Annexure-V

PROGRESS REPORT

1. Project Title: **Computational Studies of Bare and Zeolite-Supported Palladium Nanoclusters and their Application in Catalysis.**	DST No: SR/S1/PC-24/2007
2. PI (Name & Address): Ramesh C. Deka, Department of Chemical Sciences, Tezpur University, Napaam, Tezpur – 784 028, ASSAM, INDIA	Date of Birth: 01-01-1970
3. Co-PI (Name & Address): N/A	Date of Birth

4. Broad area of Research: Theoretical Chemistry

   4.1 Sub Area: Nano clusters, Computational Chemistry

5. Approved Objectives of the Proposal :
   - (i) To investigate structural, electronic and magnetic properties of Pd_n (n = 1, 13) clusters using density functional methods. Stability of the clusters will be determined from their relative energies, binding energies, bond energies etc.
   - (ii) To study the adsorption of CO on the energetically most stable isomers of each of the Pd_n clusters.
   - (iii) To explore the bonding of CO on small palladium clusters in different oxidation states.
   - (iv) To understand the interplay between various factors that influence the properties of supported palladium clusters – oxidation state of the palladium atoms (charge of the cluster), cluster size, interaction with the support.
   - (iv) To explore how a support affects the structure and adsorption properties of these palladium clusters using zeolite as a support.
   - (v) To compare the obtained results with experiment, the vibrational frequencies of CO at various positions of the studied clusters, shifts of the core level binding energy of Pd atoms, and optical spectra of these systems will be simulated.

Date of Start: 28.1.2009	Total cost of Project: Rs. 30,65,400/-
Date of completion: 31.3.2013	Expenditure as on : 31-3-2013 Rs. 30,55,802/-

6. Methodology :

(i) Density functional calculations on gas phase palladium clusters and their interaction with CO will be carried out by using local density approximation (LDA) and generalized gradient approximation (GGA). At the LDA level, we intend to use the Vosko-Wilk-Nusair (VWN) local correlation functional together with the DNP basis functions. The VWN local correlation functional is the Vosko-Wilk-Nusair parameterization of Ceperley and Alder's electron gas Monte Carlo data, which can be used successfully to predict the cluster structure. The DNP basis functions are the double numerical atomic orbitals augmented by polarization functions, i.e., functions with angular momentum one higher than that of the highest occupied orbital in the free atom. For comparison, some calculations will be repeated by the generalized gradient approximation (GGA) using the Becke-Lee-Yang-Parr (BLYP) functional. All-electron calculations with scalar relativistic corrections will be used. Fine grid mesh points will be employed for the matrix integrations. Self-consistent field procedures will be done with a convergence criterion of 10^{-6} a.u. on the energy and electron density. These calculations will be carried out using the density functional package DMOL[3].

(ii) The Embedded cluster calculations will be carried out with the scalar-relativistic variant of the linear combination of Gaussian-type orbitals fitting-function density functional method (LCGTO-FF-DF) as implemented in the program ParaGauss or using the program ChemShell. The program ParaGauss is well suited for the proposed modeling as has been shown with a series of applications of similar flavor, Error! Bookmark not defined. some of which have already been mentioned above. The zeolite support can be modeled with the hybrid quantum mechanics / molecular mechanics (QM/MM) cluster embedding method denoted as Elastic Polarizable Environment (EPE). This method permits simultaneously high-level density functional modeling of the active site (the adsorbed metal cluster and a part of the oxide support in its vicinity) and features mechanical and electrostatic interactions between the QM region and its MM environment in mutually self-consistent fashion, even including long-range electrostatic interactions due to the Madelung field set up by distant parts of the zeolite support.

7. Salient Research Achievements:

7.1 Summary of Progress

The project started in January 2009. In last four years we have determined various isomers of Pd_n and Au_n (n=2-13) clusters using density functional theory. The lowest energy structures of Pd_n and Au_n clusters are shown in Figure 1. The most stable clusters, Pd_4 and Au_6, obtained from DFT calculations are chosen to investigate two important aspects of catalysis, namely CO oxidation and hydrogen spillover. We studied various adsorption modes of CO on neutral, cationic and anionic Pd_n (n=1-7) and Au_6 cluster. From the results, it is observed that the binding of CO molecule to neutral and cationic palladium clusters takes place via 1-, 2- and 3-fold coordination. On the other hand, only terminal adsorption of CO.

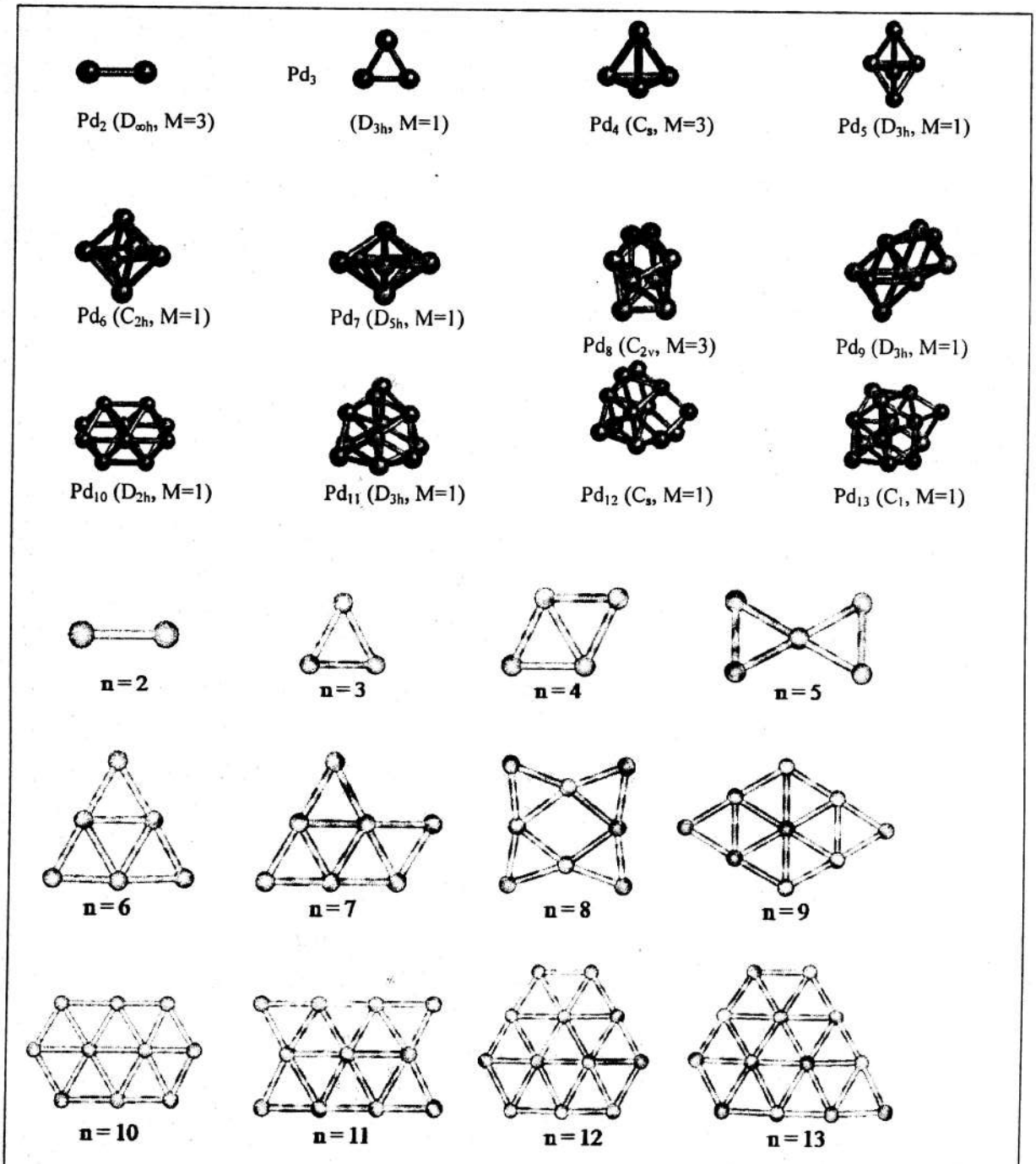

Figure 1: Lowest energy optimized structures of neutral Pd_2–Pd_{13} and Au_2–Au_{13} clusters.

molecule is possible in anionic clusters barring bridging adsorption in Pd_7^- cluster. In this study, we have examined two different spin multiplicities (M=1 and 3) for all the isomers of each cluster size of the neutral clusters. For cationic and anionic clusters, the isomers of each cluster size have been fully optimized in spin multiplicities, M=2 and 4.

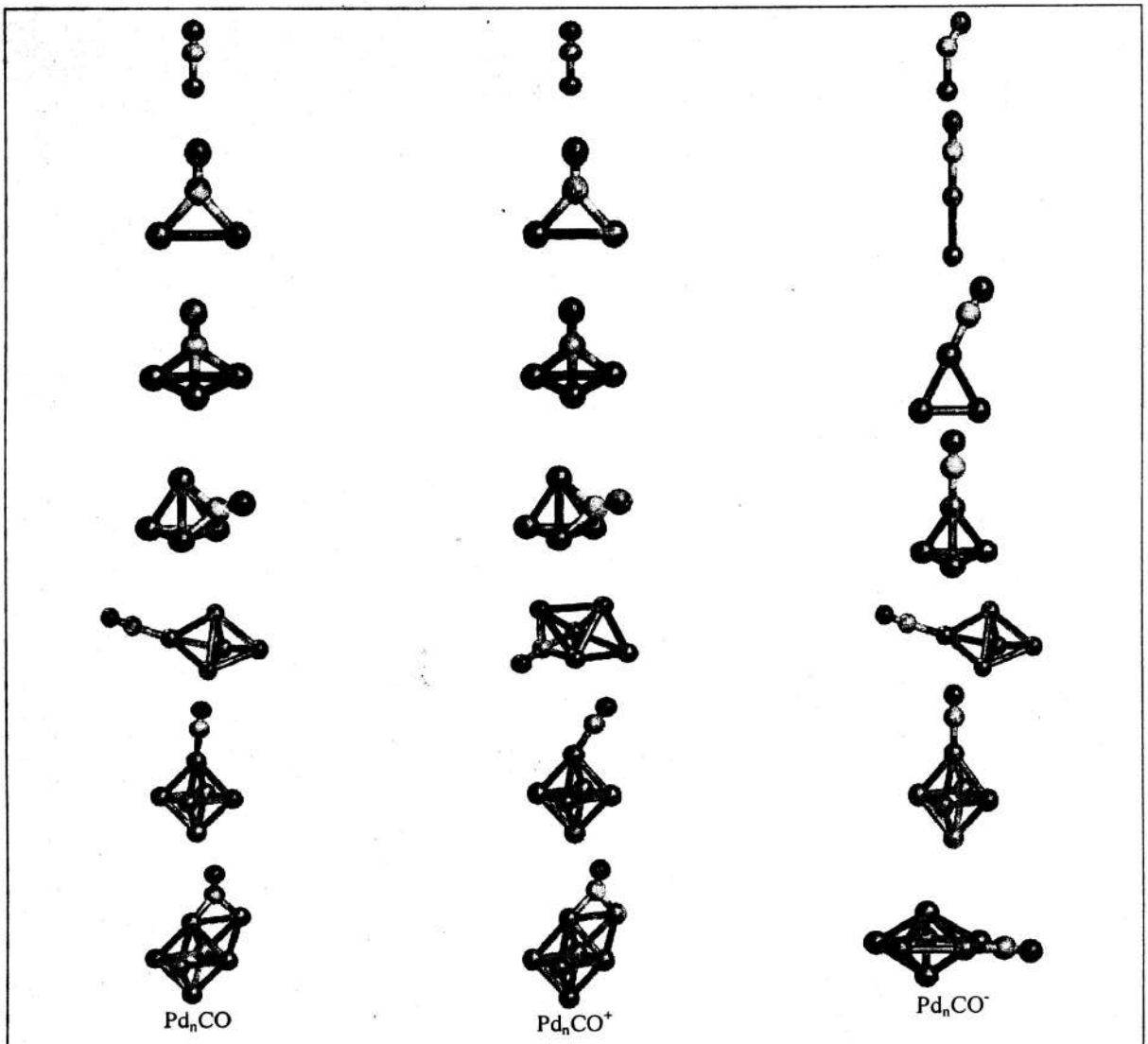

Figure 2: Optimized structures for the most stable geometries of Pd_n^qCO (q=0, 1 and -1, n=1−7) clusters. Blue, gray and red spheres represent palladium, carbon and oxygen atoms, respectively.

The elongation of Pd–Pd bond lengths of the bare clusters upon CO adsorption shows that there is a bonding interaction between the cluster and the CO molecule.The resulting most stable structures of palladium monocarbonyl complexes are shown in Figures 2.We also investigated the adsorption sites of different forms of oxygen (O_2, 2O, O) as well as their co-adsorption with CO on neutral, cationic and anionic Pd_4 clusters using DMol^3 program. For all the clusters, the dissociative adsorption of oxygen (2O) sitting on Pd bridge sites is preferred. Pre-adsorption of O_2 is found to affect the adsorption geometry as well as the binding energy of CO in the co-adsorption complexes. Binding energies of both O_2 and CO are higher in anionic Pd_4 cluster followed by cationic and neutral clusters. However, binding energies of O_2 or CO in the co-adsorption complexes follow the trend: anionic> neutral> cationic Pd_4 clusters. Based on these observations, oxygen adsorbed anionic

palladium cluster is found to be more reactive towards CO followed by neutral and cationic clusters. DFT studies on the co-adsorbate combinations, including O_2+CO, 2O+CO and O+CO and O+CO_2 on neutral, cationic and anionic Pd_4 clusters revealed the possible intermediates of: (1) $Pd_4+O_2+CO \rightarrow Pd_4O+CO_2$, (2) $Pd_4+2O+CO \rightarrow Pd_4O+CO_2$ and (3) $Pd_4+O+CO \rightarrow Pd_4+CO_2$ reactions. The results indicate that Pd_4^+ and Pd_4 are more effective for catalyzing CO in comparison with Pd_4^-. It is further observed that dissociated oxygen is a superior oxidant for CO oxidation on Pd_4^q (q=0, 1, -1) than molecular and atomic oxygen.

Zeolite supported Gold cluster:

Density Functional Theory (DFT) calculations on oxygen adsorption over gas phase and faujasite supported Au monomer has been studied using hybrid quantum mechanics/molecular mechanics method, SIMOMM (Surface Integrated Molecular Orbital Molecular Mechanics) implemented in GAMESS package. Three different oxidation states of Au (0, +1, +3) and three different adsorption modes viz. top, bridge and dissociative adsorption of oxygen have been considered in our calculations. Red shift in the ν_{O-O} value from that in gas phase O_2 indicates activation of O_2 upon adsorption over faujasite supported gold monomer. The activation of O_2 is an important step in the catalytic oxidation of CO. The presence of adsorbed O_2 increases the interaction of the Au monomer with the faujasite support. The bridged mode of O_2 adsorption is found to be more favorable in neutral Au while both bridged and dissociative modes are favorable in singly charged Au and only the dissociative mode in Au^{3+} (Figure 3).

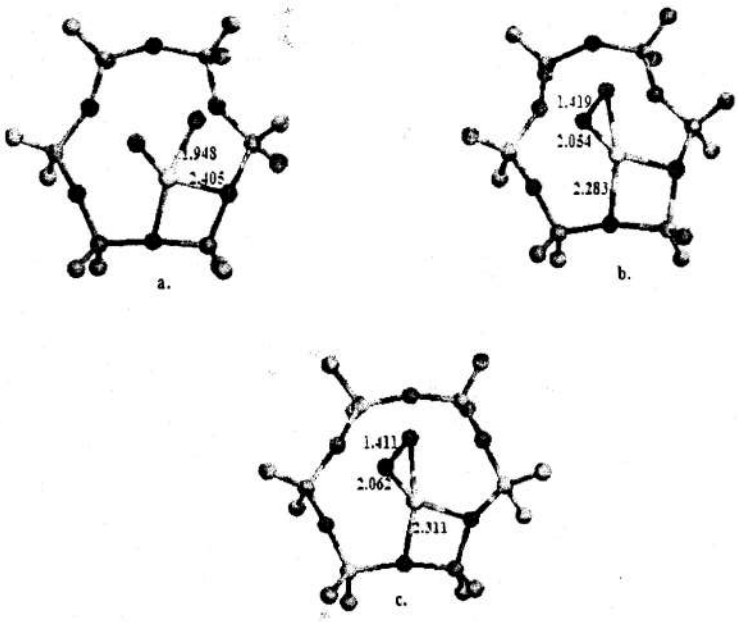

Figure 3: Optimized structures of O_2 adsorbed (dissociative coordination) on faujasite supported Au monomer; a. Au^0-O_2/FAU, b. Au^+-O_2/FAU, c. Au^{3+}-O_2/FAU

7.2 New Observations:

Pd_4 and Au_6 are found to very stable cluster. From the catalytic oxidation of CO with O_2, it was found that Pd_4 can be a very effective catalyst for CO oxidation.

Stability of metal clusters increases due to reversed hydrogen spillover from zeolite supports.

Our study on O_2 adsorption on faujasite supported Au monomer in three different oxidation states (0, +1, +3) reveals activation of O_2 indicated by the elongation of O-O bond length and corresponding red shift in the ν_{O-O} from the value in gas phase free O_2. Activation of O_2 is an important step in the catalytic oxidation of CO.

7.3 Innovations:
Method to design cluster-support interaction.

7.4 Application Potential:

7.4.1 Long Term

- Catalysts for CO oxidation and NO reduction.
- Direct synthesis of H_2O_2 from H_2 and O_2
- Propylene epoxidation
- Water to Gas Shift Reactions ($CO + H_2O \rightarrow CO_2 + H_2$)

7.4.2 Immediate

CO oxidation on Pd_4 cluster

7.5 Any other **N/A**

8. Research work which remains to be done under the project (for on-going projects) **N/A**

Ph.Ds Produced no: 2	Technical Personnel trained: Nil	Research Publications arising out of the present project: 29

List of Publications from this Project (including title, author(s), journals & year(s)

(A) Papers published only in cited Journals (SCI)

1. Nabanita Saikia, Anupam Nath Jha and **Ramesh Ch. Deka**, Dynamics of Fullerene Mediated Heat Driven Release of Drug Molecules from Carbon Nanotubes, ***J. Phys. Chem. Lett. 4 (2013) 4126-4132.***
2. Nabanita Saikia and **Ramesh C. Deka**, *Ab initio* study on the noncovalent adsorption of camptothecin anticancer drug onto graphene, defect modified graphene and graphene oxide, *J. Comput. Aided. Mol. Design. 27 (2013) 807-821.*
3. Pawan Chetri, **Ramesh Ch. Deka** and Amarjyoti Choudhury, Structural and electronic properties of stable Li_n (n=2-10) clusters: A density functional study, ***Physica B 430 (2013) 74-80.***
4. Nabanita Saikia, Anupam Nath Jha and **Ramesh Chandra Deka**, Interaction of pyrazinamide drug functionalized carbon and boron nitride nanotubes with pncA protein: a molecular dynamics and density functional approach, ***RSC Advances 3 (2013) 15102-15107.***
5. Kusum K. Bania, Galla V. Karunakar, Kommuru Goutham and **Ramesh Chandra Deka**, Enantioselective Henry Reaction Catalysed by "Ship in a Bottle" Complexes, ***Inorg. Chem. 52 (2013) 8017-8029.***
6. Kusum Kumar Bania and **Ramesh Chandra Deka**, "Zeolite-Y Encapsulated Metal Picolinato Complexes as Catalyst for Oxidation of Phenol with Hydrogen Peroxide" ***J. Phys. Chem. C, 117 (2013) 11663-11678.***
7. Nabanita Saikia, Sanchaita Rajkhowa and **Ramesh Chandra Deka**, Density functional and molecular docking studies towards investigating the role of single-wall carbon nanotubes as nanocarrier for loading and delivery of pyrazinamide antitubercular drug onto pncA protein, ***J. Comput. Aided. Mol. Design., 27 (2013) 257-276.***
8. Nabanita Saikia and **Ramesh Ch. Deka**, Density functional study on the adsorption of isoniazid drug onto pristine and B-doped single wall carbon nanotubes, ***J. Mol. Model. 19 (2013) 215-226.***
9. Nabanita Saikia and **Ramesh Ch. Deka**, A comparison of the effect of nanotube chirality and electronic properties on the $\pi - \pi$ interaction of single-wall carbon nanotubes with pyrazinamide antitubercular drug, ***Int. J. Quantum Chem. 113 (2013) 1272-1284.***
10. Nabanita Saikia and **Ramesh Ch. Deka**, First principles study on the boron-nitrogen domains segregated within (5,5) and (8,0) single-wall carbon nanotubes: Formation energy, electronic structure and reactivity, ***Comput. Theor. Chem. 996 (2012) 11-20.***

11. Kusum Bania and **Ramesh Ch. Deka**, Experimental and Theoretical Evidence for Encapsulation and Tethering of 1, 10 Phenanthroline Complexes of Fe, Cu and Zn in Zeolite-Y, ***J. Phys. Chem. C 116 (2012) 14295-14310.***
12. Subhi Baishya and **Ramesh Ch. Deka**, Exploring Structures, Electronic and Reactivity Properties of Au_6H_n (n=1-12) clusters: A DFT approach, ***Comput. Theor. Chem. 1002 (2012) 1-8.***
13. Nabanita Saikia, Swapan K. Pati and **Ramesh Ch. Deka**, First principles calculation on the structure and electronic properties of BNNTs functionalized with isoniazid drug molecule, ***Applied Nanoscience 2 (2012)389-400.***
14. Ajanta Deka and **Ramesh Chandra Deka**, A density functional study on equilibrium geometries, stabilities and electronic properties of Au_5Li binary clusters, ***Applied Nanoscience 2 (2012) 359-364.***
15. **Ramesh Ch. Deka**, Subhi Baishya, Density Functional Investigation of Reverse Hydrogen Spillover on Zeolite Supported Pd_6 and Au_6 Clusters, ***Catal. Today 198 (2013) 110-115***
16. Kusum K. Bania, Dipsikha Bharali, B. Viswanathan, **Ramesh Ch. Deka**, Enhanced Catalytic Activity of Zeolite Encapsulated Fe(III) Schiff Base Complex for Oxidative Coupling of 2-Napthol, ***Inorganic Chemistry 51 (2012) 1657-1674.***
17.
18. Bulumoni Kalita and **Ramesh C. Deka**, Reaction intermediates of CO oxidation on gas phase Pd_4 clusters: A density functional study, ***J. Am. Chem. Soc.*** **131 (2009) 13252-13254.**
19. Subhi Baishya and Ramesh C. Deka, DFT/MM studies on activated adsorption of oxygen on zeolite supported gold monomer, ***J. Chem. Phys. 135 (2011)244703.***
20. Kusum Bania and **Ramesh Ch. Deka**, Influence of zeolite framework on structure, properties and reactivity of cobalt phenanthroline complex: A combined experimental and computational study, ***J. Phys. Chem. C 115 (2011) 9601-9607.***
21. Nabanita Saikia and **Ramesh Ch. Deka**, Density functional calculations on adsorption of 2-methylheptylisonicotinate antitubercular drug onto functionalized carbon nanotube, ***Comput. Theor. Chem. 964 (2011) 257-261.***
22. Nabanita Saikia and **Ramesh Ch. Deka**, Theoretical study on pyrazinamide adsorption onto covalently functionalized (5, 5) metallic single-walled carbon nanotube, ***Chem. Phys. Lett.,500 (2010) 65.***
23. Bulumoni Kalita and **Ramesh Ch. Deka**, Nature of CO and NO interactions with Pd-H-ZSM-5 catalyst: A comparative study of DFT based cluster and ONIOM methods, ***Catalysis Letters 140 (2010) 205.***

26. Ajanta Deka, **Ramesh C. Deka** and Amarjyoti Choudhury, Adsorption of CO on gas phase and zeolite supported gold monomers: A computational study, ***Chem. Phys. Lett.* 490 (2010) 184-188.**

27. Bulumoni Kalita and **Ramesh Ch. Deka,** Adsorption of CO on oxygen preadsorbed neutral and charged gas phase Pd_4 clusters: A density function study, ***J. Comput. Chem. 31 (2010) 2476-2482.***

28. Bulumoni Kalita and **Ramesh C. Deka**, Reaction intermediates of CO oxidation on gas phase Pd_4 clusters: A density functional study, ***J. Am. Chem. Soc.* 131 (2009) 13252-13254.**

29. Bulumoni Kalita and **Ramesh C. Deka,** Investigation of reverse-hydrogen spillover on zeolite-supported palladium tetramer by ONIOM method, ***Journal of Physical Chemistry C,* 113 (2009) 16070-16076.**

Major Equipment (model and Make)

Sanctioned list	Procured (Yes/No) Model & make	Cost (Rs. In lakhs)	Working (Yes/No)	Utilization Rate(%)
High performance computing clusters (8 nodes)	High performance computing clusters	16,38,747/-	Yes	100%

Completed

Annexure-II

REQUEST FOR ANNUAL INSTALMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE

1. Sanction Order No and date: SR/S1/PC-24/2007 Dated: 15.09.2008

2. Total Project Cost: Rs. 30,65,400/-

3. Revised Project Cost: N/A
(if applicable)

4. Date of Commencement: 28.01.2009

5. Statement of Expenditure:
(month wise expenditure incurred during current financial year)

Month & year	Expenditure incurred
April 2012	Rs. 48445/-
May 2012	Rs. 961980/-
June 2012	Nil
July 2012	Nil
August 2012	Rs. 48000/-
September 2012	Rs. 32904/-
October 2012	Rs. 14000/-
November 2012	Rs. 14000/-
December 2012	Rs. 14000/-
January 2013	Rs. 14000/-
February 2013	Rs. 4985/-
March 2013	Rs. 39725/-

6. Grant received in each year:
   a. 1st Year : Rs. 20,00,000/- (Rupees twenty lakh)
   b. 2nd Year: : Rs. 5,00,000/- (Rupees five lakh)
   c. 3rd Year: : Rs. 5,50,000/- (Rupees five lakh fifty thousand only)
   d. Interest, if any:
   e. Total (a+b+c+d): Rs. 30,50,000/- (Rupees thirty lakh fifty thousand)

Statement of Expenditure

(to be submitted financial yearwise ie. DOS* to 31st March of that financial year (28.01.2009 to 31.03.2013)

Sr No	Sanctioned Heads	Funds Allocated (indicate sanctioned or revised	Expenditure Incurred					Total Expenditure	Balance as on (date) (31.3.2013) over total allocation	Remarks (if any)
			1st Year (28.01.09 to 31.03.2009)	2nd Year 1.4.2009 to 31. 3.2010	3rd Year 1.4.2010 to 31. 3.2011	4th Year 1.4.2011 to 31. 3.2012	5th Year 1.4.2012 to31.3.2013			
(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	IX		
1	Manpower costs	980400	46366	297741	230875	120000	276000	970982	9418	
2	Consumables	0								
3	Travel	60000	20781	5120	14785	6344		47030	12970	
4	Contingencies	50000	31570	29256	15936			76762	-26762	
5	Others, if any									
6	Equipment	1475000		1638747		(-)177719		1461028	13972	
7	Overhead expenses	500000		120000	163000	217000		500000	Nil	
8	Total	3065400	98717	2090864	424596	165625	276000	3055802	9598	

Fund received = Rs. 30,50,000/-
Expenditure incurred = Rs. 30,55,802/-
Excess expenditure = Rs. 5,802/-

Name and Signature of Principal Investigator:
Date: 21.10.2014
Prof. & Head
Department of Comp. Science
TEZPUR UNIVERSITY

Signature of Competent financial authority: 21.11.14
(with seal)
Date:

*** DOS – Date of Start of project**

Note :

1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of DST i.e. Figures in Column (VIII) should not exceed corresponding figures in Column (III)
2. Utilisation Certificate (Annexure III) for each financial year ending 31st March has to be enclosed along with request for carry-forward permission to the next financial year.

Annexure-III

UTILISATION CERTIFICATE (2 COPIES)
FOR THE FINANCIAL YEAR - (ENDING 31ST MARCH, 2013)

1. Title of the Project/ Scheme: **Computational Studies of Bare and Zeolite-Supported Palladium Nanoclusters and their Application in Catalysis.**

2. Name of the Institution: Tezpur University

3. Principal Investigator: Dr. Ramesh Ch. Deka

4. Department of Science & Technology sanction order No & date sanctioning the project: DST No: SR/S1/PC-24/2007 dated: 15.09.2008

5. Head of account as given in the original sanction order: Manpower: JRF-02, Equipment, Travel, Contingency and Overheads

6.	Amount brought forward from the previous Financial year quoting DST letter no and date in which the authority to carry forward the said amount was given	i. Amount : Rs. ii. Letter No/Order No. SR/S1/PC-24/2007 iii. Date: 15.09.2008
7.	Amount received during the financial year (Please give DST letter/order no and date)	i. Amount : Rs. **30,50,000/-** ii. Letter/Order No SR/S1/PC-24/2007 iii. Date : 16.05.2012
8.	Total amount that was available for expenditure (excluding commitments) during the financial year (Sr. No. 6+7)	Rs. **3050000**
9.	Actual Expenditure (excluding commitments) Incurred during the financial year (upto 31st March, 2012)	Rs. **30,55,802/-**

10. Balance amount available at the end of the financial year: Rs. **-5802**

11. Unspent balance refunded, if any (please give details of cheque no etc.): Rs. **-5802**

12. Amount to be carried forward to the next financial year : N/A

UTILISATION CERTIFICATE

Certified that out of Rs **30,65,400/-** (Rupees thirty lakh sixty five thousand four hundred only) of grants-in-aid sanctioned during the year 2009-2013 in favour of The Registrar, Tezpur University under this Ministry/ Department letter/ order No SR/S1/PC-24/2007 dated 16.05.2012 and Rs. Nil on account of unspent balance of the previous year, a sum of Rs **30,55,802/-** (Rupees thirty lakh fifty five thousand eight hundred and two only) has been utilised for the purpose of Manpower: JRF-02, Equipment, Travel, Contingency and Overheads for which it was sanctioned. The negative balance of Rs. 5802/- (Rupees five thousand eight hundred and two only) of the previous year was also adjusted from the grants received in this financial year. The excess expenditure of **Rs 5,802/-** (Rupees five thousand eight hundred and two only) should be released for adjustment.

Ramesh Ch. Deka

Signature of PI

Date 21.10.2014

Prof. & Head
Department of Chem Science
TEZPUR UNIVERSITY

Signature of Registrar/Signature of Head

Date

Registrar
Tezpur University

B Lammoo
14.11.14

Accounts Officer
of the Institute

Date

Finance Officer
Tezpur University

(To be filled in by DST)

Certified that I have satisfied that the conditions on which the grants-in-aid was sanctioned have been fulfilled/ are being fulfilled and that I have exercised the following checks to see that the money was actually utilised for the purpose for which it was sanctioned:-

Kinds of checks exercised.

1.
2.
3.
4.
5.

Signature:_____
Designation:_____
Date:_____