังงานศักย์พื้นผิวของ สภาวะ doublet และสภาวะ quartet ถูกศึกษา ซึ่งพบว่าปฏิกิริยาทั้งหมดไม่เกิดการซ้อนทับกันของ สภาวะ doublet และสภาวะ quartet จากการศึกษาพบว่าปฏิกิริยาทั้งหมดไม่เกิดการซ้อนทับกันของ สภาวะ doublet และสภาวะ quartet จากการศึกษาขบว่าปฏิกิริยาทั้งหมดไม่เกิดการซ้อนทับกันของ ปฏิกิริยานี้คือการเกิดผ่านผิวหน้าได้ดีกว่าขอบของคลัสเตอร์ชนิด Ag<sub>7</sub>Au<sub>6</sub> ขั้นกำหนดปฏิกิริยาของ ปฏิกิริยานี้คือการเกิดดีออกซิจีเนชันของ NO เพื่อสร้างโมเลกุล N<sub>2</sub>O ซึ่งการเกิดดีออกซิจีเนชันของ NO โดยใช้ CO จะเกิดได้ง่ายกว่าการเกิดดีออกซิจีเนชันของ NO โดยไม่ใช้ CO จากผลการคำนวณแสดงให้ เห็นว่าปฏิกิริยานี้บนกลุ่มอะตอม Ag<sub>7</sub>Au<sub>6</sub> มีความเหมาะสมทั้งอุณหพลศาสตร์และจลนศาสตร์ ดังนั้น กลุ่มอะตอม Ag<sub>7</sub>Au<sub>6</sub> สามารถนำไปใช้เป็นตัวเร่งปฏิกิริยาสำหรับการเปลี่ยนแก็ส NO และ CO ที่มี ความเป็นพิษไปเป็นผลิตภัณฑ์ที่ไม่เป็นอันตรายภายใต้สภาวะมาตรฐาน

#### ABSTRACT

TITLE	:	THEORETICAL STUDY ON THE CATALYTIC REDUCTION
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The potential of  $Ag_7Au_6$  alloy nanocluster to be a catalyst for the reduction of NO by CO has been examined by density functional theory calculations. This reaction is mainly divided into two reaction stages, NO deoxygenation to generate N<sub>2</sub>O and then the deoxygenation of N<sub>2</sub>O with CO to form N<sub>2</sub> and CO<sub>2</sub>. Finally, the product N<sub>2</sub> and CO<sub>2</sub> desorbs easily from the active  $Ag_7Au_6$  site, thus avoiding catalyst poisoning. The potential energy surfaces of the doublet- and quartet-states have been systematically elucidated. There is no spin crossing found for the entire reaction and the results show that the reaction preferably follows the doublet state pathway. The main reaction pathways take place on the facet site rather than the edge site of the  $Ag_7Au_6$  cluster. The crucial reaction step deals with the NO deoxygenation to generate N<sub>2</sub>O catalyzed by  $Ag_7Au_6$  cluster, in which the deoxygenation of NO by CO reaction pathway is kinetically more preferable than that in the absence of CO. The results reveal that this catalysed reaction is both thermodynamically and kinetically favourable. Therefore, the  $Ag_7Au_6$  nanocluster is predicted to be a promising and highly active catalyst for conversion of CO and NO pollutants to non-harmful products under ambient conditions.

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## LIST OF ABBREVIATIONS

#### ABBREVIATION

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## DEFINITION

DFT	density functional theory
GGA	gradient approximation
НОМО	highest occupied molecular orbitals
LDA	local density approximation
LUMO	lowest unoccupied molecular orbitals
XC	exchange-correlation
HEG	homogeneous electron gas
ECPs	effective core potentials
REPs	relativistic effective potentials
AREP	averaged relativistic effective potential
Ψ	wave function
Ε	energy
Ĥ	hamiltonian operator
ρ	electron density
Т	kinetic energy
ν	exchange-correlation potential
f	oscillator strengths

## CHAPTER 1 INTRODUCTION

#### 1.1 Nitric oxide (NO)

Nitric oxide (nitrogen oxide, nitrogen monoxide) is a molecular, chemical compound with chemical formula of NO. One of several oxides of nitrogen, it is a colorless gas under standard conditions. Nitric oxide is a free radical i.e., its bonding structure includes an unpaired electron, [1] represented by the dot ( $\cdot$ ) on the nitrogen atom and it is in the class of heteronuclear diatomic molecules that are of historic theoretical interest. It is a particularly important intermediate in the chemical industry.

#### 1.1.1 The sources of nitric oxide

The main sources of nitrogen oxides emissions (including nitric oxide) are combustion processes. Fossil fuel power stations, motor vehicles and domestic combustion appliances emit nitrogen oxides, mostly in the form of nitric oxide. The chemical is used occupationally in the bleaching of rayon and in the manufacture of nitric acid. Nitric oxide can be present at significant concentrations in ambient and indoor air. It is used medically by inhalation to produce selective pulmonary vasodilation and to improve oxygenation in patients with various forms of pulmonary hypertension.

#### 1.1.2 The toxicity of nitric oxide

Nitric oxide is a gas; therefore, absorption can only occur through the eyes and lungs. However, it will have contact effects with the skin. In the presence of moisture and oxygen, corrosive conditions will develop as a result of the formation of nitric and nitrous acids. The major proportion of inhaled nitric oxide reaches the deeper parts of the lung and reacts with hemoglobin in erythrocytes to form nitrosylhemoglobin which is converted immediately to nitrite and nitrate. [2] The nitrite and nitrate are then transferred to the serum, and the greater part of the nitrate is excreted into the urine through the kidneys. Most of the inhaled nitric oxide is eventually eliminated from the body as nitrate

#### 1.2 Carbon monoxide (CO)

Carbon monoxide (CO) is a colorless, odorless, and tasteless gas that is slightly less dense than air. It is toxic to hemoglobic animals (both invertebrate and vertebrate, including humans) when encountered in concentrations above about 35 ppm, although it is also produced in normal animal metabolism in low quantities, and is thought to have some normal biological functions. In the atmosphere, it is spatially variable and short lived, having a role in the formation of ground-level ozone. Carbon monoxide consists of one carbon atom and one oxygen atom, connected by a triple bond that consists of two covalent bonds as well as one dative covalent bond. It is the simplest oxocarbon and is isoelectronic with the cyanide anion, the nitrosonium cation and molecular nitrogen. In coordination complexes the carbon monoxide ligand is called carbonyl.

#### 1.2.1 The sources of carbon monoxide

Carbon monoxide is produced from the partial oxidation of carboncontaining compounds; it forms when there is not enough oxygen to produce carbon dioxide (CO<sub>2</sub>), such as when operating a stove or an internal combustion engine in an enclosed space. In the presence of oxygen, including atmospheric concentrations, carbon monoxide burns with a blue flame, producing carbon dioxide. [3] Coal gas, which was widely used before the 1960s for domestic lighting, cooking, and heating, had carbon monoxide as a significant fuel constituent. Some processes in modern technology, such as iron smelting, still produce carbon monoxide as a byproduct. [4]

Worldwide, the largest source of carbon monoxide is natural in origin, due to photochemical reactions in the troposphere that generate about  $5 \times 10^{12}$  kilograms per year. [5] Other natural sources of CO include volcanoes, forest fires, and other forms of combustion.

In biology, carbon monoxide is naturally produced by the action of heme oxygenase 1 and 2 on the heme from hemoglobin breakdown. This process produces a certain amount of carboxyhemoglobin in normal persons, even if they do not breathe any carbon monoxide. Following the first report that carbon monoxide is a normal neurotransmitter in 1993, [6] as well as one of three gases that naturally modulate inflammatory responses in the body (the other two being nitric oxide and hydrogen sulfide), carbon monoxide has received a great deal of clinical attention as a biological regulator. In many tissues, all three gases are known to act as anti-inflammatories, vasodilators, and promoters of neovascular growth. [7] Clinical trials of small amounts of carbon monoxide as a drug are ongoing. Too much carbon monoxide causes carbon monoxide poisoning.

#### 1.2.2 The toxicity of carbon monoxide

Carbon monoxide poisoning is the most common type of fatal air poisoning in many countries. [8] Carbon monoxide is colorless, odorless, and tasteless, but highly toxic. It combines with hemoglobin to produce carboxyhemoglobin, which usurps the space in hemoglobin that normally carries oxygen, but is ineffective for delivering oxygen to bodily tissues. Concentrations as low as 667 ppm may cause up to 50% of the body's hemoglobin to convert to carboxyhemoglobin. [9] A level of 50% carboxyhemoglobin may result in seizure, coma, and fatality. In the United States, the OSHA limits long-term workplace exposure levels above 50 ppm.

The most common symptoms of carbon monoxide poisoning may resemble other types of poisonings and infections, including symptoms such as headache, nausea, vomiting, dizziness, fatigue, and a feeling of weakness. Affected families often believe they are victims of food poisoning. Infants may be irritable and feed poorly. Neurological signs include confusion, disorientation, visual disturbance, syncope (fainting), and seizures. [10]

Some descriptions of carbon monoxide poisoning include retinal hemorrhages, and an abnormal cherry-red blood hue. [11] In most clinical diagnoses these signs are seldom noticed. [10] One difficulty with the usefulness of this cherryred effect is that it corrects, or masks, what would otherwise be an unhealthy appearance, since the chief effect of removing deoxygenated hemoglobin is to make an asphyxiated person appear more normal, or a dead person appear more lifelike, similar to the effect of red colorants in embalming fluid. The "false" or unphysiologic red-coloring effect in anoxic CO-poisoned tissue is related to the meat-coloring commercial use of carbon monoxide, discussed below.

Carbon monoxide also binds to other molecules such as myoglobin and mitochondrial cytochrome oxidase. Exposures to carbon monoxide may cause significant damage to the heart and central nervous system, especially to the globus pallidus, [12] often with long-term chronic pathological conditions. Carbon monoxide may have severe adverse effects on the fetus of a pregnant woman. [13]

#### 1.3 The conventional methods for removal of NO and CO

#### 1.3.1 The reduction of NO by CO

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The reduction of NO by CO, which is of great practical importance with respect to automotive exhaust gas catalysis, can be catalyzed by many transition metals. [14-16] Emission of these pollutants is highly undesirable due to its high toxicity and other harmful effects such as acidifying the environment forming smog and impairing human health. [17, 18] The problems caused by emission of those pollutants urged us to develop methods to protect the environment from being polluted by CO and NO in the automobile exhaust gas. [19]

#### 1.3.2 The catalyst for NO reduction by CO

Bimetallic nanoclusters (also called "nanoalloys" [20]) are of theoretical interest because of their unique electronic and geometric properties. They are also of interest for their potential applications in catalysis, [21, 22] optics, [23, 24] nanoelectronics, [25] and sensing. [26] In particular, silver-gold (Ag-Au) clusters have been investigated extensively by both computation and experiment. [27-29] The unique physicochemical properties of these nanoclusters depend on their shape, structure, surface segregation, and their alloying extent or atomic distribution. The adsorption of small gas molecules on nanoclusters has also been investigated in theoretical and experimental studies. [30, 31] Experimental investigations reveal that CO adsorption on  $Au_nAg_m$  (n = 10-45, m = 0, 1, 2) clusters at 140 K is greatest for closed electronic shell systems. [32] A combined experimental and theoretical study by Neumaier et al. investigated the preferable adsorption sites of CO on Au<sub>n</sub>Ag<sub>m</sub> (n + m < 7) clusters at low-pressure. [33] They determined that CO preferentially binds to an Au atom on the cluster surface, that Au-CO bond strength decreases with increasing cluster size, and that that the maximum number of adsorbed CO molecules strongly depends on cluster charge and composition. [34]

Recently, a 13-atom nanoalloy Ag<sub>7</sub>Au<sub>6</sub> cluster was experimentally synthesized from silver clusters by a galvanic exchange reaction. [35] This alloy cluster exhibits room temperature luminescence, and is of particular interest because it has a number of closed-shell high-symmetry "magic" structures that are precursors of larger, stable structures with high symmetry. [36] The use of this alloy cluster for theoretical chemisorption studies was suggested for the first time by Yongliang et al. [37] Using density functional theory (DFT) calculations, they reported that the CO, HCN, and NO molecules can chemisorb to the Ag<sub>7</sub>Au<sub>6</sub> cluster with exothermic adsorption energies in the range -0.474 to -1.039 eV. It was additionally predicted that that the conductivity of Ag<sub>7</sub>Au<sub>6</sub> alloy clusters is extremely sensitive to CO and NO adsorption, and hence these clusters may hold promise as potential sensors for CO and NO gases.

Despite many contributions from experimental and theoretical studies, the elementary reaction steps for reaction of NO with CO on the Ag<sub>7</sub>Au<sub>6</sub> cluster have not yet been elucidated. Thus, a description of detailed reaction mechanisms at the atomic level is needed. On the basis of previous work, herein we present the results of DFT calculations performed to investigate the reaction mechanisms of NO reduction by CO over the Ag<sub>7</sub>Au<sub>6</sub> cluster.

#### 1.4 Computational chemistry

#### 1.4.1 Density functional theory

Density functional theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. Using this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry.

DFT has been very popular for calculations in solid-state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. Computational costs are relatively low when compared to traditional methods, such as exchange only Hartree–Fock theory and its descendants that include electron correlation.

Despite recent improvements, there are still difficulties in using density functional theory to properly describe intermolecular interactions (of critical importance to understanding chemical reactions), especially van der Waals forces (dispersion); charge transfer excitations; transition states, global potential energy surfaces, dopant interactions and some other strongly correlated systems; and in calculations of the band gap and ferromagnetism in semiconductors. [38] Its incomplete treatment of dispersion can adversely affect the accuracy of DFT (at least when used alone and uncorrected) in the treatment of systems which are dominated by dispersion (e.g. interacting noble gas atoms) [39] or where dispersion competes significantly with other effects (e.g. in biomolecules). [40] The development of new DFT methods designed to overcome this problem, by alterations to the functional [41] or by the inclusion of additive terms, [42-44] is a current research topic.

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In physics and quantum chemistry, specifically density functional theory, the Kohn–Sham equation is the Schrödinger equation of a fictitious system (the "Kohn–Sham system") of non-interacting particles (typically electrons) that generate the same density as any given system of interacting particles. [45, 46] The Kohn–Sham equation is defined by a local effective (fictitious) external potential in which the non-interacting particles move, typically denoted as  $v_s(r)$  or  $v_{eff}(r)$ , called the Kohn–Sham potential. As the particles in the Kohn–Sham system are non-interacting fermions, the Kohn–Sham wavefunction is a single Slater determinant constructed from a set of orbitals that are the lowest energy solutions to

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(r)\right)\phi_i(r) = \varepsilon_i\phi_i(r)$$
(1.1)

This eigenvalue equation is the typical representation of the Kohn–Sham equations. Here,  $\varepsilon_i$  is the orbital energy of the corresponding Kohn–Sham orbital,  $\phi_i$ , and the density for an N-particle system is

$$\rho(r) = \sum_{i}^{N} |\phi_{i}(r)|^{2}$$
(1.2)

In Kohn-Sham density functional theory, the total energy of a system is expressed as a functional of the charge density as

$$E[\rho] = T_s[\rho] + \int dr v_{ext}(r)\rho(r) + E_H[\rho] + E_{xc}[\rho]$$
(1.3)

where  $T_s$  is the Kohn–Sham kinetic energy which is expressed in terms of the Kohn– Sham orbitals as,

$$T_s[\rho] = \sum_{i=1}^{N} \int dr \phi_i^*(r) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(r)$$
(1.4)

 $v_{ext}$  is the external potential acting on the interacting system (at minimum, for a molecular system, the electron-nuclei interaction),  $E_H$  is the Hartree (or Coulomb) energy,

$$E_{H} = \frac{e^{2}}{2} \int dr \int dr' \frac{\rho(r)\rho(r')}{|r-r'|}$$
(1.5)

and  $E_{xc}$  is the exchange-correlation energy. The Kohn–Sham equations are found by varying the total energy expression with respect to a set of orbitals, subject to constraints on those orbitals, to yield the Kohn–Sham potential as

$$v_{eff}(r) = v_{ext}(r) + e^{2} \int \frac{\rho(r')}{|r-r'|} dr' + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$
(1.6)

where the last term

4

$$\nu_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \tag{1.7}$$

is the exchange-correlation potential. This term, and the corresponding energy expression, are the only unknowns in the Kohn–Sham approach to density functional theory. An approximation that does not vary the orbitals is Harris functional theory.

#### **1.4.2 Functionals**

1.4.2.1 The local density approximation

Local-density approximations (LDA) are a class of approximations to the exchange–correlation (XC) energy functional in density functional theory (DFT) that depend solely upon the value of the electronic density at each point in space (and not, for example, derivatives of the density or the Kohn–Sham orbitals). Many approaches can yield local approximations to the XC energy. However, overwhelmingly successful local approximations are those that have been derived from the homogeneous electron gas (HEG) model. In this regard, LDA is generally synonymous with functionals based on the HEG approximation, which are then applied to realistic systems (molecules and solids). In general, for a spin-unpolarized system, a local-density approximation for the exchange-correlation energy is written as

$$E_{xc}^{LDA}[n] = \int \varepsilon_{xc}(n)n(\vec{r})d^3r \qquad (1.8)$$

where n is the electronic density and  $\varepsilon_{xc}$  is the exchange-correlation energy per particle of a homogeneous electron gas of charge density n. The exchange-correlation energy is decomposed into exchange and correlation terms linearly,

$$E_{xc} = E_x + E_c \tag{1.9}$$

so that separate expressions for  $E_x$  and  $E_c$  are sought. The exchange term takes on a simple analytic form for the HEG. Only limiting expressions for the correlation density are known exactly, leading to numerous different approximations for  $\varepsilon_c$ .

Local-density approximations are important in the construction of more sophisticated approximations to the exchange-correlation energy, such as generalized gradient approximations or hybrid functionals, as a desirable property of any approximate exchange-correlation functional is that it reproduce the exact results of the HEG for non-varying densities. As such, LDA's are often an explicit component of such functionals.

#### 1.4.2.2 Generalized gradient approximation

To correct for this tendency, it is common to expand in terms of the gradient of the density in order to account for the non-homogeneity of the true electron density. This allows for corrections based on the changes in density away from the coordinate. These expansions are referred to as generalized gradient approximations (GGA) [47-49] and have the following form:

$$E_{xc}^{GGA}[n_{\uparrow},n_{\downarrow}] = \int \varepsilon_{xc}(n_{\uparrow},n_{\downarrow},\vec{\nabla}n_{\uparrow},\vec{\nabla}n_{\downarrow})n(\vec{r})d^{3}r \qquad (1.10)$$

Using the latter (GGA), very good results for molecular geometries and ground-state energies have been achieved. One of the most commonly used versions is PBE functional.

#### 1.4.2.3 Hybrid exchange and correlation functional

Hybrid functionals are a class of approximations to the exchange– correlation energy functional in density functional theory (DFT) that incorporate a portion of exact exchange from Hartree–Fock theory with exchange and correlation from other sources (ab initio or empirical). [50] The exact exchange energy functional is expressed in terms of the Kohn–Sham orbitals rather than the density, so is termed an implicit density functional. One of the most commonly used versions is B3LYP, which stands for Becke, 3-parameter, Lee-Yang-Parr.

#### 1.4.3 Basis sets

A basis set in theoretical and computational chemistry is a set of functions (called basis functions) that is used to represent the electronic wave function in the Hartree–Fock method or density-functional theory in order to turn the partial differential equations of the model into algebraic equations suitable for efficient implementation on a computer.

The use of basis sets is equivalent to the use of an approximate resolution of the identity. The single-particle states (molecular orbitals) are then expressed as linear combinations of the basis functions.

The basis set can either be composed of atomic orbitals (yielding the linear combination of atomic orbitals approach), which is the usual choice within the quantum chemistry community, or plane waves which are typically used within the solid state

community. Several types of atomic orbitals can be used: Gaussian-type orbitals, Slatertype orbitals, or numerical atomic orbitals. Out of the three, Gaussian-type orbitals are by far the most often used, as they allow efficient implementations of Post-Hartree– Fock methods.

1.4.3.1 Minimal basis sets

Minimal basis sets contain the minimum number of basis functions needs for each atom, as these examples:

H: 1s

C: 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>

Minimal basis sets use fixed-size atomic-type orbitals. The STO-3G basis set is a minimal basis set. It use three gaussian primitives per basis function, which accounts for the "3G" in its name. "STO" stands for "Slater-type orbitals," and the STO-3G basis set approximates Slater orbitals with guassian functions.

1.4.3.2 Split valence basis sets

The first way that a basis can be made larger is to increase the number of basis functions per atom. Split valence basis sets, such as 3-21G, have two sizes of basis function for each valence orbital. For example, hydrogen and carbon are represented as:

H: 1s, 1s'

C: 1s, 2s, 2s', 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>, 2p<sub>x</sub>', 2p<sub>y</sub>', 2p<sub>z</sub>'

where the primed and unprimed orbitals differ in size. The triple-zeta valence (TZV) basis sets use three sizes of contracted functions for each orbital-type.

1.4.3.3 Polarized basis sets

Split valence basis sets allow orbitals to change size, but not to change shape. Polarized basis sets remove this limitation by adding orbitals with angular momentum beyond what is required for the ground state to the description of each atom. For example, Polarized basis sets add d functions to carbon atoms and f functions to transition metals, and some of them add p functions to hydrogen atoms. So far, the only polarized basis sets we've used is TZVP. Its name indicates that it is the TZV basis sets with polarized functions added to heavy atoms. This basis sets is becoming very common for calculations involving up to medium-sized systems.

#### 1.4.3.4 Diffuse functions

Diffuse functions are large-size versions of s- and p-type functions. They allow orbitals to occupy a larger region of space. Basis sets with diffuse functions are important for systems where electrons are relatively far from the nucleus: molecules with lone pairs, anions, and other systems with significant negative charge, systems in their excited state, systems with low ionization potentials, descriptions of absolute acidities, and so on. The aug-TZVP basis set is the TZVP basis set with diffuse functions added to heavy atoms. [51]

#### 1.4.3.5 Effective core potentials

Effective core potentials (ECPs) are a useful means of replacing the core electrons in a calculation with an effective potential, thereby eliminating the need for the core basis functions, which usually require a large set of Gaussians to describe them. In addition to replacing the core, they may be used to represent relativistic effects, which are largely confined to the core. In this context, both the scalar (spin-free) relativistic effects and spin-orbit (spin-dependent) relativistic effects may be included in effective potentials.

A brief recapitulation of the development of RECPs is given here, following Pacios and Christiansen. The process can be viewed as starting from an atomic Dirac-Hartree-Fock calculation, done in jj coupling, and producing relativistic effective potentials (REPs) for each l and j value,  $U_{lj}^{REP}$ . From these, a local potential is extracted, which for example contains the Coulomb potential of the core electrons balanced by the part of the nuclear attraction which cancels the core electron charge. The residue is expressed in a semi-local form,

$$U^{REP} = U_{LJ}^{REP}(r) + \sum_{l=0}^{L-1} \sum_{j=l-1/2}^{l+1/2} \left[ U_{lj}^{REP}(r) - U_{LJ}^{REP}(r) \right] \sum_{m} \left| ljm \right\rangle \left\langle ljm \right|$$
(1.11)

where L is one larger than the maximum angular momentum in the atom. The scalar potential is obtained by averaging the REPs for each j for a given l to give an averaged relativistic effective potential, or AREP,

$$U_{l}^{AREP}(r) = \frac{1}{2l+1} \left[ l U_{l-1/2}^{REP}(r) + (l+1) U_{l+1/2}^{REP}(r) \right]$$
(1.12)

These are summed into the full potential. The spin-orbit potential is obtained from the difference between the REPs for the two j values for a given l, and may be represented in terms of an effective spin-orbit operator,

$$H^{SO} = s \cdot \sum_{l=1}^{L-1} \frac{2}{2l+1} \Delta U_l^{REP} \sum_{mm'} |lm\rangle \langle lm|\hat{l}|lm'\rangle \langle lm'|$$
(1.13)

Where

$$\Delta U_{l}^{REP} = U_{l+1/2}^{REP}(r) - U_{l-1/2}^{REP}(r)$$
(1.14)

The spin-orbit integrals are the integrals over the sum, including the factor of 2/(2l+1), so that they may be treated as an effective spin-orbit operator without further factors introduced. The effective potentials, both scalar and spin-orbit, are fitted to Gaussians with the form

$$r^{2}U_{l}(r) = \sum_{k} A_{lk} T^{n_{lk}} e^{-B_{lk}T^{2}}$$
(1.15)

where  $A_{lk}$  is the contraction coefficient,  $n_{lk}$  is the exponent of the "r" term (r-exponent), and  $B_{lk}$  is the Gaussian exponent. The  $n_{lk}$  is shifted by 2, in accordance with most of the ECP literature and implementations, i.e., an  $n_{lk} = 0$  implies r<sup>-2</sup>. The current implementation allows  $n_{lk}$  values of only 0, 1, or 2.

The optional directive ECP allows the user to describe an effective core potential (ECP) in terms of contracted Gaussian functions as given above. Potentials using these functions must be specified explicitly by user input in the ECP directive. This directive has essentially the same form and properties as the standard BASIS directive, except for essential differences required for ECPs. Because of this, the ECP is treated internally as a basis set. ECPs are automatically segmented, even if general contractions are input. The projection operators defined in an ECP are spherical by default, so there is no need to include the CARTESIAN or SPHERICAL keyword as there is for a standard basis set. ECPs are associated with centers in geometries through tags or names of centers. These tags must match in the same manner as for basis sets the tags in a GEOMETRY and ECP directives, and are limited to sixteen characters. Each center with the same tag will have the same ECP. By default, the input module prints each ECP that it encounters. The NOPRINT option can be used to disable printing. There can be only one active ECP, even though several may exist in the input deck. The ECP modules load "ecp basis" inputs along with any "ao basis" inputs present. ECPs may be used in both energy and gradient calculations.

ECPs are named in the same fashion as geometries or regular basis sets, with the default name being "ecp basis". It should be clear from the above discussion on geometries and database entries how indirection is supported. All directives that are in common with the standard Gaussian basis set input have the same function and syntax. As for regular basis sets, ECPs may be obtained from the standard library such as Lanl2dz ECP and Stuttgart ECP, respectively

#### 1.5 Aims and scope of thesis

1.5.1 To provide reliable structures and vibration frequencies of the reactants, intermediates, transition states, and products as well as their chemically accurate energetics

1.5.2 To obtain a better understanding of the preference of reaction pathway

1.5.3 To gain a deep insight into the cooperativeness of Ag-Au cluster on the catalytic reduction of NO with CO

1.5.4 To understand the charge effect of  $Ag_7Au_6$  cluster on the catalytic reduction of NO with CO.

## CHAPTER 2 LITERATURE REVIEWS

This chapter surveys the catalysts widely used in NO reduction by CO, especially, the catalysts widely used as metal cluster. Furthermore, the way of the development of Ag<sub>7</sub>Au<sub>6</sub> cluster for NO reduction by CO are reviewed.

#### 2.1 The Catalysts for NO reduction by CO

In 2013, Qian-Qian Xu et al. [52] have investigated the gas-phase reaction mechanism of NO and CO catalyzed by included Rhodium (Rh) atom. This reaction is mainly divided into two reaction stages, NO deoxygenation to generate N<sub>2</sub>O and then the deoxygenation of N<sub>2</sub>O with CO to form N<sub>2</sub> and CO<sub>2</sub>. The crucial reaction step deals with the NO deoxygenation to generate N<sub>2</sub>O catalyzed by Rh atom, in which the selfdeoxygenation of NO reaction pathway is kinetically more preferable than that in the presence of CO. The minimal energy reaction pathway includes the rate-determining step about N-N bond formation. Once the NO deoxygenation with CO catalyzed by Rh atom takes place, the reaction results in the intermediate RhN. Then, the reaction of RhN with CO is kinetically more favorable than that with NO, while both of them are thermodynamically preferable. These results can qualitatively explain the experimental finding of N<sub>2</sub>O, NCO, and CN species in the NO + CO reaction. For the N<sub>2</sub>O deoxygenation with CO catalyzed by Rh atom, the reaction goes facilely forward, which involves the rate-determining step concerning CO<sub>2</sub> formation. CO plays a dominating role in the RhO reduction to regenerate Rh atom. The complexes, OCRhNO, RhON<sub>2</sub>, RhNNO, ORhN<sub>2</sub>, RhCO<sub>2</sub>, RhNCO, and ORhCN, are thermodynamically preferred. However, Rh atom possesses weaker capability for the N<sub>2</sub>O deoxygenation than Rh cluster.

In 2015, Ben-Fang Su et al. [53] have investigated the catalytic reduction of NO by CO on  $Rh_4^+$  clusters. The main reaction pathway includes the following elementary steps: (1) the coadsorption of NO and CO; (2) the recombination of NO and CO

O atoms; (3) the reaction of the N atom with the second adsorbed NO to form  $N_2O$ ; (4) the decomposition of N<sub>2</sub>O to N<sub>2</sub> molecules and O atoms; and (5) the recombination of O atoms and CO to form CO<sub>2</sub>. At low temperatures (300-760 K), the turnover frequency (TOF)-determining transition state (TDTS) is the simultaneous C-O bond formation and N–O bond cleavage, with a rate constant (s<sup>-1</sup>) of  $k_{Ps} = 4.913 \times 1012 \exp(-272,724/RT)$ . The formation of CO<sub>2</sub> should originate in half from the reaction between the adsorbed CO and NO. The presence of CO in some degree decreases the catalytic reduction temperature of NO on the  $Rh_4^+$  clusters. At high temperatures (760–900 K), the TDTS is applied to the N–O bond cleavage, with a rate constant (s<sup>-1</sup>) of  $k_{Pa} = 6.721 \times 10^{15}$ exp(-318,376/RT). The formation of CO<sub>2</sub> should stem solely from the surface reaction between the adsorbed CO and the O atom, the latter originating from NO decomposition. The rate constant ratio as a function of temperature T in the 2NO + 2CO  $\rightarrow$  N<sub>2</sub> + 2CO<sub>2</sub> reaction catalyzed on the Rh4<sup>+</sup> cluster are shown in Figure 2.1. The bridge N<sub>b</sub>Rh4<sup>+</sup> is thermodynamically preferred. Once the bridge N<sub>b</sub>Rh<sub>4</sub><sup>+</sup> is formed, N<sub>2</sub>O- and NCOcontained species are predicted to exist, which is in good agreement with the experimental results.



Figure 2.1 The rate constant ratio as a function of temperature T in the  $2NO + 2CO \rightarrow N_2 + 2CO_2$  reaction catalyzed on the Rh<sub>4</sub><sup>+</sup> cluster.

In 2015, Hua-Qing Yang et al. [54] have investigated the catalytic mechanism of  $2NO + 2CO \rightarrow N_2 + 2CO_2$  on Rh<sub>4</sub> cluster. For the overall reaction of  $2NO + 2CO \rightarrow N_2$ + 2CO<sub>2</sub>, the main reaction pathways take place on the facet site rather than the edge site of the Rh<sub>4</sub> cluster. The turnover frequency (TOF) determining transition states are characteristic of the second N–O bond cleavage with rate constant  $k_4$  = 1.403  $\times$   $10^{11}$ exp(-181,203/RT) and the N-N bond formation for the intermediate N<sub>2</sub>O formation with rate constant  $k_2 = 3.762 \times 10^{12} \exp(-207,817/\text{RT})$ . The TOF-determining intermediates of <sup>3</sup>N<sub>b</sub>Rh<sub>4</sub>NO and <sup>3</sup>N<sub>b</sub>Rh<sub>4</sub>O<sub>b</sub>(NO) are associated with the nitrogen-atom molecular complex, which is in agreement with the experimental observation of surface nitrogen. The branch ratios of  $k_2/(k_2 + k_4)$  and  $k_4/(k_2 + k_4)$  as a function of temperature are shown in Figure 2.2. On the facet site of Rh<sub>4</sub> cluster, the formation of CO<sub>2</sub> stems solely from the recombination of CO and O atom, while N<sub>2</sub> originates partly from the recombination of two N atoms and partly from the decomposition of N<sub>2</sub>O. For the N-O bond cleavage or the synchronous N-O bond cleavage and C-O bond formation, the neutral Rh<sub>4</sub> cluster exhibits better catalytic performance than the cationic Rh<sub>4</sub><sup>+</sup> cluster. Alternatively, for N-N bond formation, the cationic Rh4<sup>+</sup> cluster possesses better catalytic performance than the neutral Rh<sub>4</sub> cluster.



Figure 2.2 The branch ratios of k<sub>2</sub>/(k<sub>2</sub> + k<sub>4</sub>) and k<sub>4</sub>/(k<sub>2</sub> + k<sub>4</sub>) as a function of temperature.

#### 2.2 The development of Ag7Au6 cluster

In 2011, Denisia M. Popolan et al. [34] have investigated the binding energies of carbon monoxide to triatomic silver-gold binary cluster cations and anions. The binding energies of the first CO molecule to the trimer clusters increase with increasing gold content and with changing charge from negative to positive, which are shown in Figure 2.3. Thus, the reactivity of the binary clusters can be sensitively tuned by varying charge state and composition. Also, multiple CO adsorptions on the clusters were investigated. The maximum number of adsorbed CO molecules was found to strongly depend on cluster charge and composition as well. Most interestingly, the cationic carbonyl complex  $Au_3(CO)_4^+$  is formed at cryogenic temperature, whereas for the anion, only two CO molecules in the case of the cations and are completely inert to CO in their experiment in the case of the anions.



Figure 2.3 The binding energies of CO to the cluster trimers as a function of the cluster charge and composition

In 2011, Jorg De Haeck et al. [32] have investigated the reactivity of gold clusters in the gas phase focused on charged, small sized clusters. Here, reactivity measurements in a low-pressure reaction cell were performed to investigate carbon monoxide adsorption on neutral bare and silver doped gold clusters (Au<sub>n</sub>Ag<sub>m</sub>; n = 10-45; m = 0, 1, 2) at 140 K (Figure 2.4). The size dependence of the reaction probabilities reflects the role of the electronic shells for the carbon monoxide adsorption, with closed electronic shell systems being the most reactive. In addition, the cluster's reaction probability is reduced upon substitution of gold atoms for silver. Inclusion of a single silver atom causes significant changes in the reactivity only for a few cluster sizes, whereas there is a more general reduction in the reactivity with two silver atoms in the cluster. The experimental observations are qualitatively explained on the basis of a Blyholder model, which includes dopant induced features such as electron transfer from silver to gold, reduced s-d hybrization, and changes in the cluster geometry.



Figure 2.4 The carbon monoxide adsorption on neutral bare and silver doped gold clusters (Au<sub>n</sub>Ag<sub>m</sub>; n = 10-45; m = 0, 1, 2) at 140 K.

In 2012, Thumu Udayabhaskararao et al. [35] have investigated an alloy cluster containing a 13-atom core, with a composition  $Ag_7Au_6(H_2MSA)_{10}$  (H<sub>2</sub>MSA=mercaptosuccinic acid). The composition  $Ag_7Au_6(H_2MSA)_{10}$  is shown in Figure 2.5, which was synthesized from silver clusters by a galvanic exchange reaction. The clusters were characterized by several spectroscopic and microscopic methods. The alloy cluster shows luminescence with a quantum yield of  $3.5 \times 10^{-2}$  at room temperature. Theoretical calculations for  $Ag_7Au_6(SCH_3)_{10}$  suggest a distorted icosahedral core.



## Figure 2.5 The composition Ag7Au<sub>6</sub>(H<sub>2</sub>MSA)<sub>10</sub> was synthesized from silver clusters by a galvanic exchange reaction.

In 2013, Hector Barron et al. [36] have investigated on structures, electronic and magnetic properties of 13-atom Ag-Au nanoalloys, using spin-polarized ab initio calculations based on density functional theory. To this end, they use all possible chemical configurations of four different initial symmetries as starting structures: icosahedra, decahedra, cuboctahedra, and the buckled biplanar (BBP) cluster (Figure 2.6). Mixing is energetically favored; there is no indication of segregation. They find a general tendency to minimize the number of Au-Au bonds. Many of the clusters undergo strong morphology changes. The resulting structures of lowest energy, independent of the starting geometry, are distorted biplanar clusters. The cuboctahedra are a rather stable local minimum against geometry changes following the introduction of the mixing. All the lowest-energy structures have a Kohn-Sham HOMO-LUMO gap of about 0.2 eV and a total spin of 1 µB. Higher total spin values are found for some of the icosahedra and decahedra, but they have an energy much higher than that of the lowest-energy structures of the respective compositions. The quasi-particle gap is about 3.7 eV across the composition range. It does not vary appreciably with the composition and structural details of the clusters.



Figure 2.6 Excess energy of the LE structures for each starting geometry, referred to the energies per atom of the pure Ag and Au BBP clusters.

In 2015, Yongliang Yong et al. [37] have investigated the Ag–Au bimetallic clusters, which can be theoretically explained by the conductivity change of the clusters induced by the absorption process, to molecules such as CO, H<sub>2</sub>S, and so forth. Recently, a 13-atom alloy quantum cluster (Ag<sub>7</sub>Au<sub>6</sub>) has been experimentally synthesized and characterized. Here, the adsorption of CO, HCN, and NO on the Ag<sub>7</sub>Au<sub>6</sub> cluster (Figure 2.7) was investigated using density functional theory calculations in terms of geometric, energetic, and electronic properties to exploit its potential applications as gas sensors. It is found that the CO, HCN, and NO molecules can be chemisorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster with exothermic adsorption energy ( $-0.474 \sim -1.039$  eV) and can lead to finite charge transfer. The electronic properties of the Ag7Au<sub>6</sub> cluster present dramatic changes after the adsorption of the CO, HCN, and NO molecules, especially its electric conductivity. Thus, the Ag<sub>7</sub>Au<sub>6</sub> cluster is expected to be a promising gas sensor for CO, HCN, and NO detection.



Figure 2.7 The stable configurations of the CO, HCN, and NO molecule adsorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster. Distances are in angstroms. The O atom is red, the C atom is gray, and the N atom is blue.

## CHAPTER 3 METHODOLOGY

#### 3.1 Computational detail

All calculations were carried out with the Gaussian 09 program package. [55] Full geometric optimizations were done to locate all the intermediates and transition state (TS) structures on potential energy surfaces (PES). Since the Ag<sub>7</sub>Au<sub>6</sub> alloy cluster can be stable in both doublet and quartet states, we therefore have systematically investigated the PES in both states. The DFT calculations were performed using the PBE functional with the TZVP basis set being used for carbon, nitrogen, and oxygen atoms, and the LanL2DZ basis set used for gold and silver atoms.Frequency calculations were performed to characterize the obtained stationary points and to take corrections of Gibbs free energy into account under room temperature and atmospheric pressure (300 K and 1 atm). The adsorption, reaction and activation energies provided in the results are included the Gibbs free energy. The TS structures were confirmed by vibrational frequency calculations to ensure that each TS has only one imaginary frequency. The natural population analysis (NPA) charges on atoms and amount of charge transfer between donor and acceptor molecules have been analyzed by natural bond orbital (NBO) analysis.

#### 3.2 The optimized Ag7Au6 cluster structure

Figure 3.1 shows the side view of the optimized Ag<sub>7</sub>Au<sub>6</sub> cluster structure with yellow spheres represent carbon atoms and light blue spheres represent carbon atoms.



Figure 3.1 The side view of the optimized Ag7Au6 cluster structure

The adsorption energy  $(E_{ads})$  of the molecule on the Ag<sub>7</sub>Au<sub>6</sub> cluster is defined as follow:

$$E_{ads} = E_{cluster-molecule} - E_{cluster} - E_{molecule}$$

Where E<sub>cluster-molecule</sub>, E<sub>cluster</sub>, and E<sub>molecule</sub> represent the total energies of the product adsorbed molecule-cluster complex, isolated Ag<sub>7</sub>Au<sub>6</sub> cluster, and isolated molecule, respectively.

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## CHAPTER 4 RESULT AND DISCUSSION

#### 4.1 The Ag7Au6 cluster model

According to a previous study, [37] the Ag<sub>7</sub>Au<sub>6</sub> cluster has six stable isomers. In this work, we chose the most stable one as our catalytic model. This structure (shown in Figure 1a), has C<sub>3v</sub> symmetry and an Au surface-segregated hollow structure. The NBO analysis of Ag<sub>7</sub>Au<sub>6</sub> cluster predicts atomic NPA charges as follow: +0.017e on the edge Au atoms, +0.230e on edge Ag atoms and -0.412e on the center Ag atom. This result indicates that the electron density on the edge Ag and Au atoms transfers to the center Ag atom. The electrophilic and nucleophilic Fukui function indices of Ag7Au6 cluster were then examined to verify the preferable adsorption sites for adsorption of the reactant molecules. The active sites for electrophilic  $(f_A^-)$  and nucleophilic attacks  $(f_A^+)$ were calculated by the equations  $f_A^- = q_N^A - q_{N-1}^A$  and  $f_A^+ = q_{N+1}^A - q_N^A$ , respectively. The values of  $q_N^A$ ,  $q_{N-1}^A$  and  $q_{N+1}^A$  represent NPA charges of various atoms in the Ag<sub>7</sub>Au<sub>6</sub> cluster in neutral, cation, and anion forms, respectively. Relatively large values of  $(f_A^{\mp})$  are indicative of preferred active sites. The results in Table 4.1 show that the Au atoms at the corner (Au1, Au5, Au13) are the active sites for electrophilic attack, while the Ag atoms at the edge (Ag8, Ag6, Ag2) are the active sites for nucleophilic attack. The frontier molecular orbitals, i.e. HOMO and LUMO, are consistent with the results of the Fukui analysis. For the HOMO, the electron density is localized on the corner Au atoms, which suggests that these are active sites for adsorbing electrophile probe molecules (Figure 4.1b). On the other hand, the electron density of the LUMO is localized on the edge Ag atoms (Figure 4.1c). This indicates that these edge Ag atoms are actives site for the adsorption of nucleophilic probe molecules.



Figure 4.1 The structure and frontier molecular orbitals of the Ag7Au6 cluster: (a) the most stable configuration of the Ag7Au6 cluster; (b) HOMO of Ag7Au6 cluster; (c) LUMO of Ag7Au6 cluster. Yellow- and light blueballs represent gold and silver atoms, respectively.

	Table 4.1 The electro	philic and nucleophilic Fukui	function of Ag7Au6 cluster.
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Atoms	Electrophilic properties (e)			Nucleophilic properties (e)		
Atoms	Ag7Au <sub>6</sub> (N)	Ag7Au6 (N-1)	$f_A^-$	Ag7Au6 (N+1)	Ag7Au <sub>6</sub> (N)	$f_A^+$
Au1	0.030	0.138	0.108	-0.048	0.030	0.078
Ag2	0.230	0.247	0.017	0.101	0.230	0.129
Au3	0.017	0.083	0.066	-0.059	0.017	0.076
Ag4	0.230	0.247	0.017	0.104	0.230	0.126
Au5	0.030	0.138	0.108	-0.046	0.030	0.076
Ag6	-0.139	-0.074	0.065	-0.251	-0.139	0.112
Ag7	-0.412	-0.185	0.227	-0.425	-0.412	0.013
Ag8	0.230	0.246	0.016	0.072	0.230	0.158
Ag9	-0.139	-0.072	0.067	-0.141	-0.139	0.002
Au10	0.017	0.083	0.066	-0.034	0.017	0.051
Au11	0.018	0.083	0.065	-0.035	0.018	0.053
Ag12	-0.141	-0.073	0.068	-0.149	-0.141	0.008
Au13	0.030	0.138	0.108	-0.088	0.030	0.118

#### 4.2 Molecular Adsorption

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In the next phase of this study, we investigated the adsorption of CO,  $N_2O$ ,  $CO_2$  and  $N_2$  molecules on the Ag<sub>7</sub>Au<sub>6</sub> cluster. In order to find the most stable configurations of the four molecules adsorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster, the molecules were initially placed on all possible sites of the cluster surface. The optimized structures of the molecule-cluster complexes are displayed in Figure 4.2. The obtained results (such as adsorption energy, the shortest intermolecular distances, and charge transfer between molecule and cluster) are listed in Table 4.2.

First, we considered CO adsorption on the Ag<sub>7</sub>Au<sub>6</sub> cluster. After full relaxation, the CO molecule adopts an orientation in which the C and O atoms point to the Ag and Au atoms of the cluster. Also, the configuration of the CO molecule located on top of an edge Ag atom (CO-a) is the most stable (structure show in Figure 4.2). The calculated adsorption energy for this structure is -50.2 kJ/mol, and the molecule-cluster intermolecular distance is 2.15 Å, indicating that CO is chemisorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster. This result is close to a previous value that was calculated using spin-polarized density functional theory (DFT) implemented in the Dmol<sup>3</sup> program, where the adsorption was reported to be -63.6 kJ/mol. For the most stable structure of the CO molecule binding to an Ag atom in the cluster, we found that a charge of 0.182 e transfers from the CO molecule to the Ag<sub>7</sub>Au<sub>6</sub> cluster is nucleophilic probe molecule. This agrees with the results of our Fukui function index and frontier molecular orbital analyses, which predicted that surface Ag atoms are indeed active sites for the adsorption of nucleophilic probe molecules.

Second, we considered NO adsorption on the  $Ag_7Au_6$  cluster. After full relaxation, the NO molecule adopts an orientation in which the N atom point to the Au atoms, bridge Ag-Au, and bridge Ag-Ag of the cluster. Also, the configuration of the NO molecule located on bridge Ag-Au (NO-b) is the most stable (structure show in Figure 4.2). The calculated adsorption energy for this structure is -54.0 kJ/mol, and the molecule-cluster intermolecular distance is 2.24 Å, indicating that NO is chemisorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster. For the most stable structure of the NO molecule binding to an Ag atom in the cluster, we found that a charge of 0.246 e transfers from the Ag<sub>7</sub>Au<sub>6</sub> cluster is electrophilic probe molecule. This agrees with the results of our Fukui function index and frontier molecular orbital analyses, which predicted that surface Au atoms are indeed active sites for the adsorption of electrophilic probe molecules.

In order to determine the most stable configuration for adsorption of a N<sub>2</sub>O molecule on the Ag<sub>7</sub>Au<sub>6</sub> cluster, various possible initial adsorption geometries were considered. Initial geometries for calculations included those with N and O atoms interacting with different Ag and Au atoms on the cluster surface. The results of our calculations are summarized in Table 4.2, and the final optimized configurations are shown in Figure 4.2. We found that the structure in which the N atom of the N<sub>2</sub>O molecule binds to an Ag atom of the Ag<sub>7</sub>Au<sub>6</sub> cluster (N<sub>2</sub>O-b) is the most stable. The adsorption energy of this structure is -18.0 kJ/mol which is about 5.9 kJ/mol lower than that of the second most stable configuration (N2O-a). It can be seen from Figure 4.2 that the two most stable configurations have slight structural differences, which are mainly reflected on the adsorption side of N2O molecule. For the two most stable configurations, there is a charge transfer of 0.091 e and 0.067 e from the N<sub>2</sub>O molecule to the Ag<sub>7</sub>Au<sub>6</sub> cluster, and the distance between the molecule and cluster is less than 2.8 Å. Although we have considered as many initial structures as possible, we found that the N<sub>2</sub>O molecule does not adsorb to any of the Au atoms in the Ag<sub>7</sub>Au<sub>6</sub> cluster, which indicates that adsorption of the N<sub>2</sub>O molecule on an Au atom, is hence energetically unfavorable. This agrees with the results of our Fukui function index and frontier molecular orbital analyses, which predicted that surface Ag atoms are indeed active sites for the adsorption of nucleophilic probe molecules like N<sub>2</sub>O.

In the next phase of this study, we considered the adsorption of CO<sub>2</sub> and N<sub>2</sub> molecules (i.e., the products of the oxidation of CO by N<sub>2</sub>O) on the Ag<sub>7</sub>Au<sub>6</sub> cluster. The most stable configurations of CO<sub>2</sub> and N<sub>2</sub> molecules adsorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster (CO<sub>2</sub> and N<sub>2</sub>-a) are shown in Figure 4.2, and the relevant results are summarized in Table 4.2. It is found that CO<sub>2</sub> and N<sub>2</sub> are physisorbed on the cluster with adsorption energies of -11.7 and -13.4 kJ/mol, respectively. The charge transfer from CO<sub>2</sub> (or N<sub>2</sub>) to the Ag<sub>7</sub>Au<sub>6</sub> cluster is only 0.056 e (or 0.122 e), which is much smaller than the case of CO adsorption on the Ag<sub>7</sub>Au<sub>6</sub> cluster. Note that all probe molecules transferred electron density to the Ag<sub>7</sub>Au<sub>6</sub> cluster, indicating that the cluster has relative

nucleophilicity. Thus, all probe molecules prefer to adsorb on an Ag atoms at the facet of  $Ag_7Au_6$  cluster.



Figure 4.2 The structures of the CO, NO, N<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub> molecules adsorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster. Distances are in angstroms. The gray-, red- and blue-spheres represent C, O, and N atoms, respectively.

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Table 4.2 Calculated adsorption energy (Eads), shortest distance (d) between the molecule and Ag7Au6 cluster, and amount of charge transfer from molecule to the Ag7Au6 cluster (CT) for the (CO, N2O, CO2, and N2) molecule adsorption on the Ag7Au6 Cluster.

Molecule	Eads (kJ/mol)	d (Å)	Ст (е)
CO-a	-50.2	2.15	0.182
CO-b	-5.9	2.96	0.069
CO-c	-38.9	2.08	0.021
CO-d	-2.1	3.67	0.028
NO-a	-49.8	2.21	-0.086
NO-b	-54.0	2.24	-0.246
NO-c	-35.6	2.41	-0.305
N <sub>2</sub> O-a	-12.1	2.80	0.067
N <sub>2</sub> O-b	-18.0	2.48	0.091
N2 <b>O-c</b>	-4.6	3.20	0.021
CO <sub>2</sub>	-11.7	2.79	0.056
N2-a	-13.4	2.50	0.122
N2-b	-3.3	3.38	0.044

#### 4.3 The NO reduction by CO (2NO + 2CO $\rightarrow$ N<sub>2</sub> + 2CO<sub>2</sub>)

In the case of the Ag<sub>7</sub>Au<sub>6</sub> cluster, the structure optimization with spin multiplicity of 2, 4, and 6 are convergent. Moreover, the structure with multiplicity 2 is more stable than that of multiplicity 4 and 6 by 127.4 and 337.7 kJ/mol, respectively. These results indicate that the reaction is easier to take place on Ag<sub>7</sub>Au<sub>6</sub> cluster with spin multiplicity of 2. Thus, in the present calculations, the two state reactivity were not considered owing to the system size and complexity, which would lead to a prohibitively large number of calculations. As a result, the Ag<sub>7</sub>Au<sub>6</sub> cluster with spin multiplicity 2 was taken into account as the initial catalyst for NO and CO reduction reaction.

Achieving the main reaction in equation of  $2NO + 2CO \rightarrow N_2 + 2CO_2$ , there are two kinds of catalytic cycles. One is through N–O bond cleavage in the absence of CO. Another is through N–O bond cleavage in the presence of CO. Accomplishing the side reaction in equation of NO +  $2CO \rightarrow NCO + CO_2$ , there is a unique reaction pathway, which is composed of Ag<sub>7</sub>Au<sub>6</sub>N + CO  $\rightarrow$  Ag<sub>7</sub>Au<sub>6</sub> + NCO. In this work, we will mainly discuss the following three parts

#### 4.3.1 Through N–O Bond Cleavage in the Absence of CO.

This overall reaction occur via NO reduction without CO, which is divided into three sequent reactions of equation 4.1, 4.2, and 4.3.

$$Ag_7Au_6 + 2NO \rightarrow Ag_7Au_6O + N_2O \tag{4.1}$$

$$Ag_7Au_6 + N_2O \rightarrow Ag_7Au_6O + N_2 \tag{4.2}$$

$$Ag_7Au_6O + CO \rightarrow Ag_7Au_6 + CO_2$$
 (4.3)

Thus, it is necessary to investigate the above three reactions, both thermodynamically and kinetically.

4.3.1.1 N<sub>2</sub>O formation without CO.

The geometric structures and the schematic energy diagrams for reaction 4.1 (Ag<sub>7</sub>Au<sub>6</sub> + 2NO  $\rightarrow$  Ag<sub>7</sub>Au<sub>6</sub>O + N<sub>2</sub>O) are depicted in Figure 4.3a, 4.3b and 4.3c. The reaction 4.1 can be divided into three kinds of reaction pathways, through N-O bond cleavage in the absence of another NO molecule on edge site of Ag<sub>7</sub>Au<sub>6</sub> cluster, through N-O bond cleavage in the presence of another NO molecule on edge site of Ag<sub>7</sub>Au<sub>6</sub> cluster and through N-O bond cleavage in presence of another NO molecule on facet site of Ag<sub>7</sub>Au<sub>6</sub> cluster. As indicated in Figure 4.3a-c, the reaction 4.1 is calculated to be exergonic by 153.6 kJ/mol on its minimal energy reaction pathway (MERP). It is shown that this reaction is thermodynamically preferable. Then we will discuss its kinetics from potential energy surfaces (PESs).

As shown in Figure 4.3a, the initial step of reaction is the addition of a single NO molecule on edge site of the Ag<sub>7</sub>Au<sub>6</sub> cluster, followed by decomposition to generate O and N atoms disperse on the Ag<sub>7</sub>Au<sub>6</sub> cluster. The formation of intermediate IS1-a is significantly exergonic by 46.0 kJ/mol. Then, the FS1-a can be formed via transition state (TS1-a) with the energy barrier around 419.7 kJ/mol approximately. After breaking of N– O bond, once the NO molecule binds to the Ag<sub>7</sub>Au<sub>6</sub>, the FS1-a can lead to intermediate IS1-a2 by releasing the energy of about 65.1 kJ/mol. Next, the FS1-a2 can be formed via transition state (TS1-a2) with the energy barrier of about 16.0 kJ/mol. cluster. Finally, the nitrogen atom resulting from the NO decomposition reacts with adsorbed the second NO molecule to form  $N_2O$  that desorbs from the Ag<sub>7</sub>Au<sub>6</sub> cluster.

As shown in Figure 4.3b, the initial step of reaction is the addition of two NO molecule on edge site of the Ag<sub>7</sub>Au<sub>6</sub> cluster, followed by decomposition to generate O and N atoms dispersed on the Ag<sub>7</sub>Au<sub>6</sub> cluster. The formation of intermediate IS1-b is significantly exergonic by 107.7 kJ/mol. Next, the Int1-b can be formed via transition state (TS1-b) with the barrier energy of about 357.9 kJ/mol. After breaking of N–O bond, the FS1-b can be formed via transition state (TS1-b2) with the barrier energy of about 16.0 kJ/mol. Finally, the nitrogen atom resulting from the NO decomposition reacts with adsorbed NO to form N<sub>2</sub>O that desorbs from the Ag<sub>7</sub>Au<sub>6</sub> cluster.

As shown in Figure 4.3c, the initial step of reaction is the addition of two NO molecule on facet site of the Ag<sub>7</sub>Au<sub>6</sub> cluster, followed by decomposition to generate O and N atoms dispersed on the Ag<sub>7</sub>Au<sub>6</sub> cluster. The formation of intermediate IS1-c is significantly exergonic by 75.7 kJ/mol. Next, the Int1-c can be formed via transition state (TS1-c) with the barrier energy of about 346.5 kJ/mol. After breaking of N–O bond, the Int1-c2 can be formed via transition state (TS1-c2) with the barrier energy of about 0.5 kJ/mol. Next, the FS1-c can be formed via transition state (TS1-c3) with the barrier energy of about 10.6 kJ/mol. Finally, the nitrogen atom resulting from the NO decomposition reacts with adsorbed NO to form N<sub>2</sub>O that desorbs from the Ag<sub>7</sub>Au<sub>6</sub> cluster.

In view of Figure 4.3a–c, Comparing with the reaction pathway in Figure 4.3a, the reaction pathway in Figure 4.3b exhibits better catalytic performance in view of the energy barrier for N–O bond cleavage because of its lower energy barrier. One can see that the N–O bond cleavage with two NO molecule occurs more easily than with one NO molecule. Comparing with the reaction pathway in Figure 4.3a-b, the reaction pathway in Figure 4.3c possesses better catalytic performance, considering the energy barrier for the N–O bond cleavage because of its lowest energy barrier. One can see that the N–O bond cleavage because of its lowest energy barrier. One can see that the N–O bond cleavage because of its lowest energy barrier. One can see that the N–O bond cleavage because of its lowest energy barrier. One can see that the N–O bond cleavage occurs more easily on the facet site than on the edge site of the  $Ag_7Au_6$  cluster.







Figure 4.3 Geometric structures of the reactants, intermediates, TSs, and products, and the schematic energy diagrams for the reaction of Ag<sub>7</sub>Au<sub>6</sub> + 2NO → Ag<sub>7</sub>Au<sub>6</sub>O + N<sub>2</sub>O: (a) one NO molecule; (b) two NO molecule is initially adsorbed on edge site of Ag<sub>7</sub>Au<sub>6</sub>; (c) two NO molecule is initially adsorbed on facet site of Ag<sub>7</sub>Au<sub>6</sub>



Figure 4.3 Geometric structures of the reactants, intermediates, TSs, and products, and the schematic energy diagrams for the reaction of Ag7Au<sub>6</sub> + 2NO → Ag7Au<sub>6</sub>O + N<sub>2</sub>O: (a) one NO molecule; (b) two NO molecule is initially adsorbed on edge site of Ag7Au<sub>6</sub>; (c) two NO molecule is initially adsorbed on facet site of Ag7Au<sub>6</sub> (Continued)

4.3.1.2 Reduction of  $N_2O$ .

Figure 4.4a and b shows structures and schematic energy diagrams for the Ag<sub>7</sub>Au<sub>6</sub> cluster-catalyzed reduction of N<sub>2</sub>O (Ag<sub>7</sub>Au<sub>6</sub> + N<sub>2</sub>O  $\rightarrow$  Ag<sub>7</sub>Au<sub>6</sub>O + N<sub>2</sub>). This reaction may proceed two possible reaction pathways depending on the N<sub>2</sub>O adsorption mode. In the N-bound pathway, the N atom of the N<sub>2</sub>O molecule adsorbs to an Ag atom in the Ag<sub>7</sub>Au<sub>6</sub> cluster (Figure 4.4a). In O-bound pathway, the O atom adsorbs on an Ag atom of the cluster (Figure 4.4b). As shown, the Ag<sub>7</sub>Au<sub>6</sub> cluster preferentially populates the doublet state. The quartet state of the cluster lies 123.8 kJ/mol above the doublet state. We determined that the N<sub>2</sub>O reduction reaction on the Ag<sub>7</sub>Au<sub>6</sub> cluster is exothermic by -23.5 and -40.2 kJ/mol for the doublet and quartet state PESs, respectively.Thus, this reaction is thermodynamically favorable.





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For N-bound pathway (Figure 4.4a), an N<sub>2</sub>O molecule adsorbs on an Ag atom of the cluster through one of the N atoms. The intermediate IS2a is significantly more stable (by 15.5 kJ/mol) than the isolated form R2a. Then, cleavage of the N-O bond and formation of the new Ag<sub>7</sub>Au<sub>6</sub>–O bond are predicted to proceed via transition state TS2a to generate a molecular complex FS2a, with a activation energy barrier of 122.0 kJ/mol. Thus, in the final step, the product N<sub>2</sub> molecule rapidly desorbs from the Ag<sub>7</sub>Au<sub>6</sub>O cluster.

An N<sub>2</sub>O molecule initially adsorbs on an Ag atom via its O atom (Figure 4.4b, O-bound pathway). The energy of intermediate IS2b is -7.5 kJ/mol. Then, cleavage of the N–O bond and formation of the Ag<sub>7</sub>Au<sub>6</sub>–O bond proceeds via transition state TS2b, with an activation barrier of 103.2 kJ/mol, to generate the FS2b complex. In the final step, the N<sub>2</sub> molecule similarly rapidly desorbs from the cluster.

The PES for N<sub>2</sub> formation via the N-bound pathway includes the energy barrier of 122.0 kJ/mol at the IS2a  $\rightarrow$  TS2a reaction step. However, for the O-bound pathway, PES reveals an energy barrier of 103.2 kJ/mol for the IS2b  $\rightarrow$  TS2b reaction step. These results indicate that the N-bound pathway exhibits better catalytic performance in view of the energy barrier for the N–O bond cleavage. In other words, one can say that the N–O bond cleavage preferably occurs when the N<sub>2</sub>O molecule is adsorbed on the Ag atom of Ag<sub>7</sub>Au<sub>6</sub> cluster via the O-bound.

4.3.1.3 Oxidation of CO.

The geometric structures and schematic energy diagrams for reaction 4.3 (Ag<sub>7</sub>Au<sub>6</sub>O + CO  $\rightarrow$  Ag<sub>7</sub>Au<sub>6</sub> + CO<sub>2</sub>) are depicted in Figure 4.5. As shown in Figure 4.5, reaction 4.3 is calculated to be exergonic by 316.3 kJ/mol on its MERP. Therefore, this reaction is thermodynamically favorable. First, one CO molecule is adsorbed on Ag<sub>7</sub>Au<sub>6</sub>O. The formation of intermediate IS3 is significantly exergonic by 39.2 kJ/mol. Next, the FS3 can be formed via transition state (TS3) with the barrier energy of about 44.1 kJ/mol. The final step, the CO<sub>2</sub> molecule desorbs from the Ag<sub>7</sub>Au<sub>6</sub> cluster.



# Figure 4.5 Geometric structures of the reactants, intermediates, TSs, and products, and the schematic energy diagrams for the reaction of Ag7Au6O + CO → Ag7Au6 + CO2.

In view of through N–O bond cleavage in the absence of CO, the rate determining step is N–O bond cleavage without CO. this reaction occur via transition states with energy barrier of 346.8 kJ/mol. It is indicated that this reaction can't occur under room temperature because of its high energy barrier. Therefore, we study another situation, which is through N–O bond cleavage in the presence of CO.

#### 4.3.2 Through N-O Bond Cleavage in the Presence of CO.

This overall reaction occur via NO reduction with CO, which is divided into four sequent reactions (reactions 4.4, 4.5, 4.2, and 4.3).

$$Ag_7Au_6 + NO + CO \rightarrow Ag_7Au_6N + CO_2$$
(4.4)

$$Ag_7Au_6N + NO \rightarrow Ag_7Au_6 + N_2O \tag{4.5}$$

$$Ag_7Au_6 + N_2O \rightarrow Ag_7Au_6O + N_2 \tag{4.2}$$

$$Ag_7Au_6O + CO \rightarrow Ag_7Au_6 + CO_2$$
 (4.3)

Because reaction 4.2 and 4.3 has been discussed earlier, it is necessary to investigate reactions 4.4 and 4.5, both thermodynamically and kinetically.

4.3.2.1 N<sub>2</sub>O formation with CO part 1.

The geometric structures and schematic energy diagrams for reaction 4.4 (Ag<sub>7</sub>Au<sub>6</sub> + NO + CO  $\rightarrow$  Ag<sub>7</sub>Au<sub>6</sub>N + CO<sub>2</sub>) are depicted in Figure 4.6a and 4.6b. This reaction can be divided into two kinds of reaction pathways, through N–O bond cleavage in presence of CO molecule on edge and facet site of Ag<sub>7</sub>Au<sub>6</sub> cluster. As shown in Figure 4.6a-b, reaction 4.4 is calculated to be exergonic by 115.9 kJ/mol on its MERP. Therefore, this reaction is thermodynamically favorable.

As shown in Figure 4.6a, at the beginning, the NO and CO molecules are adsorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster. The formation of intermediate IS4-a is significantly exergonic by 64.6 kJ/mol. Next, from IS4-a, the N–O bond cleavage takes place on edge site of the Ag<sub>7</sub>Au<sub>6</sub> cluster via transition state (TS4-a) with the barrier energy of about 225.1 kJ/mol to form CO<sub>2</sub> molecule on edge site of Ag<sub>7</sub>Au<sub>6</sub> cluster. Finally, the CO<sub>2</sub> molecule desorbs from the Ag<sub>7</sub>Au<sub>6</sub>N cluster.

As shown in Figure 4.6b, at the beginning, the NO and CO molecules are adsorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster. The formation of intermediate IS4-b is significantly exergonic by 74.5 kJ/mol. Next, from IS4-b, the N–O bond cleavage takes place on facet site of the Ag<sub>7</sub>Au<sub>6</sub> cluster via transition state (TS4-b) with the barrier energy of about 148.1 kJ/mol to form CO<sub>2</sub> molecule on facet site of Ag<sub>7</sub>Au<sub>6</sub> cluster. Finally, the CO<sub>2</sub> molecule desorbs from the Ag<sub>7</sub>Au<sub>6</sub>N cluster.

As indicated in Figure 4.6a, the MERP should proceed via transition state with the energy barrier of 225.1 kJ/mol at the IS4-a  $\rightarrow$  TS4-a reaction step. As shown in Figure 4.6b, the MERP should proceed via transition state with the energy barrier of 183.3 kJ at the IS4-b  $\rightarrow$  TS4-b reaction. One can see that the reaction pathway in Figure 4.6b is the more kinetically favorable than the reaction pathways in Figure 4.6a, because of its lowest energy barrier.



Figure 4.6 Geometric structures of the reactants, intermediates, TSs, and products, and the schematic energy diagrams for the reaction of  $Ag_7Au_6 + NO + CO \rightarrow Ag_7Au_6N + CO_2$ .

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4.3.2.2 N<sub>2</sub>O formation with CO part 2.

The geometric structures and schematic energy diagrams for reaction 4.5 (Ag<sub>7</sub>Au<sub>6</sub>N + NO  $\rightarrow$  Ag<sub>7</sub>Au<sub>6</sub> + N<sub>2</sub>O) are depicted in Figure 4.7. As shown in Figure 4.7, reaction 4.5 is calculated to be exergonic by 354.1 kJ/mol on its MERP. Hence, this reaction is thermodynamically favorable. At the beginning, the NO molecule is adsorbed on the R5. The formation of intermediate IS5 is significantly exergonic by 37.6 eV. Next, the FS5 can be formed via transition state (TS5) with the barrier energy of about 5.4 kJ/mol. The final step, the N<sub>2</sub>O molecule desorbs from the Ag<sub>7</sub>Au<sub>6</sub> cluster.



Figure 4.7 Geometric structures of the reactants, intermediates, TSs, and products, and the schematic energy diagrams for the reaction of Ag<sub>7</sub>Au<sub>6</sub>N + NO → Ag<sub>7</sub>Au<sub>6</sub> + N<sub>2</sub>O.

For N–O bond cleavage, there are two reaction pathway. The first is N–O bond cleavage without CO. this reaction pathway occur via transition states with energy barrier of 346.8 kJ/mol. The second is N–O bond cleavage with CO. this reaction pathway occur via transition states with energy barrier of 148.1 kJ/mol. It is indicated that N–O bond cleavage with CO can occur easier than in the absence of CO because of its lower energy barrier.

#### 4.3.3 Formation of the NCO side product

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Accomplishing the side reaction in equation of NO +  $2CO \rightarrow NCO + CO_2$ , there is a unique reaction pathway, which is composed of Ag<sub>7</sub>Au<sub>6</sub>N + CO  $\rightarrow$  Ag<sub>7</sub>Au<sub>6</sub> + NCO. The geometric structures and schematic energy diagrams for this reaction is depicted in Figure 4.8. It is necessary to investigate this reaction, both thermodynamically and kinetically. As shown in Figure 4.8, this reaction is calculated to be exergonic by 116.1 kJ/mol on its MERP. Hence, this reaction is thermodynamically favorable. At the beginning, the CO molecule is adsorbed on the R6. The formation of intermediate IS6 is significantly exergonic by 40.3 eV. Next, the FS6 can be formed via transition state (TS6) with the barrier energy of about 26.7 kJ/mol. The final step, the NCO molecule desorbs from the Ag<sub>7</sub>Au<sub>6</sub> cluster.





For the formation of NCO side product, the energy barrier of NCO formation is 26.7 kJ/mol, which is higher than N<sub>2</sub>O formation in Figure 4.7 (5.4 kJ/mol). It indicated that N<sub>2</sub>O formation can occur easier than NCO formation because of its lower energy barrier.

## CHAPTER 5 CONCLUSIONS

#### 5.1 Molecular adsorption

In this work, we investigated the adsorption of CO, NO, N<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub> molecules on the Ag<sub>7</sub>Au<sub>6</sub> cluster. In order to find the most stable configurations of the five molecules adsorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster, the molecules were initially placed on all possible sites of the cluster surface. The results show that the CO and NO molecule are chemisorbed on Ag<sub>7</sub>Au<sub>6</sub> cluster with adsorption energies of -50.2 and -54.0 kJ/mol, respectively. It show that the NO reduction by CO can occur on Ag<sub>7</sub>Au<sub>6</sub> cluster. Moreover, the CO<sub>2</sub> and N<sub>2</sub> molecule are physisorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster with adsorption energies of -11.7 and -13.4 kJ/mol, respectively. It show that the CO<sub>2</sub> and N<sub>2</sub> molecule are physisorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster with adsorption energies of -11.7 and -13.4 kJ/mol, respectively. It show that the CO<sub>2</sub> and N<sub>2</sub> molecule are physisorbed on the Ag<sub>7</sub>Au<sub>6</sub> cluster with adsorption energies of -11.7 and -13.4 kJ/mol, respectively. It show that the CO<sub>2</sub> and N<sub>2</sub> molecule cluster.

#### 5.2 The NO reduction by CO

In this work, a systematic investigation of the catalysis of the oxidation of CO by NO by Ag<sub>7</sub>Au<sub>6</sub> clusters was performed by a series of DFT calculations. Separate calculations were performed for clusters in doublet and quartet states, and both stepwise adsorption and coadsorption mechanisms were analyzed. The overall reaction of  $2NO + 2CO \rightarrow N_2 + 2CO_2$ , the main reaction pathways take place on the facet site rather than the edge site of the Ag<sub>7</sub>Au<sub>6</sub> cluster. The crucial reaction step deals with the NO deoxygenation to generate N<sub>2</sub>O, in which the deoxygenation of NO by CO reaction pathway is kinetically more preferable than that in the absence of CO. The main reaction pathways is the reaction pathways through N–O bond cleavage in the presence of CO, which is related to simultaneous C–O bond formation and N–O bond cleavage. The reaction pathway includes five steps: (1) the coadsorption of NO and CO; (2) the recombination of CO and NO molecules to form a CO<sub>2</sub> molecule and N atom; (3) the reaction of N atoms with the second adsorbed NO to form N<sub>2</sub>O; (4) the decomposition of N<sub>2</sub>O to a N<sub>2</sub> molecule and O atom; and (5) the recombination of an O atom and CO to again form  $CO_2$ . The formation of  $CO_2$  should originate in half from the reaction between the adsorbed CO and NO. The presence of CO decreases the catalytic reduction of NO on the Ag<sub>7</sub>Au<sub>6</sub> cluster. In brief, on the facet site of the Ag<sub>7</sub>Au<sub>6</sub> cluster, formation of CO<sub>2</sub> stems solely from recombination of CO and the O atom while N<sub>2</sub> originates partly from recombination of two N atoms and partly from decomposition of N<sub>2</sub>O. REFERENCES

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