BỘ GIÁO DỤC VÀ ĐÀO TẠO
TRƯỜNG ĐẠI HỌC SƯ PHẠM HÀ NỘI

PHAN THỊ THÙY

NGHIÊN CỨU CẤU TRÚC, MỘT SỐ TÍNH CHẤT CỦA CÁC CLUSTER Ag_n VÀ Ag_nM BẰNG PHƯƠNG PHÁP PHIẾM HÀM MẬT ĐỘ

Chuyên ngành: Hóa lý thuyết và Hóa lý
Mã số: 62.44.01.19

TÓM TẮT LUẬN ÁN TIẾN SĨ HÓA HỌC

HÀ NỘI - 2017

CÔNG TRÌNH ĐƯỢC HOÀN THÀNH TẠI
TRƯỜNG ĐẠI HỌC SƯ PHẠM HÀ NỘI

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Luận án sẽ được bảo vệ trước Hội đồng chấm luận án tiến sĩ cấp Trường
họp tại Trường Đại học sư phạm Hà Nội 2017
Vào hồi: giờ ngày tháng năm

Có thể tìm hiểu luận án tại:
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ABSTRACT

The birth and rapid development of a new field called nanoscience and nanotechnology has not only made a breakthrough in material chemistry, electronics, international technology, biomedical sciences but also widely applied in life such as gauze which treat burn was covered by nano silver, vegetable washing water, deodorant treat smell in air conditioning etc. Nanotechnology changes our lives because of human intervention at nanometer level (nm). At that scale, nanomaterials exhibit special and interesting properties that are distinct from their properties in atomic and cubic size. Of the nanoscale materials, clusters occupy a very important role because they are the blocks built nanosciences. Clusters are defined as a collection of from a few to thousands of atoms in size nm or smaller has individual physical and chemical properties. The clearest provableness for this phenomenon is the discovery of gold clusters, a material known for its chemical passivity in bulk, but strong chemical activity and become an excellent catalyst for many reactions such as CO oxidation, NO reduction, etc. It has opened up new era in research and application of cluster into many different fields as the useful catalyst of many industrial processes. it is noteworthy that clusters are used in catalytic converters in cars and catalytic carbonylation of methanol to product acetic acid via Monsanto process. Clusters are also used in science and biochemical technologies for sickness treatment as marking drug delivery in cancer treatment, imaging diagnosis. The weak-point of this potential material is thermodynamical unstableness. Therefore, in order to find new materials with different features, we have to determine the durable structures as well as physical and chemical properties of the clusters. Quantum chemistry is a useful tool in this case, it go ahead and guide the experiment studies to determine the appropriate cluster structure for use in different fields. ". In particular, cluster of precious metals as Cu, Ag, Au ... and transition metals has d subshell are not saturated, attracting a lot of research interest in both theory and experiment. The electrons in unsaturated d orbitals contribute an important role in the formation of chemical bonds and determine the particular characteristics of the cluster. However, we has just a few knowledge of the complex relationship between structure, electrons and atoms with the durability and properties of bimetallic clusters, in particular, its applicable in the search for new generation materials in a variety of fields such as optical materials, magnetic materials, semiconductor materials and catalyst materials etc.

Derived from the fact that the importance of transition metallic clusters in science and life, with the desire to understand the nature and applicability of clusters, we choose the topic: "**Study on structures and properties of some Ag_n and Ag_nM some clusters by using density functional theory methods**".

The scientific purpose of the thesis is:

Using the DFT method and suitable basis set to determine the durable structure, electron properties and catalytic ability of some metallic clusters and bimetallic clusters to orient for experimental studies.

To achieve that purpose, the thesis has the following contents:

1. Determination of structures and electron properties of some metallic and bimetallic clusters: silver clusters Ag_n (n = 1-20) and silver bimetallic clusters Ag_nM (n = 1-9, M = Fe, Co, Ni, Cu, Au, Pd, Cd).

2. Study reaction mechanism of N_2O direct decomposition and indirect decomposition by CO, H_2 and CH_4 on Ag_7, Ag_7^+ and Cu_7 clusters. This results orient for catalytic role of some metallic clusters.

The new points of the thesis is

1. Determine durable structures and some electron properties of some metallic and bimetallic clusters such as Ag_n (n = 2-20), Ag_nM (n = 1-9, M = Fe, Co, Ni), Ag_nM (n = 1-9, M = Cu, Au, Pd, Cd).
2. Determine that Fe doped into Ag_nM clusters make spin magnetic moment increase. Cu and Au doped make stableness increase, E_{gap} values decrease with Ag_3M và Ag_8M.
3. Determine reaction mechanism of N_2O dissociation and dissociation of N_2O with CO, H_2 and CH_4 on Ag_7, Ag_7^+ and Cu_7, proved catalytic role of clusters.

CHAPTER 1. OVERVIEW

This chapter presents an overview of the basis of quantum chemical theory and the fundament of calculation methods. At the same time, an overview of nanomaterials and the special properties of nanomaterials. The work shows the important role of quantum chemistry to describe molecules, atoms and materials in general. It gives us a clear view about structure and properties of clusters.

Chapter 2. OVERVIEW OF RESEARCH SYSTEM AND COMPUTATIONAL METHODS

2.1. Overview of the research system

In chemistry, a cluster is defined as a set of atoms linked together and have nm size or smaller. Studies on metallic clusters have been strongly developed in both academic and industrial fields since the late 1970s. In this area, the theory of atomic structure and the electron structure of the clusters has provided the basic directions for the creation of new nanomaterials for use in modern and future technologies. Nano-sized molecules and compounds also open up potential opportunities for applications in the fields of chemical glue, medicine, and especially in catalysis. The physical and chemical properties of small and medium sized clusters are strongly dependent on their size and shape, and these characteristics are completely different from those of metallic atoms and metallic crystals.

2.2.1. Computational software

To study the metallic and bimetallic clusters (Ag_n and Ag_nM) by quantum chemistry, we used two major software, Gaussian 09 and Gaussview. When applying this software for research substance will get many results. Based on these results, it is possible to predict many characteristic properties of molecules. Examples: Parameters of the geometry and total energy of molecules; linked energy, multi-force moment; atomic and electric charge; frequency range, IR spectrum, UV-VIS spectrum, infrared spectrum; the Gaussview software allows the description of the shape of the molecular structure, the charge on the atoms, the spectrum and the molecular vibration. Also, use the Chemcraft software to draw molecular structures; excel software for processing results, ...

2.2.2. Research Methods

Density Funtional Theory (DFT) has been used by many scientists to study the theory of metallic clusters in general and clusters of precious metals in particular. It gave good approximate results with empirical and well-suited for the silver cluster. Hence, we choose to explore some methods within the DFT framework to choose the suitable method. We select some commonly used methods to determine the structure and properties of metallic clusters such as B3LYP, B3PW91, PB86. The results of the Ag_2 cluster were compared with the empirical data for the method selected using Table 2.1.

Table 2.1: Ag-Ag binding length (Å) and vibration frequency (cm^{-1})

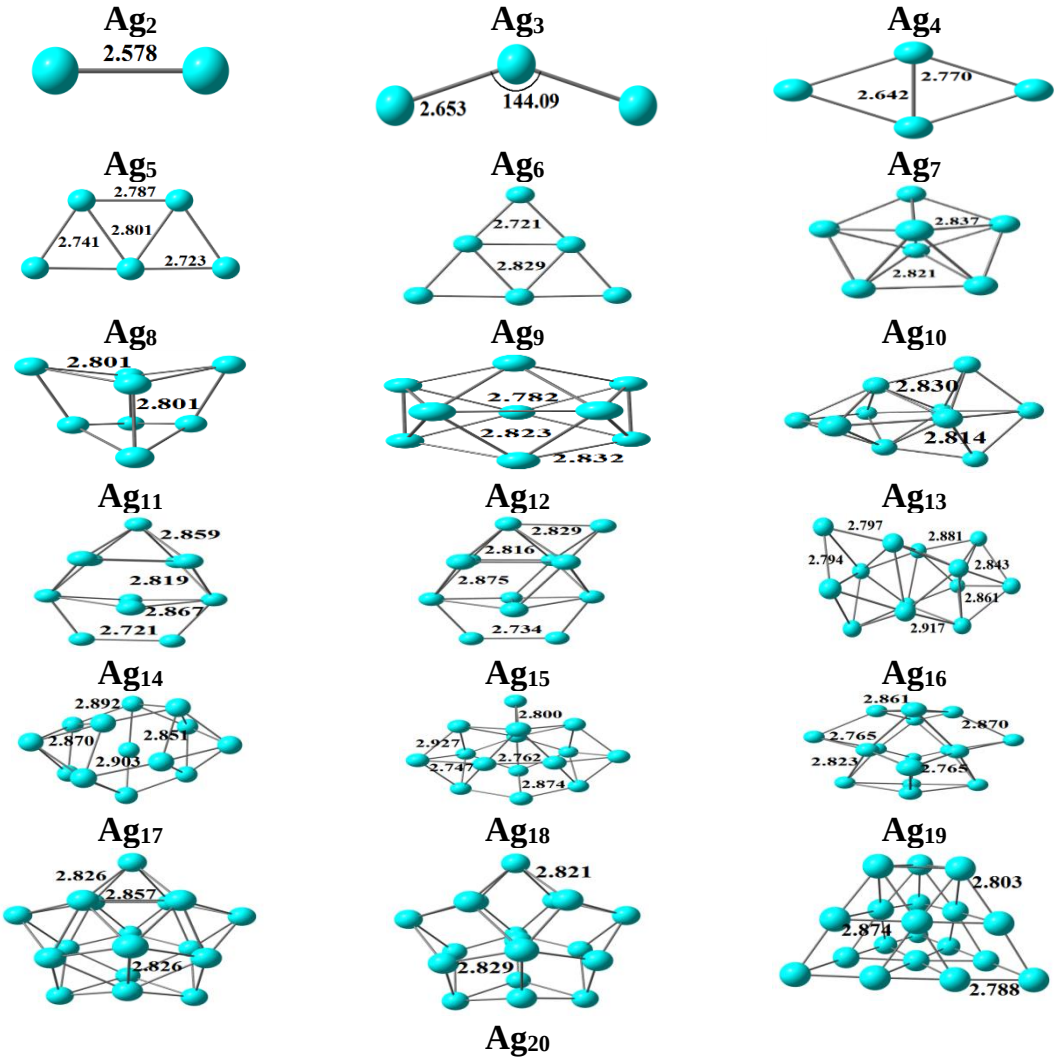
Ag_2	PB86	B3LYP	B3PW91	Thực nghiệm
r(Å)	2,548	2,580	2,558	2,530
V(cm^{-1})	191,07	180,29	187,35	192,40

Analysis of the above results shows that the use of the BP86 method for calculation results in terms of binding length and vibration frequency does not deviate much from the experimental results (Table 2.1). Thus, BP86 method is the most suitable method within the framework of the survey methods.

CHAPTER 3. RESULTS AND DISCUSSION

3.1. Structure and electron properties of Ag_n cluster (n = 2-20) and Ag_nM bimetallic clusters (n=1-9, M= Fe, Co, Ni, Cu, Au, Pd, Cd)

3.1.1. Structure and electron properties of Ag_n cluster (n = 2-20)



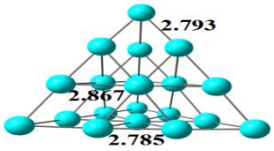


Figure 3.2: Ag_n cluster stable structure (n = 2-20)

Calculation results allow to determine the durable structure of the Ag_n cluster as shown in Figure 3.2. Durable forms are highly symmetric in the structure group have low energy. With small atoms ($n \leq 6$) there is a flat structure, a cluster with silver atoms greater than 7 is not flat, some repeating structures such as Ag_7 and Ag_9, or Ag_8 and Ag_{10}. When the number of atoms in the structure increases, the structure complexly changes.

From the stable isomers defined above, we compute some characteristic properties of silver metallic clusters such as the symmetry point group, the first ionization energy, the Ag-Ag binding energy, and the average binding energy.

With

$$I_{Agn} = E_{(Agn+)} - E_{(Agn)}$$
$$E_{Ag\text{-}Ag} = E_{(Agn+1)} - E_{(Ag)} - E_{(Agn)}$$
$$E_b = n.E(Ag) - E(Ag_n)/n$$

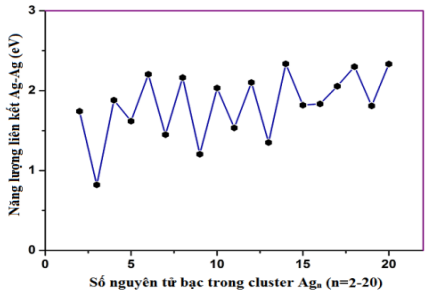


Figure 3.3: $E_{Ag\text{-}Ag}$ transformation Graph of the Ag_n cluster (eV)

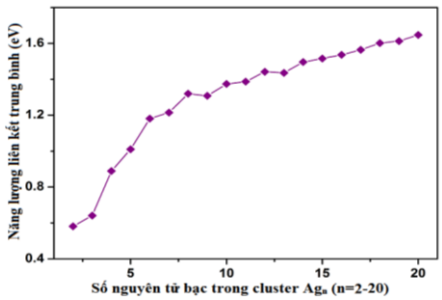


Figure 3.4: E_{LKTB} transformation graph (eV)

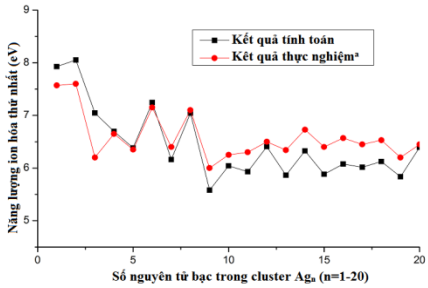


Figure 3.5: I_1 transformation graph of Ag_n cluster (eV)

Calculation results allow to construct graphs of energy conversion by the number of silver atoms in the clusters. From the graph it is found that binding energy depends on the number of atoms in the cluster and their parity directly determines the value obtained. Clusters with even numbers of silver atoms generally have greater energy values than adjacent clusters. The average binding energy is between 0.581 and 1.647 eV, where the smallest value of the Ag_2 cluster and the largest value of Ag_{20}.

The first ionization energy values of the silver metallic clusters were made in the same method and function for durable structures. Ionization potential values range from 5,580 to 8,051 eV. Cluster Ag_9 with C_{2V} point group is the easiest to release electrons with ionization potential is 5,580 eV. The give electrons is the most difficult to occur for Ag_2 clusters. Comparing the results of first ionization energy calculation with empirical data, it was found that the results of the calculation were well matched with the experimental values obtained. Many of the ionization potential values of the cluster had very tiny difference.

From the values of HOMO, LUMO, and energy difference values between LUMO-HOMO in Table 3.5, we plot the change in these values by the number of silver atoms in the Ag_n cluster as follows:

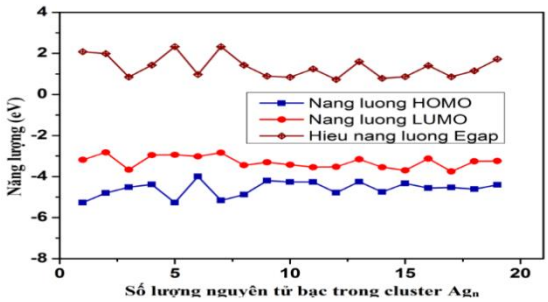


Figure 3.6: E_{HOMO} (eV), E_{LUMO} (eV) and E_{gap} (eV) transformation charts of the Ag_n cluster

Analysis of the graph above shows that E_{gap} varies uneven change. The highest value of the Ag_5 cluster was 2,326 eV and the lowest of the Ag_{13} cluster was 0.725 eV. From Ag_n (n = 5-16) with uneven atomic numbers have lower E_{gap} than adjacent even-numbered clusters, this is similar to the change rule of E_{HOMO} value. Cluster Ag_{13}, Ag_{15} and Ag_4 have low E_{gap} value, which can guide the study of the applicability in semiconductor technology.

Using the TD-DFT method and the LANL2DZ-based function set to determine the UV-VIS spectrum of the Ag_4 cluster, the results were compared with the experimental spectrum determined in the Argon gas environment determined by Félix et al.

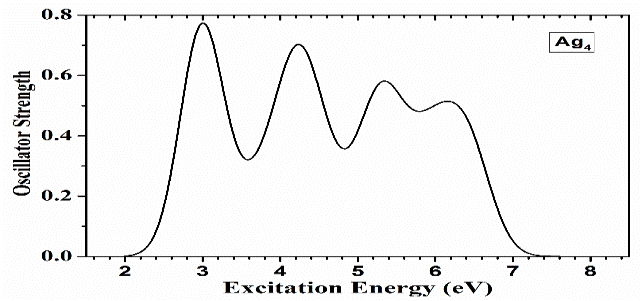


Figure 3.8: UV-VIS spectrum of Ag_4 calculated using the TD-DFT method

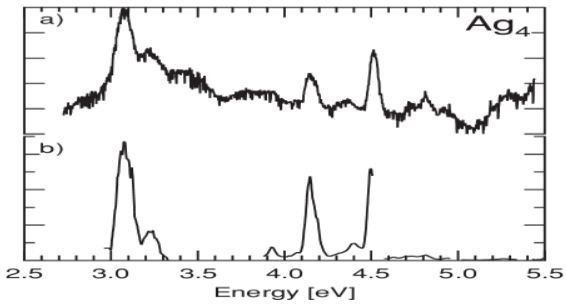
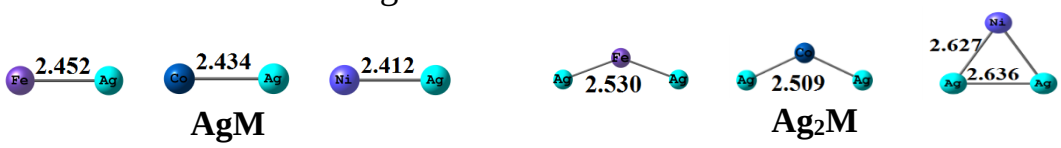


Figure 3.9: Experimental UV-Vis spectrum of Ag_4 in the Argon at 28K; (a) adsorption spectrum; (b) emission spectrum

From the empirical absorption spectra obtained by Felic et al., Experimenting in Argon at 28K of Ag_4, we found that there were three strong peaks, pic at 3.07 eV; 4.15 eV and 4.50 eV. Calculated results for Ag_4 with D_{2h} structure show strong peak of 3.00 eV; 4.20 eV and 5.35 eV. This helps us confirm the good approximation of this method and function to the theoretical calculations used.

3.1.2. Structure and electron properties of Ag_nM bimetallic clusters (n = 1-9, M = Fe, Co, Ni)

Investigation of cluster structure at different spin states has identified many geometries of the Ag_nM clusters (n = 1-9, M = Fe, Co, Ni). In the resulting isomeres, the lowest energy-efficient and highly symmetric structure was the durable form of Ag_nM bimetallic clusters was shown in Figure 3.8.



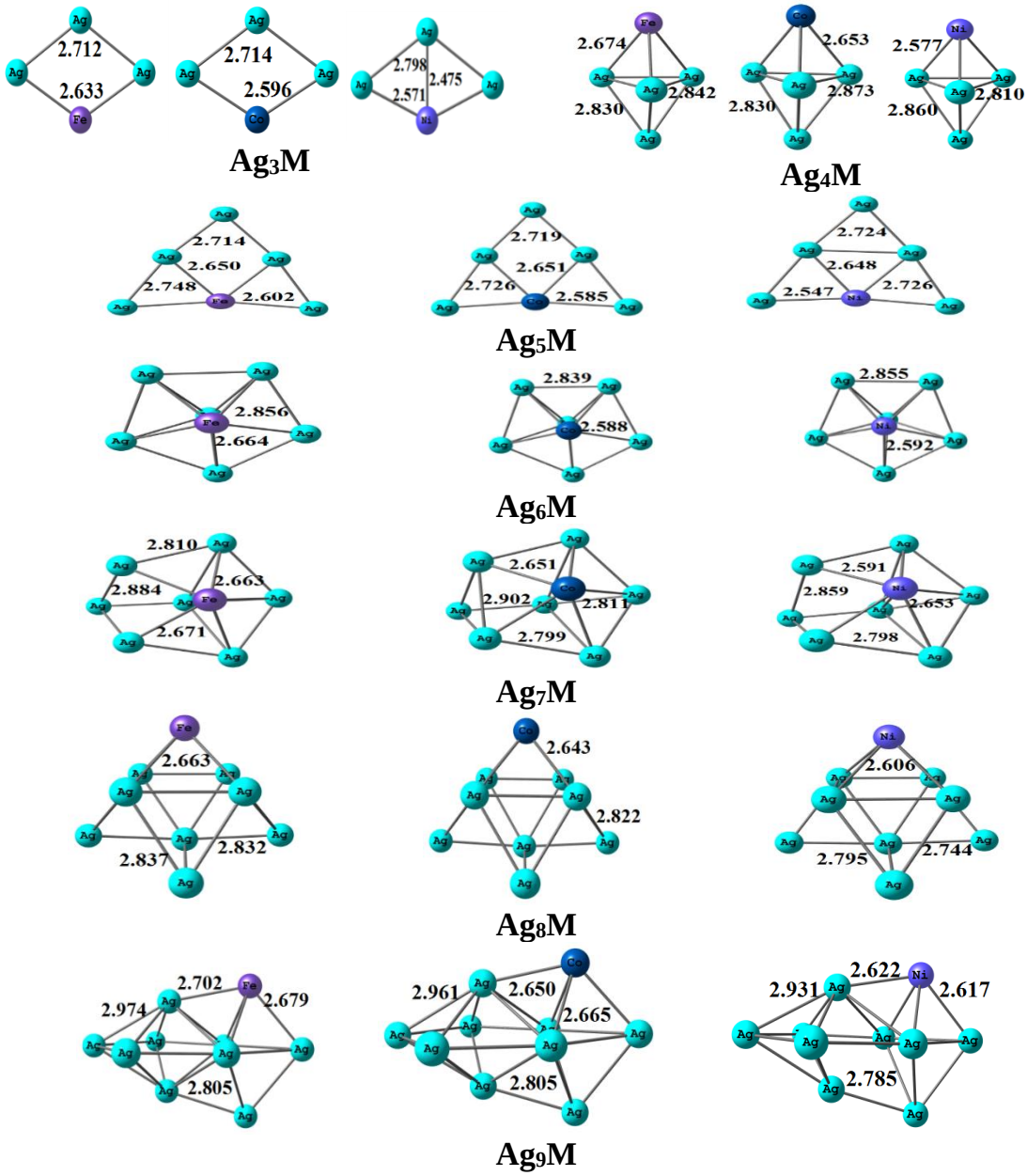


Figure 3.12: Durable structure of Ag_nM clusters (n = 1-9, M = Fe, Co, Ni)

AgM cluster is structured in the form $C_{\infty v}$, the spin multiplicity of M = Fe, Co, Ni, respectively, is 4, 3 and 2 (clusters have 3, 2 and 1 single electron). This suitable to VERSP rules. The most durable form of the Ag_2M cluster is a C_{2V} flat structure with spin multiplicity 5, 4 and 3, respectively. When the transition to the Ag_3M structure, the number of bonds increases with the excitation of electrons from ns subshell to np subshell in atom of M (M = Fe, Co, Ni) to form two bonds with two silver atoms.

For the Ag_4M molecule, the durable structure has the trigonal bipyramid structure. M binding concurrently with three other atoms. The bond Ag-Ni has a minimum length of 2.571 Å. The most durable structure of the Ag_5M cluster is C_{2V}, the same flat structure as the Ag_6 cluster. The C_{5V} pentagonal bipyramid structure is respectively the Ag_6M durable structure, with corresponding spin multiplications of M = Fe, Co, Ni is 2, 3, and 1. In the Ag_6M structures, the bond Ag-Co is the shortest with a value of 2,588 Å. Ag_7M cluster have durable structure are C_1 form, with spin values of 3, 4, 2, respectively, of M = Co, Fe, Ni, the Ag-Ni bond is the smallest length. We obtained a C_s durable structure

with spin multiplicity values is 2, 3, 1 for the Ag_8M cluster (M = Co, Fe, Ni). Ag_9M cluster after examining many different structural forms obtained the durable structure has C_1 point group, incorporating two pentagonal pyramid. The M-Ag binding length is the smallest value when M is Ni and decreasing in order from Fe, Co, Ni. From the durable Ag_nM clusters identified above, we obtain the spin quantum numbers, the E_{gap} energy, the charge on the M atom, the symmetry point group, the first ionization energy value (I_1), the average binding energy (E_b) results was shown in Table 3.5.

Table 3.5: Parameters (PG) about symmetry point group, spin multiplicity, E_{gap} (eV), average binding energy E_b (eV) the first ionization energy value (I_1) and charge on M atom (M = Fe, Co, Ni)

Ag_nM	PG	Mul. Spin	E_b (eV)	I_1 (eV)	E_g (eV)	q_M ($\bar{e}$)
AgFe	$C_{\infty v}$	Quartet	0,680	6,889	2,31	0,142
Ag_2Fe	C_{2v}	Quintet	1,021	6,945	2,62	0,171
Ag_3Fe	C_{2v}	Sextet	1,111	6,355	2,67	0,111
Ag_4Fe	C_{3v}	Triplet	1,159	6,109	1,97	0,181
Ag_5Fe	C_{2v}	Quartet	1,407	7,085	2,96	–0,146
Ag_6Fe	C_{5v}	Triplet	1,465	6,729	1,42	–0,693
Ag_7Fe	C_1	Quartet	1,532	6,018	2,01	–0,334
Ag_8Fe	C_s	Triplet	1,478	5,628	2,25	0,188
Ag_9Fe	C_1	Quartet	1,550	6,183	1,47	0,286
AgCo	$C_{\infty v}$	Triplet	0,895	8,029	3,08	0,087
Ag_2Co	C_{2v}	Quartet	1,023	6,907	2,56	–0,013
Ag_3Co	C_{2v}	Quintet	1,109	6,289	2,26	–0,035
Ag_4Co	C_{3v}	Doublet	1,176	6,696	1,60	0,047
Ag_5Co	C_{2v}	Triplet	1,463	7,062	2,98	–0,151
Ag_6Co	C_{5v}	Doublet	1,499	6,578	2,37	–0,725
Ag_7Co	C_1	Triplet	1,551	6,418	2,04	–0,386
Ag_8Co	C_s	Doublet	1,527	6,277	2,33	0,019
Ag_9Co	C_1	Triplet	1,565	6,071	1,70	0,269
AgNi	$C_{\infty v}$	Doublet	0,981	7,892	3,10	0,072
Ag_2Ni	C_{2v}	Triplet	0,986	5,965	2,78	0,251
Ag_3Ni	C_{2v}	Doublet	1,262	6,667	1,82	0,017
Ag_4Ni	C_{3v}	Singlet	1,234	6,552	1,49	–0,150
Ag_5Ni	C_{2v}	Doublet	1,491	7,263	2,99	–0,190
Ag_6Ni	C_{5v}	Singlet	1,577	6,585	2,13	–0,869
Ag_7Ni	C_1	Doublet	1,582	6,370	1,91	–0,678
Ag_8Ni	C_s	Singlet	1,550	5,761	1,64	– 0,058
Ag_9Ni	C_1	Doublet	1,584	6,145	1,71	0,215

From the data obtained, the average binding energy value in Ag_nM clusters (M = Fe, Co, Ni) increased when n increased from 1 to 9 except n = 8. The value of Ag_8M is lower than the two adjacent clusters. Besides, the first ionization energy value ranged from 6 to 8 eV close to the value of the silver cluster.

The determination of the E_{gap} value of Ag_nM clusters will guide further research into the applicability of the bimetallic cluster. Specific data are shown in table 3.2, which

shows that the E_{gap} varies uneven, with the highest value is 3.1 eV in AgNi cluster and the lowest value is 1.4 eV in Ag_6Fe cluster. Hence, those values within the allowable range of magnetic material or good transmission of heat and electricity.

Fe, Co, Ni elements are known as typical magnetic elements, the dope into the silver cluster to study the magnetic increment of the silver cluster. From the durable structure obtained above, consider magnetic properties for the entire Ag_nM cluster and determine the spin local moment value on each atom and on the important AO. By using calculations on Dmol3 software.

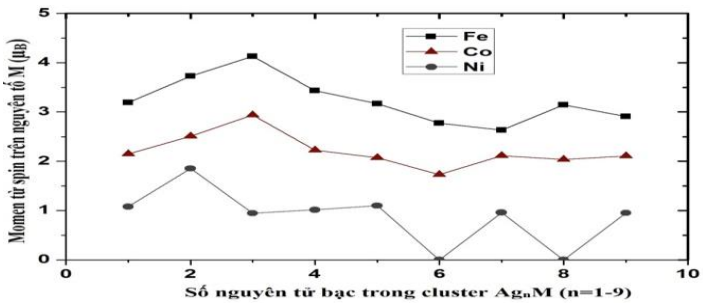
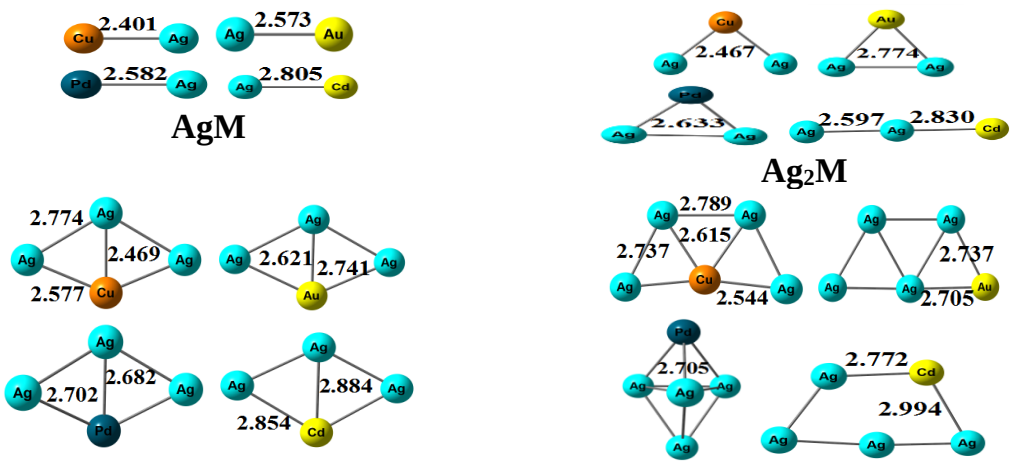


Figure 3.16: Variable graphs of spin magnetic moment of clusters Ag_nM (n = 1-9, M = Fe, Co, Ni)

The graph shows that the spin magnetic moment on the Fe atom in the Ag_nM clusters is the greatest. For clusters with the same number of silver atoms, the order of magnitude of spin magnetic moment of M is Fe, Co, Ni. With the Ag_3M cluster, the spin magnetic moment of Fe has a maximum value of 4.218 μB. It shows that magnetism mainly focuses on the M atom in each cluster. For more details, consider the orbital of the external subshell (n-1)d, ns, np of M metal. The results show that subshell (n-1)d has maximum spin magnetic moment. The ns subshell contributes a fraction of the remaining np is almost negligible. This is perfectly consistent with the e-shell characteristics of the M elements because the (n-1)d subshell contains as many electrons as the large number of single electrons so that the spin magnetic moment is large.

3.1.3. Structure and electron properties of bimetallic clusters Ag_nM (n = 1-9, M = Cu, Au, Pd, Cd)

We have identified many different geometries of the Ag_nM clusters (n = 1-9, M = Au, Cu, Pd, Cd). In the resulting isomeres, the lowest energy-efficient and highly symmetric structure was the durable form of bimetallic clusters Ag_nM (shown in Figure 3.18).



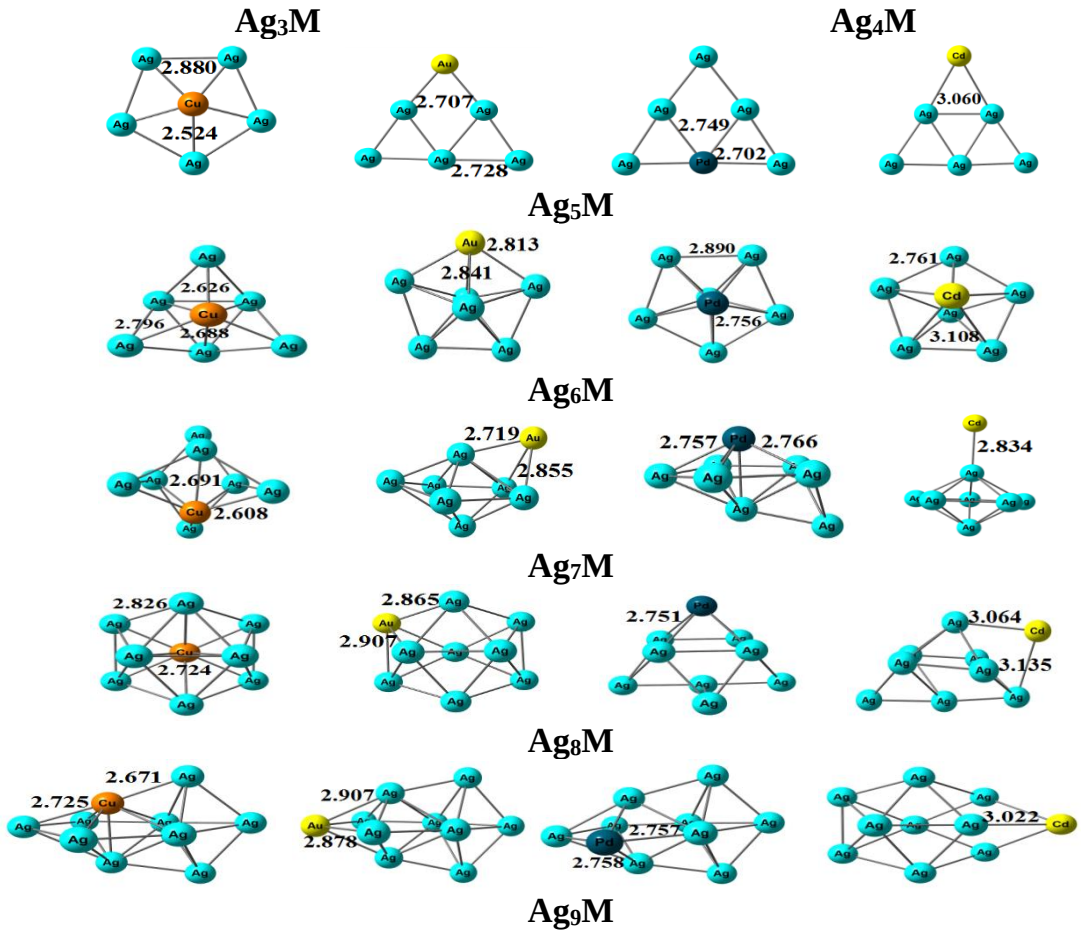


Figure 3.18: Ag_nM cluster stable structure (n = 1-9, M = Cu, Au, Pd, Cd)

From the durable structure of the Ag_nM cluster, we obtain the parameters of the symmetric point group, spin quantum number and calculate some characteristic parameters such as Ag-M binding energy, First ionization energy, HOMO energy values, LUMO energy and band gap energy.

$$E_b = (n.E_{Ag} + E_M - E_{AgnM}) / (n + 1)$$

$$E_{Ag\text{-}M} = (E_{Agn} + E_M - E_{AgnM}) / (n + 1)$$

$$I_{AgnM} = E_{(AgnM+)} - E_{(AgnM)}$$

The calculated results show that the durable form of the symmetry structure with the spin multiplicity is 1 and 2, respectively. That suitable with electron configuration of the elements with the saturated subshell (n-1)d. When forming bonding in the cluster, the electron excitation will produce the corresponding spin states.

Table 3.7: Parameter about symmetry point group (PG), spin multiplicity, Ag-M binding energy (eV), average binding energy (eV) and ionic strength of Ag_nM clusters (n = 1-9, M = Cu, Au, Pd, Cd)

Ag_nM	PG	Mul. Spin	E_{Ag-M} (eV)	E_b (eV)	I_1 (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
AgCu	$C_{\infty v}$	Singlet	2,021	1,010	8,093	–3,031	–4,914	1,883
Ag_2Cu	C_{2v}	Doublet	1,283	1,008	6,297	–3,546	–5,639	2,093
Ag_3Cu	C_{2v}	Singlet	2,450	1,253	6,761	–3,579	–4,542	0,964
Ag_4Cu	C_{3v}	Doublet	2,264	1,342	6,429	–2,791	–4,397	1,606
Ag_5Cu	C_{2v}	Singlet	2,901	1,494	7,143	–2,868	–5,104	2,236

Ag_6Cu	C_{5v}	Doublet	2,045	1,473	6,205	–2,833	–4,289	1,456
Ag_7Cu	C_1	Singlet	2,907	1,578	7,073	–2,839	–5,136	2,296
Ag_8Cu	C_s	Doublet	2,257	1,553	5,462	–3,262	–3,74	0,478
Ag_9Cu	C_1	Singlet	2,808	1,591	6,051	–3,328	–4,314	0,986
AgAu	$C_{\infty v}$	Doublet	2,174	1,087	8,928	–3,773	–5,907	2,134
Ag_2Au	C_{2v}	Singlet	1,424	1,056	6,651	–3,862	–6,235	2,373
Ag_3Au	C_{2v}	Doublet	2,033	1,149	6,739	–4,154	–4,576	0,422
Ag_4Au	C_{3v}	Singlet	2,261	1,341	6,690	–3,189	–4,661	1,472
Ag_5Au	C_{2v}	Doublet	2,895	1,493	7,487	–3,230	–5,457	2,227
Ag_6Au	C_{5v}	Singlet	1,979	1,464	6,202	–3,909	–5,209	1,300
Ag_7Au	C_1	Doublet	2,630	1,543	6,700	–3,419	–4,830	1,411
Ag_8Au	C_s	Singlet	2,010	1,526	5,871	–3,859	–4,890	1,031
Ag_9Au	C_1	Doublet	2,848	1,595	6,459	–3,339	–4,698	1,358
AgPd	$C_{\infty v}$	Singlet	1,462	0,731	7,791	–2,986	–5,029	2,043
Ag_2Pd	C_{2v}	Doublet	1,891	1,211	7,470	–3,186	–4,212	1,026
Ag_3Pd	C_{2v}	Singlet	2,433	1,249	6,586	–3,265	–4,416	1,152
Ag_4Pd	C_{3v}	Doublet	1,861	1,261	6,366	–3,70	–4,268	0,568
Ag_5Pd	C_{2v}	Singlet	2,234	1,383	7,046	–5,08	–2,991	2,089
Ag_6Pd	C_{5v}	Doublet	2,738	1,572	6,750	–4,705	3,584	1,121
Ag_7Pd	C_1	Singlet	2,756	1,559	6,130	–4,004	–4,689	0,685
Ag_8Pd	C_s	Doublet	2,567	1,588	6,488	–3,357	–4,612	1,255
Ag_9Pd	C_1	Singlet	2,725	1,583	6,014	–4,029	–4,841	0,812
AgCd	$C_{\infty v}$	Doublet	0,466	0,233	6,578	–4,150	–1,737	2,413
Ag_2Cd	C_{2v}	Singlet	0,404	0,715	7,151	–4,827	–3,019	1,808
Ag_3Cd	C_{2v}	Doublet	0,522	0,771	6,764	–4,752	–4,084	0,668
Ag_4Cd	C_{3v}	Singlet	0,697	1,028	6,675	–4,644	–3,148	1,497
Ag_5Cd	C_{2v}	Doublet	0,417	1,080	5,710	–3,897	–3,052	0,845
Ag_6Cd	C_{5v}	Singlet	0,581	1,264	6,800	–4,820	–2,951	1,869
Ag_7Cd	C_1	Doublet	0,437	1,269	5,623	–3,861	–2,848	1,013
Ag_8Cd	C_s	Singlet	0,447	1,352	6,495	–4,721	–3,268	1,453
Ag_9Cd	C_1	Doublet	0,522	1,363	5,629	–3,975	–3,315	0,661

The results of the average binding energy in the Ag_nM clusters (M = Ag, Cu, Au) increased when the number in cluster increased from 1 to 9 but with even slower growth rates. When comparing the results of M = Cu, Au with the original Ag_n cluster, we see that the rule of change is similar. That is due to the similarity of the electron shell, when the dope M = Cu, Au increases the durability. When considering two elements with the same period such as Pd and Cd, we find that the Cd atom forms weak bonds with the silver atoms due to the large radius, the average binding energy is in the range of 0.233 eV to 1.363 eV. With other elements, $E_{Ag\text{-}M}$ values often vary with atomic parity in the Ag_nM cluster. When the dope of the Cu, Au, Pd, Ag –M binding energy in Ag_nM is larger than the Ag-Ag binding energy in the Ag_{n+1} cluster.

It is possible to study the optoelectronics processes of nanomaterials which are closely related to the stimulus mechanisms and the internal energy conversion mechanisms. In the basic state, the HOMO region has filled electrons while the LUMO region has no electrons. When there are stimulant such as light, temperature etc the electrons in the HOMO region get their energy converted to the excited state, if the

energy is large enough, they can jump to the LUMO region, which is the same as the electron process from the valence region jumps to the conduction region when the electron is excited in the solid semiconductor material. Thus, there would exist a overlap between the electron clouds between the two HOMO and LUMO regions that constitute the semiconductor of the transition metallic clusters.

Therefore, study about HOMO, LUMO and E_{gap} energy of clusters are important and crucial factors for the application of optical properties. The calculation results are shown in Table 3.7. It shows that the different energy between LUMO-HOMO uneven, the highest value is 2.4 eV in AgCd and 0.4 eV in Ag_3Au. When the dope of Cu and Au atoms in their silver clusters, the E_{gap} value changes according to the parity of the atomic number in the cluster. The lowest E_{gap} value when Cu dope is 0.5 eV in Ag_8Cu, while Au dope has the lowest value is 0.4 eV in Ag_3Au cluster respectively.

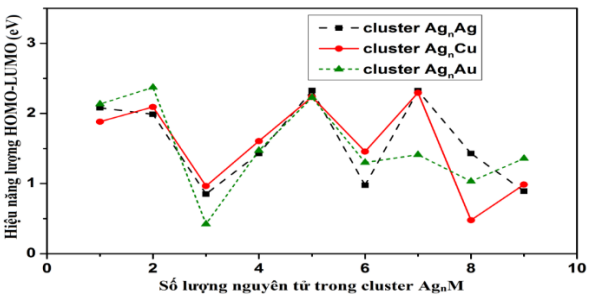


Figure 3.25: Energy E_{gap} (eV) of Ag_nM clusters (n = 1-9, M = Ag, Cu, Au)

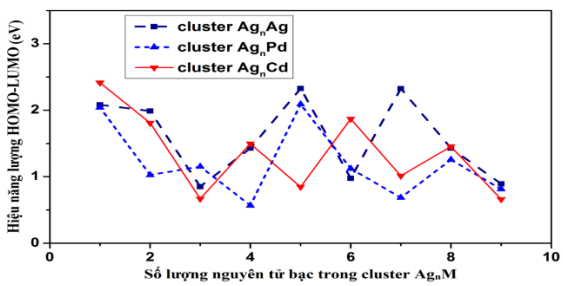


Figure 3.26: Energy E_{gap} (eV) of Ag_nM clusters (n = 1-9, M = Ag, Pd, Cd)

When the Pd and Cd atom were doped except the AgM, the other Ag_nM clusters have E_{gap} values smaller than the Ag_{n+1} cluster. This shows that when a silver atom in the silver cluster was replaced by another element, the electron interaction between them reduces the HOMO and LUMO energy difference as the E_{gap} value decreases.

Compared to the LUMO-HOMO energy exception of some commonly used semiconductor materials (Table 3.9), it can be predicted that Ag_nM clusters will become potential materials in semiconductor technology. in particular, the Ag_3Cd, Ag_3Pd, Ag_3Au and Ag_8Cu clusters.

Table 3.9 Value of the LUMO-HOMO energy difference of some common semiconductor materials

STT	Some common semiconductor material	ΔE_{gap} (eV)	Application
1	Si	1,11	Making integrated cỉcuits…
2	GaAs	1,43	As a substrate for semiconductor material III–IV (InGaAs và GaInNAs), used in infrared LED…
3	SiC	2,30 – 3,00	Used in LED
4	InN	0,7	Used in solar cell…
5	GaN	3,44	Used in blue LED, blue lase …
6	BN	5,96 – 6,36	Used in UV LED
7	ZnTe	2,25	Used in solar cell, LED, laser ..
8	TiO2	3,20	Used as a optical catalyst.

To better understand the interaction of light and electrons in the cluster, the characteristic peak of Ag_3M clusters in the UV-VIS spectrum were considered, which is located in the range of 200-600 nm in the ultraviolet-visible range. Ag_3M cluster absorb radiation with a maximum wavelength of 310 - 490 nm, the purple absorber. The radiation absorbance of the cluster on the corresponding stimulant mainly originates from electrons in the vicinity of the HOMO region excited on the LUMO region.

3.2. Catalytic properties of transition metallic clusters

From the study of the structure and properties of the silver cluster obtained, the calculated results show that the Ag_7 cluster is the smallest structure that is not a flat structure. The analysis of MO energy in N_2O molecules and Ag_7 cluster yields their molecule-based energy pattern, shown in Figure 3.28. From the diagrams, the energy lever of bonding MOs of 7σ, 2Π and antibonding MO_s of 3Π, 8σ in N_2O are near the energy level of MOs in the Ag_7 cluster. The bonding MO_s of 7σ, 3Π ensure symmetry, which can overlap with MOs in the HOMO area of the Ag_7 cluster. In addition, bonding MO of 7σ, 2Π contain pairs of electrons that can transfer electron to the region of the HOMO area of the cluster, while in these MOs can yield to the 3Π antibonding MOs of N_2O. Therefore, we selected the Ag7 cluster with the spin-point D_{5h} spin-doubles group to study the N_2O decomposition and indirectly decompose CO. In order to select the appropriate clusters, we further investigate the processes that occur on the Ag_7^+ and Cu_7 clusters. The calculated results are analyzed and discussed in the next section.

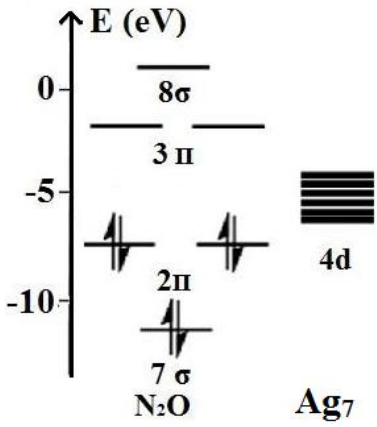


Figure 3.28: Comparison chart of MO energy of N_2O molecule and Ag_7 cluster constructed using BP86 method

3.2.1. Direct decomposition of molecules in the gas phase

Many research results show that the two N_2O molecules decomposition in the gas phase occurs at high temperature conditions, the product can be generated in the reaction process is $2N_2 + O_2$; N_2+ 2NO and $N_2 + N_2O_2$. But the detail mechanism of the that process has not clear, so we use the Density Functional Theory (DFT) at BP86/Aug-cc-pvdz to study this reaction system. Calculation results show that the $P1_g(2N_2 + O_2)$ had the lowest correlation energy value is -16.8 kcal/mol. Away from the original compound has five different paths to form the $P1_g$. Besides, there are two products $P2_g$ ($N_2O_2 + N_2$) and $P3_g$ (2NO + N_2) have energy is 17.9 kcal/mol and 24.3 kcal/mol respectively. In it, the main obtained products include N_2 and O_2, the reaction path goes through $TS0/1_g$ and $TS3/P1_g$ more favorable because of lowest barrier energy (49.7 kcal/mol).From the

potential energy surface showed two remaining products have energy barrier is 62.7 kcal/mol for the $P2_g$ (N_2O_2 + NO) and 69.6 kcal/mol for the $P3_g$ (NO + N_2). N_2O decomposition process in the gas phase occurs difficult with large energy barrier. So the selection of suitable catalysts to improve the performance and lower the activation energy of the reaction is extremely necessary. With of, Therefore, we choose the precious metallic cluster which have interesting characteristics to investigate the possibility of using the material as a catalyst for direct decomposition process gas N_2O.

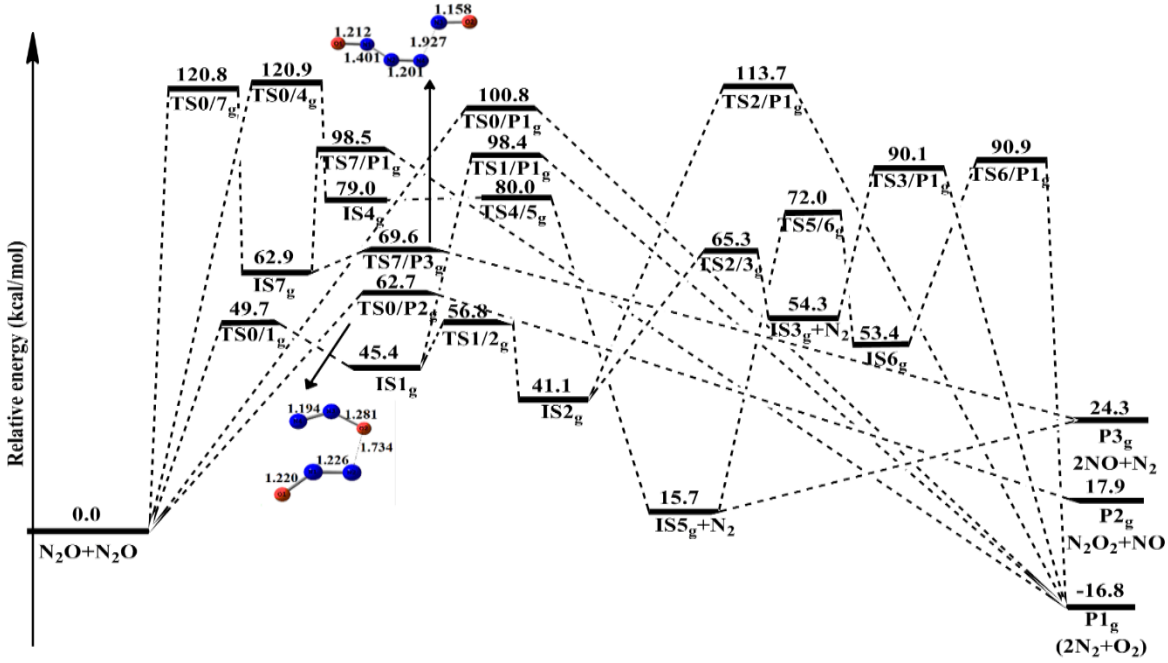
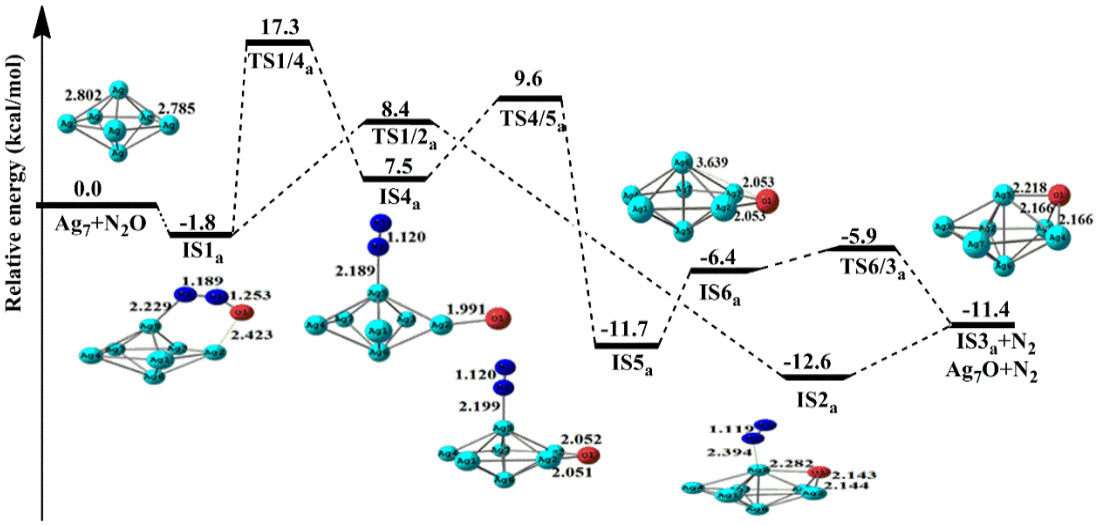


Figure 3.30: The potential energy surface (PES) of N_2O + N_2O reaction system in the gas phase using BP86 method

3.2.2. The catalytic role of Ag_7 cluster

3.2.2.1. Direct decomposition N_2O molecules on Ag_7 cluster

Using Density Functional Theory to study the decomposition of N_2O gas molecule directly on cluster Ag_7.



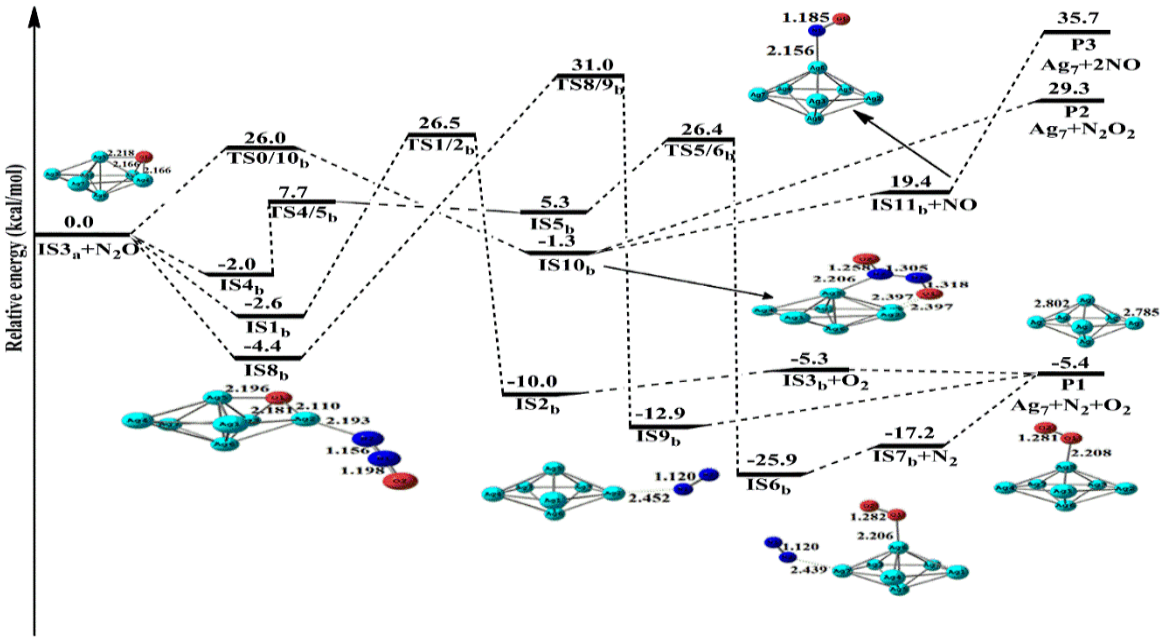


Figure 3.32: The potential energy surface (PES) of direct decomposition N_2O molecules on Ag_7 cluster using BP86 method

The survey of N_2O adsorption capacity on the silver cluster in different positions was performed through the NBO analysis and the calculation of adsorption energy value. Results of adsorption energy N_2O on the Ag_7 cluster is -1.8 kcal/mol, while forming the bond between N2 atom of N_2O and Ag5 atom of Ag_7 cluster. In the intermediate compounds Ag_7N_2O have electrons movement from the silver atom to N_2O group with overall charge of the group is -0.31e^-. Results from establishing pathway of reaction system shows the decomposition of two N_2O molecules directly on Ag_7 cluster formed two products P1 ($2N_2 + O_2$; -5.4kcal/mol), P2 ($N_2 + N_2O_2$; 29.3 kcal/mol) and P3 (N_2 + 2NO; 35.7 kcal/mol) of which the P1 is the main product. This decomposition process occurs in two stages. The first stage releases a N_2 molecules occurs due to two pathways, energy barrier for the most favorable pathway is 10.2 kcal/mol. Decomposition second N_2O molecule on silver cluster continue releasing N_2 and O_2 molecules. This process goes through three different pathway, in terms of energy-second pathway with the energy barrier of 21.1 kcal/mol is the highest priority. Compare the results obtained with the energy barrier of the processes occurring in the gas phase with the lowest energy barrier is 49.7 kcal/mol, indicating the use of Ag_7 cluster catalysis significantly reduce energy barrier the amount of N_2O decomposition process.

3.2.2.2. Indirect decomposition of N_2O molecule by CO molecule on Ag_7 cluster

Phase one respectively adsorption and decomposition of N_2O was studied above in direct response N_2O decomposition on Ag cluster. The second stage is the process of a CO molecule adsorbed on the surface of intermediate compounds that react with Ag_7O after O atoms forming CO_2 and reimbursement catalysts according to the following equation:

$$CO + O \rightarrow Ag_7 + CO_2 + Ag_7$$

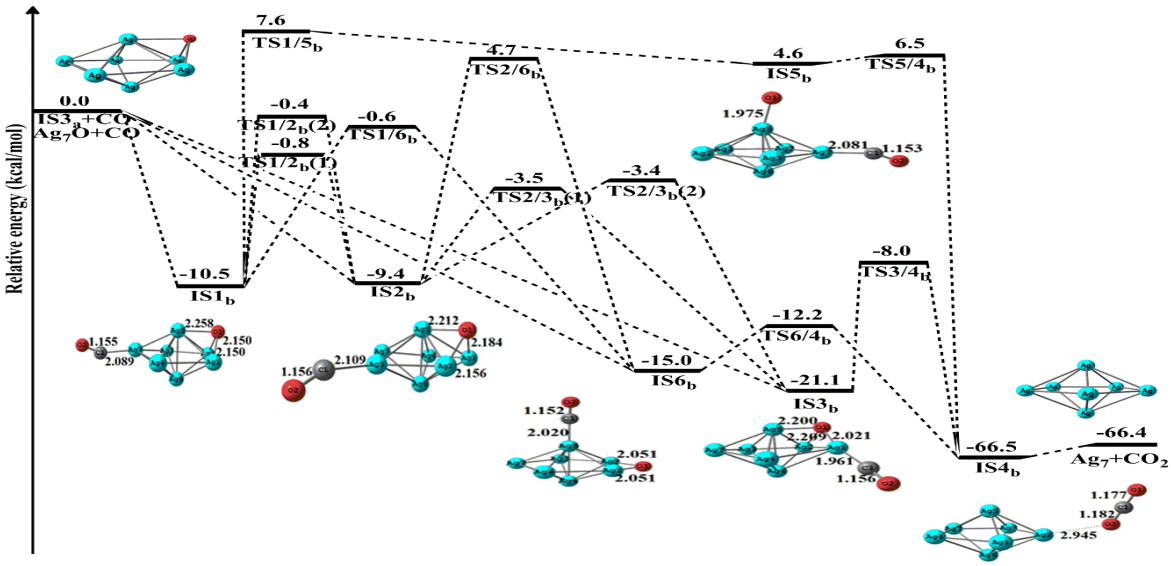


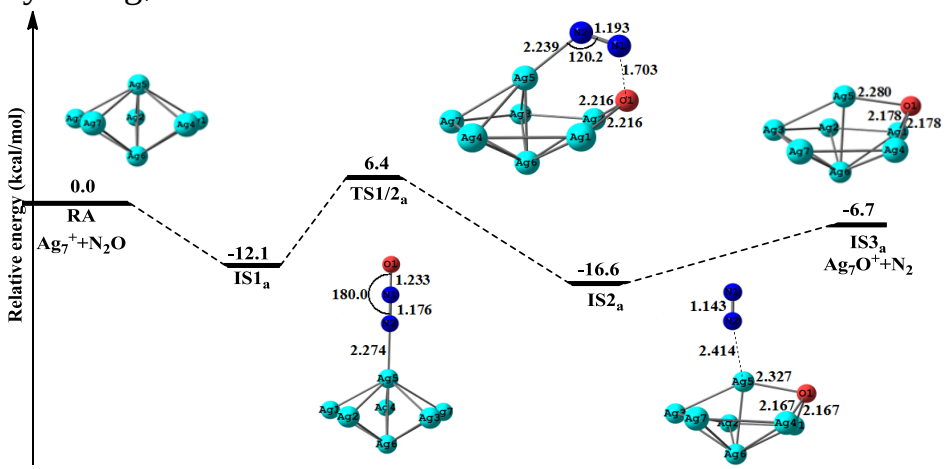
Figure 3.34: The surface potential second reaction stage of the indirect decomposition N_2O by CO molecule on the Ag_7 cluster using BP86 method.

Reaction indirect N_2O decomposition by carbon monoxide on the cluster Ag_7 been studied by density-functional theory in the BP86. Establishing road system reaction reaction mechanism that decomposes N_2O indirectly by carbon monoxide molecules on Ag_7 cluster forming N_2 + CO_2 products. This decomposition occurs in two stages, the first stage of decomposition of N_2O release of a molecule N_2 with energy barrier 10.2 kcal/mol. Phase two adsorbed CO molecules and O atoms react with dispersed cluster releasing a molecule of CO_2. This phase can go through four different reaction lines, fences, power lines corresponding to the most favorable reaction when the CO molecule adsorbed on Ag^5 value of 2.8 kcal/mol. Calculation results show that the first phase is the next decisive phase decomposition process, energy barrier of decomposition process is 10.2 kcal/ mol which shows the breakdown of CO occur indirectly through more favorable.

3.2.3. The catalytic role of Ag_7^+ cluster

3.2.3.1. Direct decomposition of N_2O molecules on Ag_7^+ cluster

Using Density Functional Theory BP86 to study the decomposition of N_2O gas molecule directly on Ag_7^+ cluster.



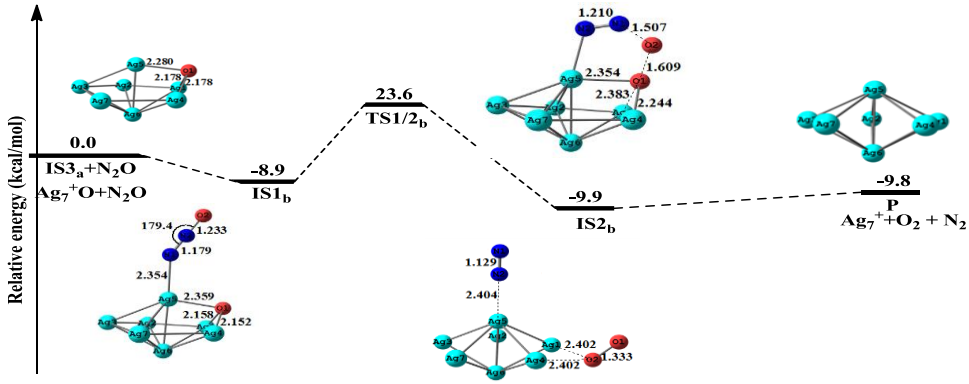


Figure 3.35: The potential energy surface (PES) of direct decomposition N_2O molecules on cation Ag_7^+ cluster using BP86 method

Results of adsorption energy N_2O on the Ag_7 cluster is -1.8 kcal/mol, while forming the bond between N_2 atom of N_2O and Ag5 atom of Ag_7 cluster. This decomposition process occurs in two stages. The first stage releases a N_2 molecules, energy barrier is 18.5 kcal/mol. Decomposition second N_2O molecule on cation silver cluster continue releasing N_2 and O_2 molecules. This process goes through three different pathway, in terms of energy-second pathway with the energy barrier of 32.5 kcal/mol is the highest priority. Compare the results obtained with the energy barrier of the processes occurring in the gas phase with the lowest energy barrier is 49.7 kcal/mol, indicating the use of Ag_7^+ cluster catalysis significantly reduce energy barrier the amount of N_2O decomposition process.

3.2.3.2. Indirect decomposition of N_2O molecule by CO molecules on Ag_7^+ cluster

Phase one respectively adsorption and decomposition of N_2O was studied above indirect response N_2O decomposition on Ag cluster. The second stage is the process of a CO molecule adsorbed on the surface of intermediate compounds that react with Ag_7O^+ after O atoms forming CO_2 and reimbursement catalysts according to the following equation:

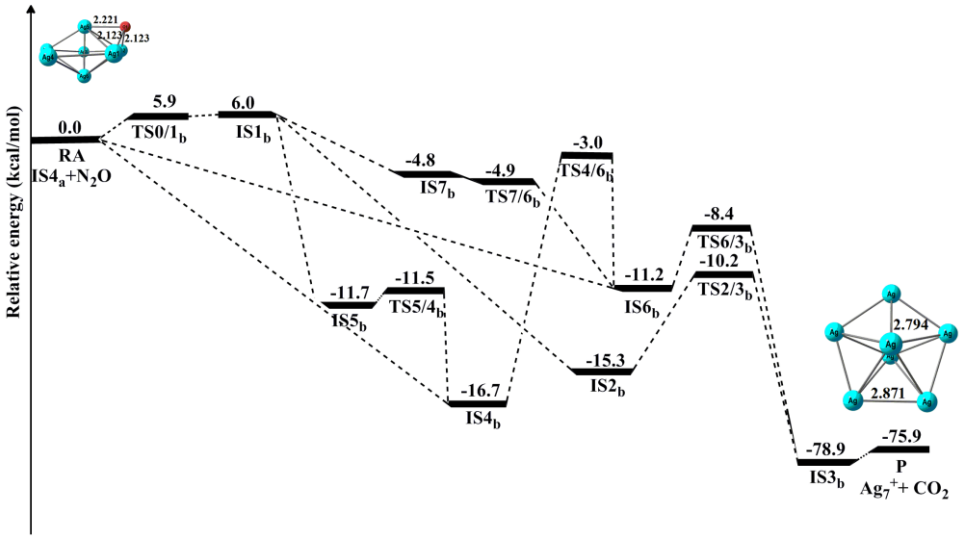


Figure 3.37: The surface potential second reaction stage of indirect decomposition of N_2O by CO molecule on Ag_7^+ cluster using BP86 method

Reaction indirect N_2O decomposition by carbon monoxide on the cluster Ag_7^+ been studied by density-functional theory in the BP86. Establishing road system reaction reaction mechanism that decomposes N_2O indirectly by carbon monoxide molecules on Ag_7^+ cluster forming N_2 + CO_2 products. This decomposition occurs in two stages, the

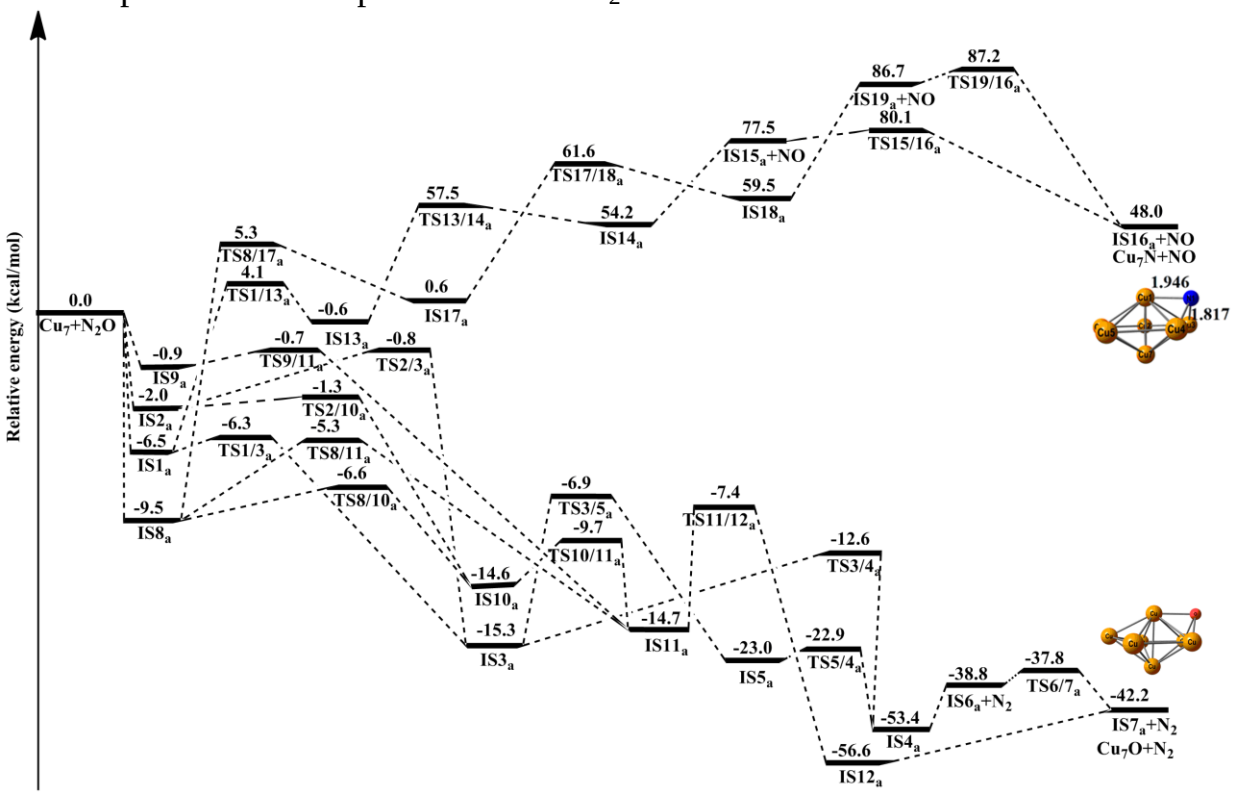
first stage of decomposition of N_2O release of a molecule N_2. Phase two adsorbed CO molecules and O atoms react with dispersed cluster releasing a molecule of CO_2. This phase can go through two different reaction lines, fences, power lines corresponding to the most favorable reaction when the CO molecule adsorbed on Ag[4]. The energy barrier of 2.8 kcal/mol is the highest priority Calculation results show that the first phase is the next decisive phase decomposition process, energy barrier of decomposition process is 18.5 kcal/mol which shows the breakdown of CO occur indirectly through more favorable.

3.2.4. The catalytic role of Cu_7 cluster

3.2.4.1. Direct decomposition of N_2O molecules on Cu_7 cluster

Adsorption of N_2O were surveyed on the durability isomer of Cu_6, Cu_7 and Cu_8, the results obtained are Cu_7 cluster has highest adsorption energy value (-9.5 kcal/mol), higher than Cu_6 (-5.2 kcal/mol) and Cu_8 (-9.3 kcal/mol). So we choose the cluster Cu_7 with geometries D_{5h} doublet spin state to study the direct decomposition of N_2O molecule.

Direct decomposition reaction of two molecules N_2O on Cu_7 catalyst, adsorption energy of N_2O on Cu_7 cluster at favoriable position has value 9.5 kcal/mol. NBO analysis results, the NPA showed that electrons are transferred from the copper atoms of the cluster into NNO group. Bond are formed through the N atom is more favorable. Results from establishing reaction road of system indicates that directly decomposition process two N_2O molecule on Cu_7 cluster made up of three products P1 ($2N_2 + O_2$; 25.4 kcal/mol)), P2 ($N_2O_2 + N_2$; 60.1 kcal/mol) and P3 ($2NO + N_2$; 66.4 kcal/mol) formed the same reactions in the gas phase. Which products P1 include N_2 and O_2 molecules is the main product advantages in terms of energy with the energy barrier is not large. This decomposition occurs in two stages, first one is the adsorption and decomposition of first N_2O molecule.



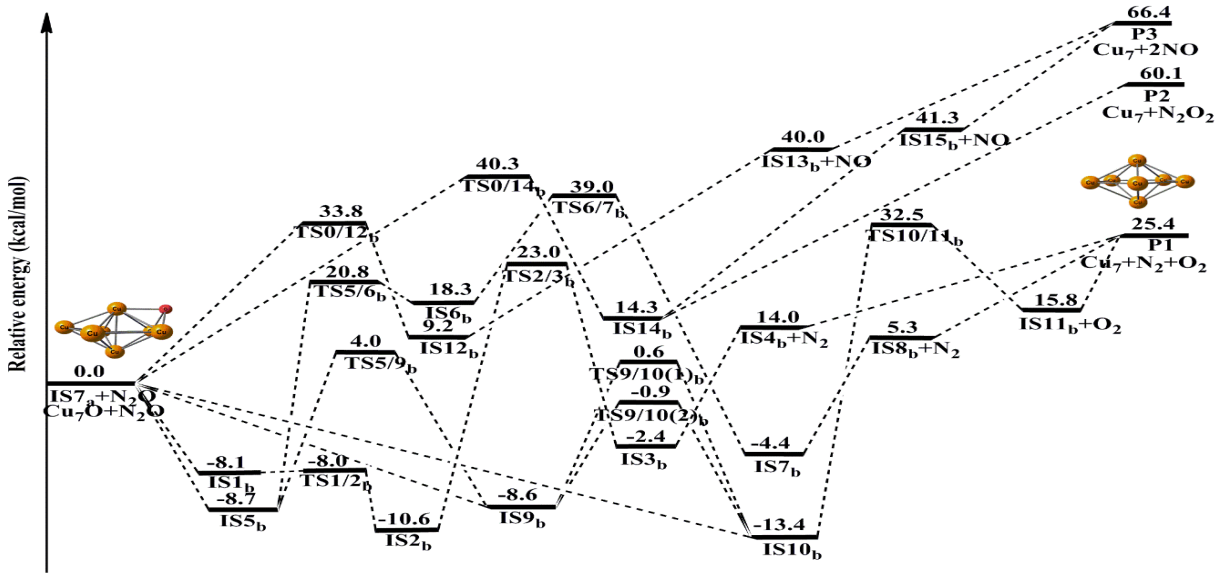


Figure 3.39: The potential energy surface (PES) of direct decomposition N_2O molecules on Cu_7 cluster using BP86 method

Then, the second N_2O molecule adsorbed on Cu_7O and react with O atoms to form three products. The most favorable path derived from adsorption N_2O on Cu(4) and Cu (1) atom and then pass the energy barrier have correlation energy is -12.6 kcal/mol in first stage and 23.0 kcal/mol in the final stage to form the P1 product. Thus, the predict energy barrier is about 33 kcal/mol (less than 50 kcal/mol in the unused catalyst reaction. Meanwhile, forming P2 and P3 have overcome the high energy barrier and correlation of them have great value 60.1 and 66.4 kcal/mol. The calculation results show that the contribution of P2 and P3 products are less important than the P1 in the two N_2O molecules decomposition.

3.2.4.2. Indirect decomposition of N_2O molecule by H_2 molecule on the Cu_7 cluster

Transform harmful emissions into the environment as N_2O quality environmentally friendly by reducing agents such as N_2 and H_2 have been attracting the attention of scientists. However, empirical studies show that the reaction occurs requiring conducted at high temperatures such as in the absence of catalysts to temperature up to 1700-3000K. The study of the role of catalyst in order to find the most favorable path to the reaction occurs is essential.

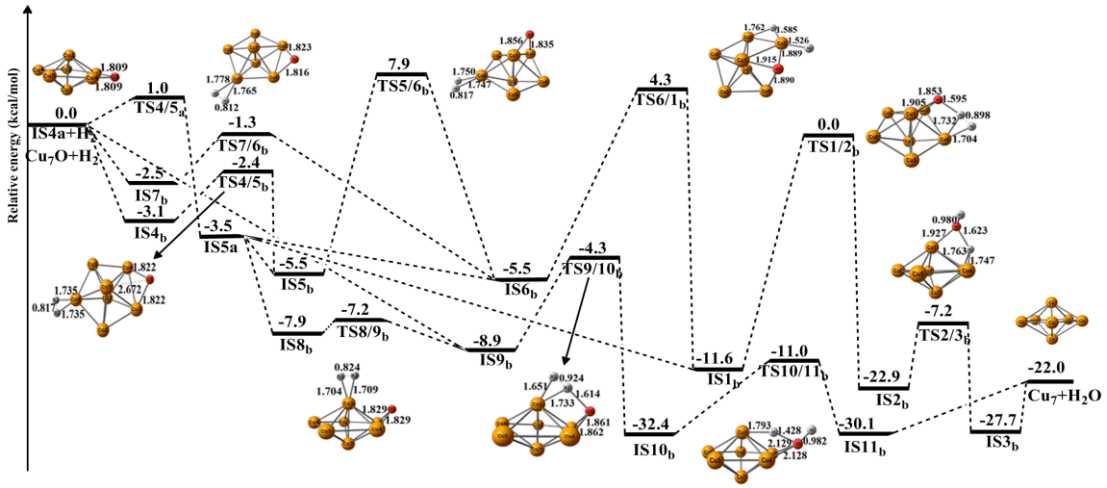


Figure 3.41: The surface potential of the second reaction stage of indirect decomposition of N_2O by H_2 molecule on Cu_7 cluster using BP86 method

Using density-functional method research decomposition N_2O molecule by H_2 molecule on Cu_2 cluster. Since the establishment of sugar reaction system shows the reaction to go through two main stages, the first stage is the process of adsorption and decompose N_2O, obtained N_2 and cluster Cu_7O the energy barrier of the favorable most only 2.7 kcal/mol. The second phase corresponds to the H_2 molecules are adsorbed onto Cu_7O reaction with O atoms to form H_2O and cluster Cu_7 products. The process goes through four different pathway with H_2 adsorption on the Cu atoms of Cu_7O. From the calculated results show that road most preferred reaction with the formation of links between H_2 molecules and Cu^1 atom of Cu_7O, with relative energy of the transition state is -4.3 kcal/mol. Compared with the decomposition direct two molecules N_2O on Cu_7 the use of more gas H2 nature reduction and to make the place more favorable, with a significant reduction in energy barrier and the clearing of energy by the exothermic process in the different stages of the reaction. Thus, the studying mechanism was launched by the mechanism of the reaction decomposes of N_2O molecule by H_2 on cluster Cu_7, suggesting the use of background catalyst cluster Cu_7 significantly reduce the energy barrier of the decomposition. Result shows that the use of cluster catalysis background Cu_7 significantly reduce the energy barrier of the decomposition of N_2O molecule by H_2 molecule.

3.2.4.3. Indirect decomposition of N_2O molecules by CH_4 molecule on the Cu_7 cluster

Similar processes N_2O decomposition reviewed by H_2 on Cu_7 cluster reducing agent to use a reducing agent is that CH_4. From the calculated results show that the reaction occurs through five stages, the first is the adsorption and decomposition of N_2O and N_2 brought an O atom in the cluster dispersed Cu_7 was discussed above. After that happens process a molecule CH_4 adsorbed on the Cu_7O cluster and participate in the reaction with O atom put product Cu_7CH_2 cluster and release a molecule of H_2O. This phase can go through three different road to travel reaction product, the most favorable in terms of energy is derived from sugar reaction CH_4 adsorption on the atom Cu^1 passing $TS1/2_b$. Potential energy surfaces from 3.43 image shows, the response speed of this stage is determined by cleavage of C-H link formed concurrently associated with OH groups make up the H_2O molecule with the energy barrier is 34.3 kcal/mol put product H_2O and Cu_7CH_2 cluster ($IS4_b$) continue to participate in the next stage of the reaction.

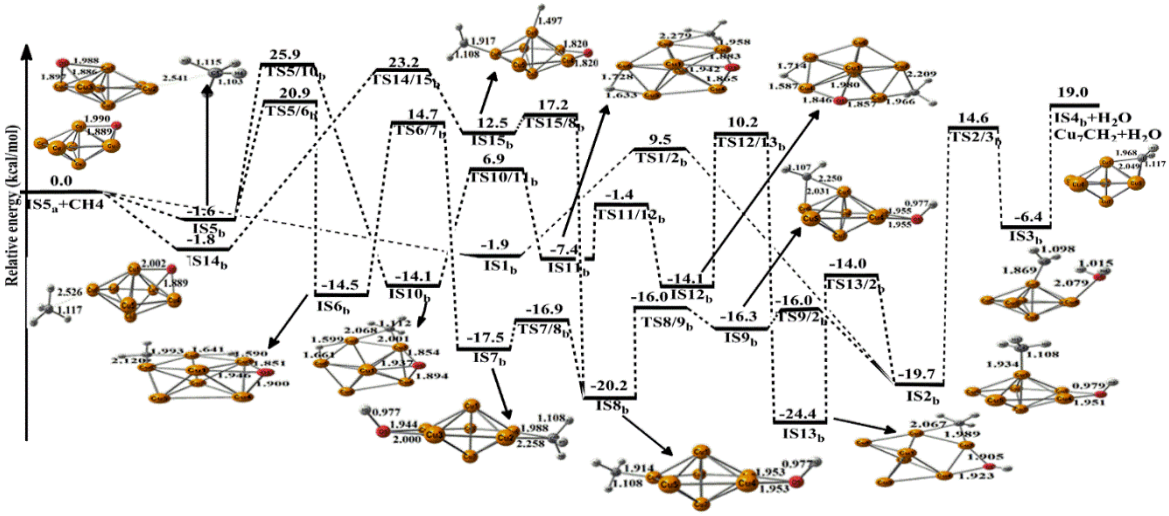


Figure 3.43: The surface potential of the second stage of indirect decomposition of N_2O by CH_4 molecule on Cu_7 cluster using BP86 method

Third phase reactions occurring process the second N_2O molecules adsorbed onto cluster Cu_7CH_2 ($IS4_b$) and then reacts with the CH_2 group formed products. This process occurs in two steps, first the adsorption and break the link N^1-O in N_2O molecule release a molecule of N_2 and O atom dispersed on the cluster Cu_7CH_2. The next step reaction occurs between O atoms and CH_2 group formed two products (H_2O + Cu_7C) and (HCHO + Cu_7).

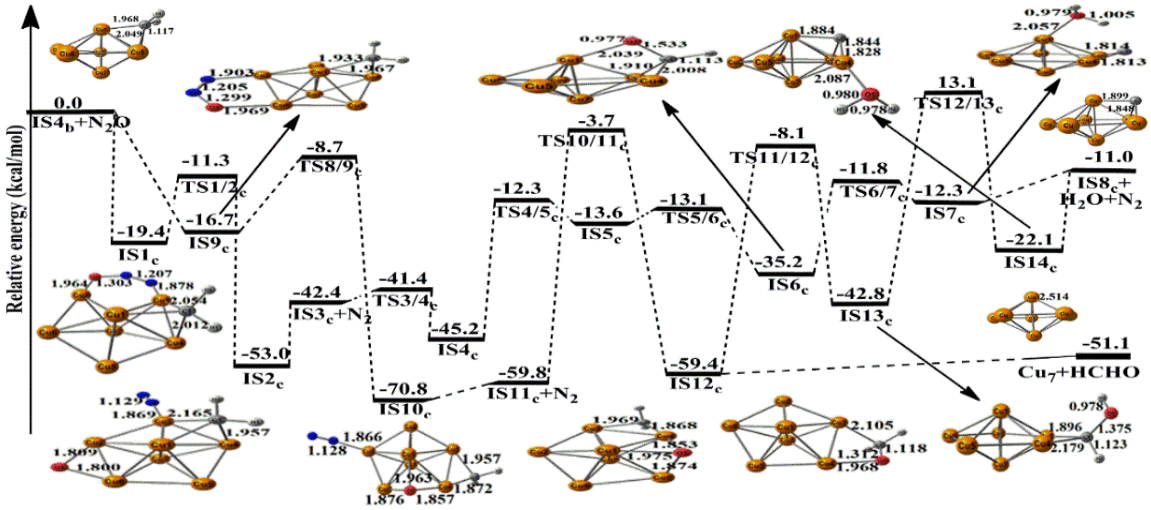


Figure 3.45: The surface potential of the third stage of indirect decomposition of N_2O by CH_4 molecule on Cu_7 cluster using BP86 method

From the calculated results surface potential shows that most compounds, intermediates and transition state for the third stage are energy correlation lower than the parent compound Cu_7CH_2 + N_2O, proves this stage advantages in terms of energy value and low energy energy barrier released in the process of forming intermediate compounds adults. N_2 + H_2O + products formed through two road Cu_7C different reactions, in which the first reaction path more favorable in terms of energy value of 32.9 kcal energy barrier / mol. Besides the N_2 + HCHO + Cu_7 formed with the energy barrier of 56.1 kcal/mol. In terms of energy products more convenient H_2O formed.

The next phase of the reaction occurs according to the equation:

$$N_2O + Cu_7C \rightarrow Cu_7CO + N_2$$

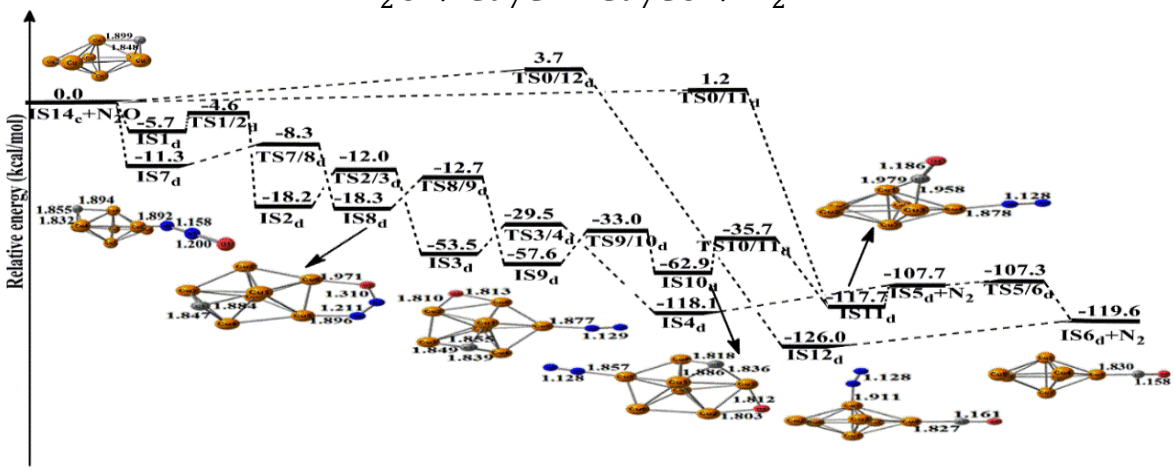


Figure 3.47: The surface potential of the fourth stage of indirect decomposition of N_2O by CH_4 molecule on Cu_7 cluster using BP86 method

Results calculated the potential energy surface for the reaction period Wednesday showed, there are four different reaction lines derived from $IS14_c$ + N_2O N_2 + product

offering Cu_7CO ($IS6_d$). Show in 3.47 figure, the surface world noticed most of the intermediate structure and the transition state energy have low correlation. The reaction rate is determined by the formation of links C-O with energy barrier relatively high approximately 30 kcal/mol, but react to favorable when the energy released by this process have value greater than 54 kcal/mol. Road second reaction most favorable in terms of energy.

The final stage of the decomposition of N_2O with CH_4 phase release of CO_2 and N_2 derived from the adsorbed molecule N_2O to intermediate compounds $IS6_d$ (Cu_7CO) then occurs the decomposition and the reaction of N_2O and CO put product group. This stage occurs through five different sugar reaction results are shown in Figure 3.49.

In this final phase, the results establish the potential energy surface for this period shows that there are five lines derived from Cu_7CO reaction ($IS6_d$) + N_2O taken N_2 + CO_2 + products Cu_7. Most of the intermediates and transition states have low correlation energy, the process can not exceed the energy barrier 25.0 kcal/mol, small steps are mainly created an exothermic process events for the reaction to occur. Road second reaction is energetically favorable with the highest energy barrier of 19.8 kcal/mol.

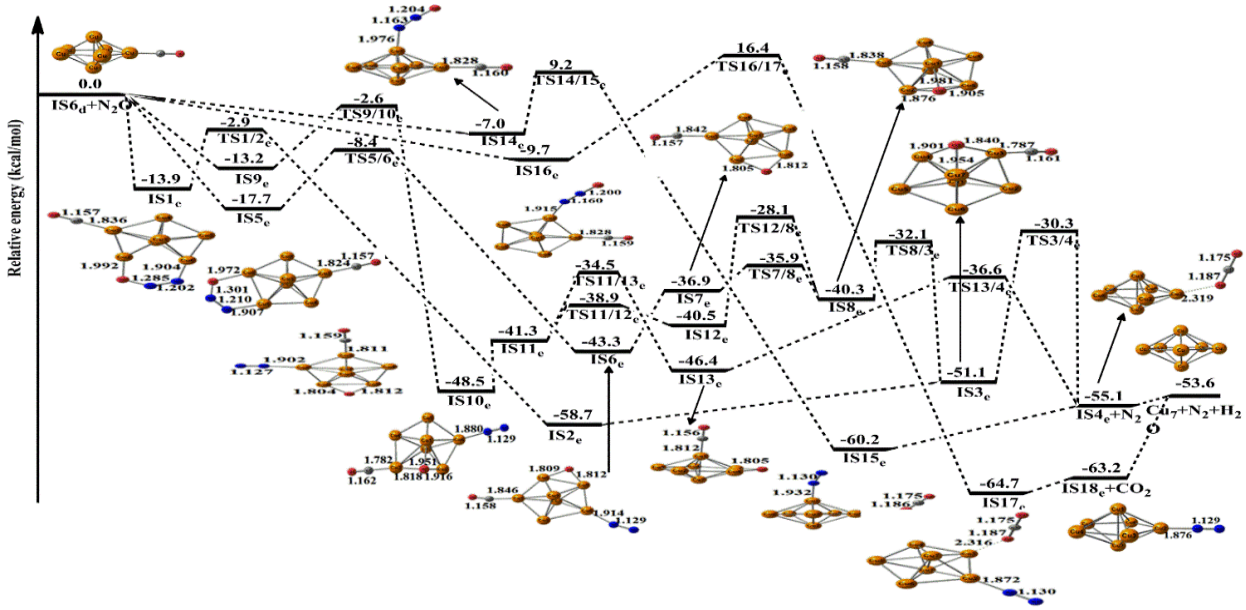


Figure 3.49: The surface potential of the fifth stage of indirect decomposition of N_2O by CH_4 molecule on Cu_7 cluster using BP86 method

N_2O decomposition process by CH_4 gas in the cluster Cu_7 undergo five stages. Calculation results obtained by using the method of density-functional theory (DFT) with the BP86 with the basic function cc-pvdz-pp for Cu and aug-cc-pvdz times for the elements N, O, C and H. We have established the potential energy surface for different stages, the process of bringing the two products P1 (N_2 + H_2O + CO_2) and P2 (N_2 + H_2O + HCHO) in which the secondary products two less priority than the energy barrier P1 with great value of 56.1 kcal/mol is not favorable in terms of energy. For products P1, phase occurs most difficult second stage corresponding molecular processes CH_4 adsorption on cluster Cu_7O reaction and liberated H_2O and Cu_7CH_2 energy barrier of the road favorable response especially 34.3 kcal/mol and correlation energy of high-energy compounds. Besides the next phase put on products with low energy barrier, and the process of releasing a large amount

of heat to facilitate the reaction process occurs. Thus the use of cluster catalysts and agents CH_4 Cu_7 create favorable conditions for the N_2O decomposition process than in the gas phase.

Comment

Study mechanism of N_2O decomposition in gas phase and on metallic clusters are performed using BP86 method and suitable basis set. Adsorption capacity of N_2O on clusters at different position is predicted via NBO analysis. Adsorption energy of N_2O on Ag_7, Ag_7^+ and Cu_7 clusters is –1.8 kcal/mol, -12.1 kcal/mol and -9.5 kcal/mol, respectively. Binding between N^2 atom of N_2O and M^5 of M clusters (M=Ag_7, Ag_7^+, Cu_7) is formed by electron movement to N_2O group in intermediate substance MN_2O. Results of establishment reaction pathways indicate that N_2O is decomposed into two products are N_2 and O_2 molecules. This decomposition occurs via two stages. First stage is formation one N_2 molecular and one O atom are dispersed on metallic clusters. Second stage is adsorption of one N_2O molecular react with O atom to form N_2 and O_2 via different reaction pathways. Energy of the most favorable reaction pathway is shown in Table 3.13.

Table 3.13: Adsorption energy and relative energy of transition state in direct decomposition of N_2O molecules on the cluster using BP86 method

Clusters	Stage	$E_{adsorption}$ (kcal/mol)	$E_{relative}$ (kcal/mol)
Gas phase	1_g		49,0
	2_g		90,1
Ag_7	1_{tt}	-1,8	8,4
	2_{tt}	-2,0	26,4
Ag_7^+	1_{tt}	-12,1	6,4
	2_{tt}	-8,9	23,6
Cu_7	1_{tt}	-6,5	-12,6
	2_{tt}	-8,1	23,0

i_g: the i stage of direct decomposition of N_2O molecules in gas phase.

i_{tt}: the i stage of direct decomposition of N_2O molecules on cluster.

Obtained results indicate that the most favorable pathways have energy barriers are 10.2 kcal/mol, 18.5 kcal/mol and 2.7 kcal/mol respect to Ag_7, Ag_7^+ and Cu_7 clusters. In second stage, favorable pathways has energy barrier is 21.1 kcal/mol, 32.5 kcal/mol, 33.6 kcal/mol respect to Ag_7, Ag_7^+ and Cu_7 clusters. This meaning second N_2O molecular decomposition is more difficult than first molecular. These results are suitable with experiment data of Kapteijn et al. and theoretical data is calculated by Liu et al. Kapteijn et al. released that O_2 desorption occur in about 673K and second N_2O decomposition hard occur. Liu et al. studied N_2O dec

omposition mechanism on binuclear Cu-ZSM-5 zeolite and released that energy barriers of two N_2O molecules dissociation is 47.2 kcal/mol and 63.9 kcal/mol, respectively. Where suggest that steps breakdown N-O bond of N_2O play decided role in entire process. Hence, obtained results proved suitability for our theoretical study to experimental data and previous theoretical calculations. Based on Table 3.13, we release that Ag_7, Ag_7^+ and Cu_7 clusters double reduce energy barrier value of N_2O

decomposition. In which, Cu_7 cluster is the most favorable catalyst because of lowest relative energy is -12.6 kcal/mol and 23.0 kcal/mol in two stages, respectively.

Besides, N_2O and CO concurrent decomposition on Ag_7 and Ag_7^+; N_2O and H_2 or CH_4 on Cu_7 also obtained remarkable results. Concurrent decomposition process occurs via two stages. First stage is N_2O adsorption and dissociation to form N_2 and intermediate substance MO (M=Ag_7, Ag_7^+, Cu_7). This stage is similar to N_2O decomposition on metallic cluster. The difference is adsorption of CO, H_2 and CH_4 onto cluster in second stage. Energies of the most favorable reaction pathway are shown in Table 3.14.

Table 3.14: Adsorption energy, energy barrier and relative energy of transition state in concurrent decomposition of N_2O and CO, H_2 CH_4 on clusters

Clusters	Stage	$E_{adsorption}$ (kcal/mol)	$E_{relative}$ (kcal/mol)
CO/Ag_7	2_{tt}	-2,0	26,4
	2_{gt}	-15,0	-12,2
CO/Ag_7^+	2_{tt}	-8,9	23,6
	2_{gt}	-11,2	-8,4
H_2/Cu_7	2_{tt}	-8,1	23,0
	2_{gt}	-7,9	-11,0
CH_4/Cu_7	2_{gt}	-1,9	14,6
	3_{gt}	-19,4	-11,3
	4_{gt}	-5,7	-4,6
	5_{gt}	-13,9	-2,9
Gas phase	1_g		49,0
	2_g		90,1

i_{gt}: the i stage of indirect decomposition of N_2O molecules on cluster.

Concurrent decomposition N_2O and CO, H_2 or CH_4 favorable occur with energy barrier is remarkable reduced when compare with N_2O decomposition. In detail, when add CO in reaction, relative energy of transition state is -12.2 kcal/mol and -8.4 kcal/mol, remarkable lower when compare with case unused CO is 26.4 kcal/mol and 23.6 kcal/mol on Ag_7 and Ag_7^+ clusters, respectively. In the case of concurrent decomposition N_2O with CH_4 or H_2 on Cu_7, the difference of energy barriers is trivial but it has energy offset. Relative energies of concurrent decomposition N_2O with H_2 is -11.0 kcal/mol; with CH_4 is 14.6 kcal/mol (remarkable reduce when compare with 23.0 kcal/mol).

Therefore, quantum chemical computation improve our knowledge about N_2O decomposition mechanism and concurrent decomposition mechanism N_2O and CO, H_2 or CH_4 to form N_2, O_2, H_2O, CO_2 catalyzed by silver and copper clusters. Using metallic clusters as catalyst force decomposition process. This work shows that potential application of silver and copper clusters to produce catalytic materials reduce environmental pollution.

CONCLUDE

Using density functional theory BP86 with suitable basis set to study structures and some electron properties of metallic and bimetallic clusters. Based on study results about

structure and electron properties of metallic clusters, we chose Ag_7, Ag_7^+ and Cu_7 to investigate catalytic role of clusters for N_2O decomposition. This work require to establish potential energy surface in detail based on geometry optimization, calculation of single point energy, zero point energy for about 250 components include reactants, intermediate substances, transition states and products for N_2O direct decomposition and indirect decomposition with agent as CO, H_2, CH_4 in gas phase and on Ag_7, Ag_7^+, Cu_7 clusters. Some obtained conclusions are:

1. Geometry optimization more than 300 structures of Ag_n clusters (n = 2-20) and bimetallic clusters of silver Ag_nM (M = Fe, Co, Ni, Cu, Au, Pd, Cd; n = 1 -9) and determine structure parameters, single point energies and vibration frequencies of each cluster. This is basic to obtain 90 durable structures. Derived from average binding energies of clusters, the stability increase when cluster size (n) increase. Cu and Au atoms doped make stability of clusters increase.

2. Calculation results of first ionization energy of Ag_n clusters and UV-VIS spectroscopy of some cluster Ag_n (n = 4, 6, 8) are good suitable with experiment and previous results. This proved truth of chosen method.

3. Determine magnetic properties of bimetallic clusters Ag_nM (M=Fe, Co, Ni; n=1–9). Results indicate that Fe, Co and Ni doped make magnetic property of clusters increase. In which, Fe doped make spin magnetic moment values of silver clusters increase, special Ag_3Fe. Spin magnetic moment major concentrate on M atom and (n-1)d atomic orbital of M.

4. Calculated results about energies of E_{gap} of durable structures with Ag_nM clusters indicate that transition metallic doped make E_{gap} of some cluster decrease, special Ag_3M và Ag_8M (M=Cu, Ag, Au, Pd, Cd). Calculated UV-Vis spectroscopy has maximun absorption region in range wavelength from 310 to 490 nm. Excited wavelength major contribute from HOMO to LUMO transform.

5. The results indicate that for direct decomposion of N_2O molecules on Ag_7, Ag_7^+ and Cu_7 clusters occur via two stages. The breakdown N-O bonding play important role in each reaction pathway. When using catalyst clusters, the energy barrier was significantly reduced compared to that in the gas phase, in which the decomposition reaction on the Cu_7 cluster was most favorable in terms of energy.

6. The indirect decomposition of N_2O molecule by some agent as CO, H_2, CH_4 on metallic clusters occur via two stages. First stage includes adsorption and decomposition of N_2O to form N_2 molecule and O atom is dispersed on the cluster. The second stages is step that further adsorbs CO, H_2 and CH_4 on the Ag_7, Ag_7^+ and Cu_7 clusters, and then reacts with O atoms to form CO_2, H_2O and CO_2. At the second, stage the reaction is very favorable in terms of energy, which is most advantageous for CO. Thus, the results show that silver and copper clusters are potentially catalytic materials for decomposition of agent which cause environmental pollution as N_2O, CO, H_2 và CH_4.