Density functional theory study of structure, electronic and magnetic properties of non-metal (Group 13) doped stable Rh_n ($n = 2-8$) clusters and their catalytic activities towards methanol activation

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Abstract. Rhodium clusters are very important finite size materials because of their unique electronic, magnetic and catalytic properties. Tuning the physical and chemical properties of rhodium clusters by incorporating different metal and non-metal atoms have found a great research interest in recent years. In this study, non-metal atoms of group 13, viz., B, Al or Ga were incorporated into the stable rhodium clusters to evaluate the structure, stability, electronic, magnetic as well as catalytic properties using density functional theory (DFT). Stability function, dissociation energy and LUMO-HOMO gap analysis reveal the higher stability of Rh_5B , Rh_4Al and Rh_4Ga clusters. Boron-doped on even-atomic rhodium clusters are more stable than odd-atomic rhodium clusters whereas both odd and even-atomic clusters were found to be stable for Al and Ga-doped rhodium clusters. Deformed electron density was found to be higher in the case of Rh_5B , Rh_4Al , Rh_7Al and Rh_4Ga clusters along all the bonds as well as at the atoms, which indicates higher stability of these non-metal doped rhodium clusters. LUMO and HOMO orbital analysis suggests that electronic redistribution occurs from HOMO (Rh) to LUMO (non-metal). DOS and COOP studies reveal the higher contribution of d electrons in the bonding region rather than s and p electrons. Spin density and magnetic moment analysis indicate zero magnetic moment for even-atomic B, Al or Ga-doped rhodium clusters due to the cancellation of spin up and spin down densities, whereas for the odd ones the magnetic moment is non-zero. Greater catalytic activity for the activation of methanol is noticed with Rh_4Al and Rh_4Ga in comparison to Rh_5 , while the activity with Rh_5B is lower.

Keywords. Rhodium; boron; aluminium; gallium; methanol activation.

1. Introduction

Transition metal clusters are considered to be important materials and have attracted much attention in recent times due to their significance in nanotechnology as well as in material science and catalysis. Properties of finite clusters of metal atoms are very much susceptible to their atomic size and composition. Clusters may be made up of identical atoms, or molecules, or two or more different species. Exploring the novel physical and chemical properties of these clusters is of great significance for developing new cluster-based materials for technological purposes. In the past two decades, several theoretical and experimental attempts have been

made to uncover the structural, electronic, optical as well as magnetic properties of atomic clusters.¹⁻⁵ Properties of atomic clusters were found to be specifically different from those of bulk materials. For example, metals like palladium which is non-magnetic in the bulk solid state, show non-zero magnetic moments in discrete clusters.^{6,7} Size-dependent properties of atomic clusters are the important cause for drawing significant attention.^{8,9} Variation of the properties of metal clusters can also be monitored by taking different metal elements to produce intermetallic clusters.¹⁰ Numerous cases have been reported where enhancement in specific properties are observed upon alloying due to synergistic effects. This affluent variety of compositions, structures and properties of metallic alloy clusters have escalated to

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extensive applications in electronics, engineering and catalysis. Chemical and physical properties of nano alloy clusters can be tuned by varying the composition and atomic ordering as well as the size of the clusters. Surface structures, compositions and segregation properties^{11,12} of nano alloy clusters are very important in determining chemical reactivity with respect to catalytic activity.^{13,14} In recent years, transition metal clusters have been widely studied due to their unique catalytic and magnetic properties. In particular, Pt, Pd and Rh finite clusters are used as heterogeneous catalyst for hydrogenation as well as for reduction of NO, oxidation of CO and unburned hydrocarbons.¹⁵ Theoretical studies of Galicia,¹⁶ Reddy *et al.*,⁶ and experimental work of Cox *et al.*,^{17,18} motivated researchers to explore different properties of rhodium nano clusters. Another fascinating characteristic showed by the rhodium clusters is its magnetism which displays that these clusters acquire super paramagnetic behaviour at very low temperature (0.35–1.061 μ_B /atom).¹⁷ To understand the stability, structural and catalytic properties of rhodium-based binary clusters, a bundle of experimental as well as theoretical studies have been executed.^{19–21} Methanol is considered to be one of the important candidates for storage and production of hydrogen and is a promising component in the next generation of renewable green fuels.²² Palladium group elements have been found to be effective for the decomposition of methanol.^{23,24} Bimetallic RhRu clusters are observed to be good catalysts for methanol activation. Pal *et al.*, showed that Ru-doped Rh₆ cluster is a better catalyst for the activation of methanol compared to pure Rh₆. It may be noted that methanol activation occurs *via* O–H bond dissociation rather than C–H bond.²⁵ Rhodium nano clusters exhibit tremendous reactivity toward hydrogenation of aromatic compounds and are also chosen as catalysts for selective hydroformylation of alkenes.^{26–31} Experimental results suggest that particle size of rhodium clusters govern the reactivity in the hydrogenation of aromatic compounds. The focus of the present investigation is to determine the variation of properties of pure rhodium clusters by incorporation of a second atom or alloying rhodium cluster with another atom. However, numerous experimental studies were performed to determine the stability and the structural and catalytic properties of the Rh-based binary clusters.^{20,21,26–31} Alloying of a second metal (Mn or W) atom with the Rh clusters show higher catalytic activity for the CO-hydrogenation in comparison to pure Rh clusters.²⁰ It was observed that the activity of Mn-doped Rh clusters is about 13 times higher than that of pure Rh clusters. Analogous outcome has also been monitored for the Pd-doped rhodium clusters where mixed bimetallic cluster shows higher catalytic activity for partial

hydrogenation of 1,3-cyclooctadiene.³² These results reveal that the reactivity of these bimetallic clusters strongly depends on the Rh/Pd ratio. Very few theoretical reports are available in the literature regarding the equilibrium geometries, stabilities, electronic and magnetic properties of doped Rh clusters.^{33–36} Electronic and magnetic properties of small Mn-doped rhodium clusters are investigated by Srivastava *et al.*,³³ and it was noticed that the Rh₂Mn₂ cluster is very stable. They also observed that electronic and magnetic properties of these clusters are strongly influenced by the ratio of Rh and Mn atoms in the cluster. Mekkath *et al.*,³⁴ studied the electronic and magnetic properties of small Fe_nRh_m ($n+m \leq 8$) clusters using the GGA exchange-correlation functional and found that the d-orbitals play a significant role in determining the magnetism of the binary clusters. Dennler *et al.*,³⁵ found the increment of local magnetic moments of Rh atoms in the presence of Co in the binary clusters. It is observed that magnetism can also contribute to the stability of Rh_nCo_m clusters. Yang *et al.*,³⁷ investigated the stability and electronic properties of Au_nRh ($n = 1–8$) clusters by using the PW91P86/LanL2DZ method and found that the ground state Au_nRh favour planar geometry. Their investigation predicted the highest stability of Au₅Rh cluster. Some non-transition metal-doped rhodium clusters are also being studied in the recent years. Soltani *et al.*,³⁸ performed DFT study on electronic and magnetic properties of Ca-doped Rh clusters and observed that ground state Rh_nCa clusters always favour three-dimensional geometry. Magnetic moment of Rh_nCa clusters is found to be independent of doped calcium atom. Lecours *et al.*,³⁹ studied the sulphur-doped neutral and ionic rhodium clusters and reveal that metal-like behaviour for rhodium sulfide is due to the electronic transition from p orbitals of sulphur to d orbitals of rhodium as well as with the back-donation to sulphur. Zhang *et al.*,⁴⁰ performed systematic theoretical investigation on structures, stabilities, and electronic properties of rhodium-doped silicon clusters Rh₂Si_n^q ($n = 1–10$; $q = 0, \pm 1$) and Rh₂Si₆[–], Rh₂Si₆, and Rh₂Si₆⁺ clusters are found to be more stable. The natural population analysis shows that the electronic charges in Rh₂Si_n^q clusters are observed to be transferred from the Si atoms to the Rh atoms except in Rh₂Si⁺. Jia *et al.*,⁴¹ theoretically investigated the geometries and stabilities of binary RhC_n and found that the clusters with odd number of carbon atoms are more stable.

In this study, we have systematically investigated the variation of geometrical, electronic, magnetic as well as catalytic activities of boron, aluminium or gallium-doped binary rhodium clusters. Methanol activation has also been carried out on stable B, Al or Ga-doped rhodium clusters. To the best of our knowledge, no

theoretical studies are available in the literature on boron, aluminium or gallium-doped rhodium nanoclusters. Therefore, a systematic investigation in this field is necessary to explore the structural, electronic, magnetic and catalytic activities of Group 13 non-metal doped small rhodium clusters.

2. Computational details

To investigate the structural, electronic and magnetic properties of non-metal doped rhodium clusters, ground state geometries of neutral Rh_n ($n = 2-8$) clusters are taken from our recent publication.⁴² Stable geometries of rhodium clusters are considered as low-lying isomers for replacement of one atom of rhodium by non-metal atoms (boron, aluminium or gallium) at different positions. Non-metal doped rhodium clusters are optimized without imposing any symmetry constraints. All calculations including transition states are performed by DFT method using DMOL3 package^{43,44} under generalized gradient approximation (GGA) with BLYP exchange correlation functional^{45,46} which incorporates exchange functional of Becke's with the gradient-corrected functional of Lee–Yang–Parr. DNP⁴⁷ basis set is chosen for geometry optimization. DNP basis set is equivalent to Gaussian split-valence 6-31G** basis set. Incorporation of relativistic effect is very important to study the heavy metals like rhodium atom. Hence, all electron relativistic correction to valence orbitals *via* a local pseudo potential are included for direct inversion in a subspace method (DIIS). Self-consistent field (SCF) procedures are utilised within the boundary condition of convergence criteria of energy 1×10^{-5} Ha, maximum force gradient 2×10^{-3} Ha $\text{\AA}^{-1}$ and displacement convergence 5×10^{-3} $\text{\AA}$ on the total energy and 10^{-6} a.u. on electron density. Symmetry restricted calculations are performed at higher spin multiplicities in order to compare energy values with the ground state geometries. B, Al or Ga atom substituted even and odd atomic rhodium clusters are optimized with multiplicities ($M = 1, 3, 5$ and 7) and multiplicities ($M = 2, 4, 6$, and 8), respectively, to evaluate stable geometrical isomers. DFT-evaluated transition states show only one imaginary frequency whereas no imaginary frequency is noticed for geometry optimization to the lowest energy state. Binding energy per atom (E_b) of alloy clusters is evaluated by using the following mathematical expression (1):

$$E_b(Rh_nX) = [nE(Rh_n) + E(X) - E(Rh_nX)] / (n + 1) \quad (1)$$

[X = B, Al or Ga]

where, $E(Rh_n)$ and $E(X)$ represent the energies of the rhodium and X atoms, $E(Rh_nX)$ is the total energy of Rh_nX cluster. Hybrid functional, B3LYP has also been used to optimize some doped clusters to compare with the results obtained with BLYP functional. Nature of bonding in clusters are analysed by Bader's quantum theory of atoms in molecules (QTAIM)^{48–50} for which AIMALL package⁵¹ is used.

3. Results and Discussion

3.1 Structural properties

DFT-optimized lowest energy geometries of Rh_nX ($n = 1-7$ and $X = B, Al$ or Ga) clusters are shown in Figure 1 and their corresponding binding energies and bond distances are reported in Tables 1 and 2, respectively. Doped isomers are obtained by replacing one of the Rh atom from bare lowest energy Rh_n clusters by different non-metal atom like boron (B), aluminium (Al) or gallium (Ga). Most stable boron, aluminium and gallium-doped diatomic RhB , $RhAl$ and $RhGa$ clusters attained $C_{\infty v}$ symmetry at the singlet state. Binding energy per atom of RhB , $RhAl$ and $RhGa$ are evaluated to be 2.7549, 1.6327 and 1.4381 eV, respectively. $Rh-B$, $Rh-Al$ and $Rh-Ga$ bond distances are found to be 1.722, 2.213 and 2.292 $\text{\AA}$, respectively. Rh_2B , Rh_2Al and Rh_2Ga clusters possess triangular geometry at the ground state having doublet multiplicity and C_{2v} symmetry. Calculated binding energy values of Rh_2B , Rh_2Al and Rh_2Ga are 2.9540, 2.0610 and 1.8601 eV/atom, respectively. $Rh-Rh$ bond distances in Rh_2B , Rh_2Al and Rh_2Ga evaluated by the DFT method are found to be 2.800, 2.527 and 2.444 $\text{\AA}$, respectively. While average $Rh-B$, $Rh-Al$ and $Rh-Ga$ bond length values are calculated to be 1.829, 2.328 and 2.464 $\text{\AA}$ in Rh_2B , Rh_2Al and Rh_2Ga , respectively.

Lowest energy geometry of Rh_3B , Rh_3Al and Rh_3Ga clusters are obtained to be tetrahedral with C_{3v} symmetry point group at the singlet multiplicity. Binding energy of the stable Rh_3B , Rh_3Al and Rh_3Ga clusters are 3.1046, 2.4535 and 2.2938 eV/atom, respectively. Average $Rh-Rh$ bond distances in Rh_3B , Rh_3Al and Rh_3Ga clusters are measured to be 2.668, 2.540 and 2.474 $\text{\AA}$, respectively, while average $Rh-B$, $Rh-Al$ and $Rh-Ga$ bond lengths in the corresponding doped clusters are found to be 1.928, 2.425 and 2.653 $\text{\AA}$. Distorted square pyramidal geometry is obtained for Rh_4B , Rh_4Al and Rh_4Ga clusters in the ground state with C_{2v} symmetry at the doublet multiplicity. 3.2165, 2.7108 and 2.5838 eV binding energy per atom is found for Rh_4B , Rh_4Al and Rh_4Ga clusters in their respective lowest energy state. Average $Rh-Rh$ bond lengths in Rh_4B , Rh_4Al and Rh_4Ga clusters are recorded to be 2.628, 2.529, and 2.513 $\text{\AA}$, respectively, while, average $Rh-B$ bond lengths in Rh_4B is 1.985 $\text{\AA}$, $Rh-Al$ in Rh_4Al is 2.690 $\text{\AA}$ and $Rh-Ga$ in Rh_4Ga is found to be 2.848 $\text{\AA}$. Ground state of Rh_5B , Rh_5Al and Rh_5Ga clusters have distorted prismatic structure with C_s point group and singlet multiplicity. Average $Rh-Rh$ and $Rh-B$ bond distances for boron doped cluster are 2.554 and 1.949 $\text{\AA}$, while the corresponding $Rh-Rh$ and $Rh-Al$ distances in

Rh ₁ B(0.034)	Rh ₁ Al(0.018)	Rh ₁ Ga(-0.062)

Rh ₂ B(-0.021)	Rh ₂ Al(0.021)	Rh ₂ Ga(0.009)

Rh ₃ B(-0.043)	Rh ₃ Al(-0.002)	Rh ₃ Ga(-0.011)

Rh ₄ B(-0.067)	Rh ₄ Al(-0.056)	Rh ₄ Ga(-0.023)

Rh ₅ B(-0.104)	Rh ₅ Al(-0.012)	Rh ₅ Ga(-0.008)

Rh ₆ B(-0.006)	Rh ₆ Al(0.021)	Rh ₆ Ga(-0.012)

Rh ₇ B(-0.009)	Rh ₇ Al(-0.033)	Rh ₇ Ga(-0.008)

Figure 1. DFT-optimized stable ground state structures of Rh_nX (n = 1-7) clusters, where X = B, Al or Ga. Formation energies (eV) are mentioned in bracket (ΔE_f).

Table 1. Binding energy per atom (eV/atom) of DFT-derived Rh_nX ($n = 1-7$ and $\text{X} = \text{Rh}^{42}$, B, Al or Ga) clusters.

Cluster	(X = B)	(X = Al)	(X = Ga)	X = Rh^{42}
Rh_1X	2.7549	1.6327	1.4381	1.5067
Rh_2X	2.9540	2.0610	1.8601	2.1276
Rh_3X	3.1046	2.4535	2.2938	2.5315
Rh_4X	3.2165	2.7108	2.5838	2.7091
Rh_5X	3.2978	2.8527	2.7037	2.8809
Rh_6X	3.3218	2.9542	2.8601	2.9045
Rh_7X	3.4229	3.0909	2.9625	3.1092

Table 2. Bond length ($\text{\AA}$) values of Rh_nX ($n = 1-7$ and $\text{X} = \text{B}$, Al or Ga) clusters derived by DFT method.

Cluster	Rh–Rh	Rh–B	Rh–Al	Rh–Ga
Rh_1B		1.722		
Rh_1Al			2.213	
Rh_1Ga				2.292
Rh_2B	2.800	1.829		
Rh_2Al	2.527		2.328	
Rh_2Ga	2.444			2.464
Rh_3B	2.668	1.928		
Rh_3Al	2.540		2.425	
Rh_3Ga	2.474			2.653
Rh_4B	2.628	1.985		
Rh_4Al	2.529		2.690	
Rh_4Ga	2.513			2.848
Rh_5B	2.554	1.949		
Rh_5Al	2.527		2.373	
Rh_5Ga	2.494			2.495
Rh_6B	2.633	2.255		
Rh_6Al	2.568		2.525	
Rh_6Ga	2.524			2.624
Rh_7B	2.499	1.970		
Rh_7Al	2.491		2.376	
Rh_7Ga	2.474			2.464

Rh_5Al are 2.527 and 2.373 as well as Rh–Rh and Rh–Ga distances Rh_5Ga clusters are 2.494 and 2.495 $\text{\AA}$, respectively. Binding energy values per atom of Rh_5B , Rh_5Al and Rh_5Ga clusters evaluated at BLYP/DNP level are 3.2978, 2.8527 and 2.7037 eV, respectively. The most stable geometry of Rh_6B , Rh_6Al and Rh_6Ga clusters are attained to be prismatic capped in the doublet multiplicity with C_s symmetry point group. Binding energies of the lowest energy state geometry of Rh_6B , Rh_6Al and Rh_6Ga clusters are 3.3218, 2.9542 and 2.8601 eV/atom respectively. For Rh_6B cluster, average Rh–Rh and Rh–B bond lengths are 2.633 and 2.255 $\text{\AA}$, while, corresponding Rh–Rh and Rh–Al bond lengths in Rh_6Al cluster are 2.568 and 2.525 $\text{\AA}$, respectively. Average Rh–Rh and Rh–Ga bond lengths in Rh_6Ga have 2.524 and 2.624 $\text{\AA}$. The distorted cubic structure is obtained for Rh_7B ,

Figure 2. Variation of Rh–Rh bond length with cluster size. (with BLYP functional).

Rh_7Al and Rh_7Ga in the ground state with singlet multiplicity and C_{3v} symmetry. The binding energy of Rh_7B , Rh_7Al and Rh_7Ga clusters is 3.4229, 3.0909 and 2.9625 eV/atom, respectively. Average Rh–Rh and Rh–B bond lengths are 2.499 and 1.970 $\text{\AA}$, respectively in Rh_7B . Rh–Rh and Rh–Al bond lengths for the Rh_7Al cluster are found to be 2.491 and 2.376 $\text{\AA}$, respectively, while the corresponding Rh–Rh and Rh–Ga distances in Rh_7Ga cluster are 2.474 and 2.464 $\text{\AA}$. Boron, aluminium and gallium-doped rhodium cluster are found to be three dimensional in the ground state as the number of rhodium atoms increase. BSSE-corrected energy values of these doped clusters are mentioned in the Supplementary Information (Table S1).

The variation of average Rh–Rh and Rh–X ($\text{X} = \text{B}$, Al or Ga) bond lengths with the cluster size for the lowest energy geometry of boron, aluminium and gallium-doped rhodium clusters are shown in Figures 2 and 3. Irregular variation of Rh–Rh and Rh–X ($\text{X} = \text{B}$, Al or Ga) bond distances with increasing cluster size is noticed. Rh–Rh bond length in Rh_2B is calculated to be higher (2.800 $\text{\AA}$) and for Rh_7B (2.499 $\text{\AA}$) it is lower, while Rh–B separation is maximum in Rh_6B (2.255 $\text{\AA}$) and in RhB (1.722 $\text{\AA}$) is minimum. Rh–Rh bond distances are found to be almost close or shows little variation in Rh_nAl when $n = (2-5)$ but higher value of Rh–Rh is noticed to be maximum for $n = 6$ cluster. Bond length Rh–Rh for Rh_nGa cluster increases from Rh_2Ga to Rh_4Ga and then follows odd-even oscillation up to Rh_7Ga . Rh–B bond length in Rh_nB clusters follows constant increasing path from Rh_1B to Rh_4B and then shows odd-even variation. Rh–Al bond length for Rh_nAl clusters smoothly increases from Rh_1Al to Rh_3Al , then a sudden sharp increase is noticed at Rh_4Al and then follows odd-even oscillation

Figure 3. Variation of Rh-X bond length with cluster size. (with BLYP functional).

like curve up to $n = 7$. Rh-Ga bond length for Rh_nGa cluster smoothly increases from Rh_1Ga to Rh_4Ga , then decreases to Rh_5Ga which again increases to Rh_6Ga and then again decreases. Overall outcome is that boron-substituted cluster possesses longer Rh-Rh and shorter Rh-X bond length than aluminium and gallium-doped bare rhodium cluster. Shorter Rh-B bond is due to the lesser number of shells in boron atom than Al and Ga. A constant increase in Rh-Rh and Rh-X bond distances are noticed at Rh_6X for all boron, aluminium and gallium incorporated rhodium clusters. For Al and Ga doped rhodium clusters a sharp increase of Rh-X bond separation is noticed at Rh_4X . More overlapping is noticed among Rh and B atoms because of the higher electron density at boron with smaller radius in comparison to aluminium and gallium, hence, Rh-B bond is stronger. For availability of vacant d orbital in Al and Ga, electron density of this two atom decreases which results in poor overlapping among Rh and Al or Ga orbitals. Bonded electron density in Rh-B bond is closer to B atom in the case of doped rhodium clusters. Rh-Rh bond distances are found to be longer in the case of Rh_nB due to stronger overlapping in Rh-B bonds. The variation of calculated binding energies per atom (E_b) with cluster size is shown in Figure 4. It is observed from Figure 4 that binding energy per atom for B, Al and Ga doped rhodium clusters increase with increasing cluster size. Rh_5B , Rh_5Al and Rh_5Ga clusters are optimized at BLYP/DND and B3LYP/DNP levels to monitor the variation of geometrical parameters in the case of both the functionals. It is noticed that Rh-Rh bond lengths of Rh_5B , Rh_5Al and Rh_5Ga are 2.547, 2.512 and 2.489 Å, respectively, for B3LYP/DNP level optimized clusters. While, 1.922, 2.298 and 2.329 Å are found to be the Rh-B, Rh-Al and Rh-Ga bond lengths in Rh_5B , Rh_5Al and

Figure 4. Variation of binding energy per atom with cluster size. (with BLYP functional).

Figure 5. Variation of binding energy per atom with cluster size. (with B3LYP functional).

Rh_5Ga , respectively. It is observed from both the functional studies that Rh-B bond lengths are smaller than Rh-Al and Rh-Ga. These results correlate well with the results obtained at BLYP/DNP level of calculation in the case of Rh_5B , Rh_5Al and Rh_5Ga finite clusters. Variation of binding energy per atom with cluster size obtained at B3LYP/DNP level is also mentioned in Figure 5. Similar trend of binding energy per atom is also noticed in the case of doped rhodium clusters evaluated using B3LYP functional (Figure 5) with the binding energies obtained using BLYP functional. It is also noticed in Figure 5 that binding energies for doped cluster also increases with the increase in cluster sizes. That is, doped clusters continue to gain energy during the growth process. Boron-doped cluster possesses higher binding energy than aluminium and gallium doped rhodium clusters. Increase of binding energy is more pronounced

in the smaller clusters than that of the larger clusters. For gallium and aluminium incorporated rhodium clusters, increase of binding energy is smooth whereas for boron-doped clusters, little variation of energy is noticed. Table 1 reveals that binding energy of boron doped rhodium clusters are higher than that of the pure rhodium clusters. In the contrary, binding energy of bare rhodium clusters are found to be higher than aluminium and gallium-doped clusters. It seems possible due to the small size of B atom where effective overlapping occurs among p orbitals of B with Rh d orbitals.

3.2 Description of dissociation energy, stability function and LUMO-HOMO gap and formation energy

The relative stability of the lowest energy structure of Rh_nX ($n = 1-7$ and $\text{X} = \text{B}, \text{Al}$ or Ga), are evaluated on the basis of the following mathematical expressions of second-order difference of energies (Δ^2E) or stability function, dissociation energies (ΔE_f) and LUMO-HOMO (ΔE) gap.

$$\Delta^2E(\text{Rh}_n\text{X}) = E(\text{Rh}_{n+1}\text{X}) + E(\text{Rh}_{n-1}\text{X}) - 2E(\text{Rh}_n\text{X}) \quad (2)$$

$$\Delta E_d(\text{Rh}_n\text{X}) = E(\text{Rh}_{n-1}\text{X}) + E(\text{Rh}) - E(\text{Rh}_n\text{X}) \quad [\text{X} = \text{B}, \text{Al} \text{ and } \text{Ga}] \quad (3)$$

$$\Delta E(\text{Rh}_n\text{X}) = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (4)$$

Where, $E(\text{Rh})$ and $E(\text{X})$ represent the energies of the individual Rh and X atoms while, $E(\text{Rh}_n\text{X})$, $E(\text{Rh}_{n+1}\text{X})$, and $E(\text{Rh}_{n-1}\text{X})$ are the total energies of the ground state geometries of Rh_nX , Rh_{n+1}X , and Rh_{n-1}X clusters. E_{LUMO} and E_{HOMO} are the energy of lowest unoccupied molecular orbital and energy of highest occupied molecular orbital respectively.

3.2a Dissociation energy: Variation of dissociation energy of non-metal doped rhodium clusters with a cluster size is shown in Figure 6. In this case, dissociation energy is evaluated by removing one rhodium atom from doped clusters. Higher dissociation energy reveals the higher stability of the finite sized clusters, *i.e.*, it is more difficult to set the constituent atoms apart and has a tendency to form a finite sized cluster. It is seen from Figure 6 that boron, aluminium or gallium-doped rhodium clusters such as Rh_5B , Rh_4Al and Rh_7Al and Rh_4Ga and Rh_6Ga possess higher dissociation energies in comparison to their respective neighbouring clusters. For Rh_nB even atomic cluster possesses higher bond dissociation energy than odd ones whereas similar dissociation energies are noticed both for even and odd atomic clusters in the case of Rh_nAl and Rh_nGa . Al and Ga possess higher coordination number because of their lesser shielding

effect which leads to similar dissociation energy for Al and Ga-doped clusters.

3.2b LUMO-HOMO gap: DFT-evaluated variation of LUMO-HOMO energy gap with cluster size is presented in Figure 7. Odd-even oscillation is observed for boron doped rhodium cluster with size *i.e.* even atoms finite sized clusters are found to be more stable than the odd atomic clusters in the case of boron doped rhodium clusters. However, both even and odd atomic Al and Ga doped rhodium clusters possess higher photo stability. It is observed from Figure 7 that Rh_5B , Rh_4Al and Rh_4Ga finite sized clusters have higher LUMO-HOMO energy gap. The above-mentioned reactivity parameters suggest the higher photo stability of the Rh_5B , Rh_4Al and Rh_4Ga clusters in comparison to their respective neighbour. B3LYP hybrid functional has also been used to calculate LUMO-HOMO gap of doped rhodium

Figure 6. Variation of dissociation Energy with cluster size. (with BLYP functional).

Figure 7. Variation of LUMO-HOMO gap with cluster size. (with BLYP functional).

Figure 8. Variation of LUMO-HOMO gap with cluster size evaluated by using B3LYP functional.

clusters for comparison. Variation of LUMO-HOMO gaps derived at B3LYP/DNP level with cluster sizes are mentioned in Figure 8. Figure 8 reveals that Rh₅B, Rh₄Al, Rh₄Ga and Rh₅Ga finite-sized clusters possess higher LUMO-HOMO energy gap. Calculated results show that values of the LUMO-HOMO gap of doped rhodium clusters depend on the choice of DFT functional. Although the overall outcome that is obtained from two functional studies is that Rh₅B, Rh₄Al and Rh₄Ga clusters are more stable than their respective neighbours.

3.2c Stability function: The second-order difference of energy or stability function is known to provide the relative stability of a finite-sized cluster (n) with respect to its neighbour. Variation of second-order difference of energy with cluster size is provided in Figure 9. It is observed from Figure 9 that Rh₅B possesses higher value of stability function among Rh_nB clusters, while, Rh₄Al and Rh₄Ga clusters are found to have higher stability function. Higher stability function of Rh₅B, Rh₄Al and Rh₄Ga signifies the higher stability of these clusters with respect to their neighbours. Variation of second-order difference of energy with cluster size derived by using B3LYP functional is provided in Figure 10. In this case also, Rh₅B is found to be the most stable among all Rh_nB clusters. In the case of aluminium doped rhodium clusters, almost equal stability is noticed for Rh₃Al and Rh₄Al while Rh₄Ga exhibits higher stability. BLYP and B3LYP derive stability parameters suggest higher stability for Rh₅B, Rh₄Al and Rh₄Ga in comparison to their respective neighbouring clusters.

3.2d Formation energy: Cluster formation energy ΔE_f is used to describe whether Rh and B or Al or

Figure 9. DFT-evaluated stability function with cluster size at BLYP/DNP level.

Figure 10. DFT-evaluated stability function with cluster size at B3LYP/DNP level.

Ga atoms tend to form binary clusters or not. Formation energy can be represented by equation 5:

$$\Delta E_f = (ERh_m - X_n) - \frac{m}{m+n} ERh_{m+n} - \frac{n}{m+n} EX_{m+n} \quad [X = B, Al \text{ or } Ga] \quad (5)$$

where, ERh_{m+n} and EX_{m+n} represent the energies of pure Rh and X clusters. Negative values of formation energy (ΔE_f) indicates for a tendency to form doped clusters whereas a positive value of formation energy signifies less favoured formation of doped clusters. All the values of formation energies that are obtained from the calculation are mentioned in single bracket in Figure 1. Figure 1 shows that except Rh₁Al, Rh₁B, Rh₂Al, Rh₂Ga and Rh₆Al all doped clusters possess negative value of formation energy. So it may be concluded that Rh₁Al, Rh₁B, Rh₂Al, Rh₂Ga and Rh₆Al clusters are less favourable than others mentioned in Figure 1. i.e., except

Table 3. Mülliken charge (Q) analysis of DFT-evaluated Rh_nX cluster ($n = 1-7$) [$X = B, Al$ and Ga].

Cluster	Q_{Rh}	Q_B	Q_{Al}	Q_{Ga}
Rh_1B	−0.083	0.083		
Rh_1Al	−0.242		0.242	
Rh_1Ga	−0.247			0.247
Rh_2B	−0.007	0.082		
Rh_2Al	−0.155		0.310	
Rh_2Ga	−0.141			0.283
Rh_3B	−0.003	0.009		
Rh_3Al	−0.094		0.282	
Rh_3Ga	−0.061			0.181
Rh_4B	−0.022	0.048		
Rh_4Al	−0.144		0.314	
Rh_4Ga	−0.119			0.248
Rh_5B	−0.034	0.084		
Rh_5Al	−0.153		0.445	
Rh_5Ga	0.084			0.249
Rh_6B	−0.026	0.079		
Rh_6Al	−0.042		0.244	
Rh_6Ga	−0.031			0.103
Rh_7B	−0.042	0.168		
Rh_7Al	−0.176		0.579	
Rh_7Ga	−0.111			0.331

these mentioned clusters, all other clusters mentioned in Figure 1 are more favourable.

3.3 Mülliken charge analysis

Mülliken charges on all the atoms of boron, aluminium or gallium-doped rhodium clusters have been evaluated to understand the electronic charge redistribution. The charges on the individual atoms evaluated at BLYP/DNP level are summarised in Table 3. It is observed in Table 3 that in most cases, doped non-metal atom bears positive charge whereas rhodium atoms carry a negative charge. Therefore, it can be noted that electronic charge redistribution occurs in doped rhodium clusters. Electrons are seen to be transferred from doped atom to rhodium atoms. This charge redistribution is observed because of the electronegativity differences, electronegativity of rhodium (2.28) being higher than that of boron (2.04), aluminium (1.61) and gallium (1.81) atoms. Electronic charge at rhodium atom (Q_{Rh}) is calculated to be higher in the case of Rh_nAl and Rh_nGa clusters which leads to charge delocalization from aluminium or gallium to vacant d-orbitals of rhodium atoms

3.4 Electric dipole moment analysis

Dipole moment values of Rh_nX ($n = 2-7$ and $X = B, Al$ or Ga) obtained by the quantum chemical method are

Table 4. Dipole moment (Debye) values of Rh_nX ($n = 1-7$ and $X = B, Al$ or Ga) clusters derived by DFT method.

Cluster	(X = B)	(X = Al)	(X = Ga)
Rh_1X	2.6215	0.3063	0.2236
Rh_2X	1.8695	0.4091	0.2640
Rh_3X	1.3734	0.1526	0.0472
Rh_4X	0.9388	0.1090	0.0393
Rh_5X	0.6799	0.4298	0.1669
Rh_6X	0.3957	0.0041	0.3275
Rh_7X	0.6736	0.6257	0.5044

listed in Table 4 and Figure S2 (in Supplementary Information). Table 4 reveals that boron-doped rhodium finite sized clusters have higher dipole moment than that of the aluminium or gallium-doped clusters. Boron, aluminium or gallium-doped rhodium clusters are more polar than that of the pure rhodium clusters (as pure clusters have small dipole values) and the highest polarity is seen in the case of Rh_nB . Larger Rh–Rh bond distances in Rh_nB than Rh_nAl and Rh_nGa are due to the higher dipole moment of Rh_nB . That is, d electron delocalization of Rh_nB are responsible for increasing polarity.

3.5 Magnetic moments analysis

Calculated magnetic moments on each of the atoms in Rh_nX ($n = 1-7$, and $X = B, Al$ or Ga) are given in the Tables 5A, 5B and 5C and their graphical representations are shown in Figure S2 (in Supplementary Information). Resultant magnetic moments of Rh_1B , Rh_3B , Rh_5B and Rh_7B are calculated to be zero. In the case of Rh_2B , Rh_4B and Rh_6B clusters, the electronic spin of the boron atom is seen to be opposite to that of the rhodium atoms (Table 5A). Zero resultant magnetic moments are noticed in the case of Rh_1Al , Rh_5Al and Rh_7Al clusters. It is noticed in Table 5B that electronic spin of rhodium and aluminium atoms are parallel in Rh_3Al , Rh_4Al and Rh_6Al clusters whereas it is in the opposite direction for Rh_2Al . Rh_1Ga , Rh_5Ga and Rh_7Ga possess zero magnetic moments, while, Rh_2Ga and Rh_3Ga have the resultant magnetic moment of 1.00 and 1.85 μ_B , respectively, on cancellation of respective electronic spin of rhodium and gallium atoms. In the case of Rh_4Ga and Rh_6Ga , the electronic spins of rhodium and gallium atoms are parallel which sum up for making the total magnetic moment of 1.00 μ_B . Among all the Rh_nB , Rh_nAl and Rh_nGa clusters, Rh_3Al and Rh_3Ga possess higher values of magnetic moment (1.19 and 1.85 μ_B). Magnetic moment values calculated at

Table 5. Total and individual atomic magnetic moment (μ_B) values of a) Rh_nB , b) Rh_nAl , c) Rh_nGa ($n = 1-7$) clusters derived by DFT method. [Numbering of Rh atoms are in Figure 1].

Cluster	Total magnetic moment (μ_B)	(B)	(Rh ₁)	(Rh ₂)	(Rh ₃)	(Rh ₄)	(Rh ₅)	(Rh ₆)	(Rh ₇)
A									
Rh ₁ B	0	0	0						
Rh ₂ B	1	-0.07	0.540	0.538					
Rh ₃ B	0	0	0	0	0				
Rh ₄ B	1	-0.033	0.221	0.209	0.221	0.382			
Rh ₅ B	0	0	0	0	0	0	0		
Rh ₆ B	1	-0.01	0.153	0.403	0.152	0.010	0.158	0.156	
Rh ₇ B	0	0	0	0	0	0	0	0	0
Cluster	Total magnetic moment (μ_B)	(Al)	(Rh ₁)	(Rh ₂)	(Rh ₃)	(Rh ₄)	(Rh ₅)	(Rh ₆)	(Rh ₇)
B									
Rh ₁ Al	0	0	0						
Rh ₂ Al	1	-0.272	0.636	0.636					
Rh ₃ Al	1.193	0.307	0.297	0.296	0.293				
Rh ₄ Al	1	0.180	0.172	0.234	0.234	0.180			
Rh ₅ Al	0	0	0	0	0	0	0		
Rh ₆ Al	1	0.007	0.134	0.133	0.228	0.229	0.135	0.134	
Rh ₇ Al	0	0	0	0	0	0	0	0	0
Cluster	Total magnetic moment (μ_B)	(Ga)	(Rh ₁)	(Rh ₂)	(Rh ₃)	(Rh ₄)	(Rh ₅)	(Rh ₆)	(Rh ₇)
C									
Rh ₁ Ga	0	0	0						
Rh ₂ Ga	1	-0.292	0.648	0.644					
Rh ₃ Ga	1.851	-0.056	0.640	0.633	0.634				
Rh ₄ Ga	1	0.048	0.192	0.284	0.284	0.192			
Rh ₅ Ga	0	0	0	0	0	0	0		
Rh ₆ Ga	1	0.016	0.127	0.127	0.238	0.237	0.128	0.127	
Rh ₇ Ga	0	0	0	0	0	0	0	0	0

B3LYP/DNP level are mentioned in Table 6. Table 6 shows higher values of magnetic moment for Rh₆B, Rh₃Al and Rh₃Ga in comparison to the other studied clusters. The almost similar trend of the magnetic moment is noticed for most of the clusters evaluated at both BLYP/DNP and B3LYP/DNP levels. However, calculated magnetic moment values evaluated at B3LYP/DNP level for Rh₆B and Rh₆Al clusters are found to be slightly higher than the corresponding values of BLYP/DNP.

Although it is noticed that the B3LYP results are qualitatively similar to those of BLYP data for many clusters, quantitative differences are observed in addressing and describing many electronic properties of these doped metal clusters such as the electronic gap, magnetic moment and the stability function, *etc.*

3.6 LUMO-HOMO orbital analysis

Isosurface diagram of LUMO and HOMO orbitals generated at BLYP level are shown in the Figures 11A,

Table 6. Total magnetic moment (μ_B) values of Rh_nX ($n = 1-7$) clusters derived with B3LYP functional.

Cluster	X = B	X = Al	X = Ga
Rh ₁ X	0	0	0
Rh ₂ X	1.00	1.00	1.00
Rh ₃ X	0	2.00	1.97
Rh ₄ X	0.96	1.00	1.00
Rh ₅ X	0	0	0
Rh ₆ X	2.89	1.95	1.00
Rh ₇ X	0	0	0

11B and 11C. It is observed from figures that electronic cloud of LUMO and HOMO orbitals are basically seen at the rhodium atoms in the boron, aluminium or gallium-doped rhodium clusters. In Rh_nB , higher orbital electron densities are noticed around rhodium atoms in the LUMO as well as in the HOMO, which reveals that d-orbitals of rhodium atoms are involved in the bond formation. But in some cases, overlapping

Figure 11. (A) DFT-computed HOMO and LUMO pictorial diagrams of Rh_nB ($n = 1-7$) clusters. (B) DFT-computed HOMO and LUMO pictorial diagrams of Rh_nAl ($n = 1-7$) cluster. (C) DFT-computed HOMO and LUMO pictorial diagrams of Rh_nGa ($n = 1-7$) clusters.

occurs among d-orbitals of Rh and p orbitals of B. In the LUMO of Rh₅B and Rh₇B, some positive overlapping occurs among d_{z2} orbitals. For Rh_nAl positive overlapping among d_{z2} orbitals occurs in the LUMO of Rh₃Al. It is noticed from Figure 11B, that orbital electron densities in Rh_nAl are found to be localised on both rhodium as well as aluminium atoms at the LUMO, whereas for almost all cluster orbital densities are mainly seen to be localised around the rhodium atoms at HOMO. This

observation suggests electronic redistribution among Rh and Al atoms in Rh_nAl clusters. Pi-bonding overlapping takes place among the d_{xy/yz} orbitals of rhodium atoms in the Al-doped rhodium clusters. Some positive overlapping occurs among d_{z2} orbitals in LUMO of Rh₆Ga and Rh₇Ga. Electronic isosurface diagram of the Rh_nGa clusters reveals that almost for all cluster LUMO electron densities are seen to be situated at Ga and Rh atoms whereas HOMO electrons are found to be at Rh

C

Cluster	HOMO	LUMO
Rh ₁ Ga		
Rh ₂ Ga		
Rh ₃ Ga		
Rh ₄ Ga		
Rh ₅ Ga		
Rh ₆ Ga		
Rh ₇ Ga		

Figure 11. continued

atoms. Therefore, it can be concluded that electrons are excited from HOMO of Rh atoms to LUMO of Ga atom in Rh_nGa. Sideways orbital overlapping are responsible for bonding among metal d orbitals whereas, for some non-metal-doped rhodium clusters p orbitals of non-metal are also seen to be involved in overlapping with Rh orbitals.

3.7 Density of states (DOS) analysis

Electron density distribution at the bonding and anti-bonding regions of B, Al or Ga doped rhodium clusters

can be evaluated based on DOS analysis. DFT evaluated DOS diagrams are given in Figures 12A, 12B and 12C. DOS diagrams reveal that density width of d-electrons are found to be in the bonding region, while the width of p-electrons is seen in the anti-bonding region in the case of B, Al or Ga doped rhodium clusters. That is, a population of p-orbitals is maximum at the anti-bonding region. The population of Rh d-orbital density in the bonding region is found to be higher than others, p and f-orbitals, which suggests that d-orbitals of Rh are involved in bond formation for B, Al or Ga doped rhodium clusters. It is also observed that the intensity of orbital electron density in bonding region is higher with the increase of cluster size.

3.8 Electron density analysis

DFT-computed electron density diagrams of Rh_nX clusters [X= B, Al or Ga] are shown in Figure 13. Stability of the metal finite sized clusters can be derived by calculating the electron density distribution. Electron density at Rh_nX (n = 1–7 and X = B, Al or Ga) clusters are evaluated by quantum chemical method. Figure 13 suggests that electron densities are found to be more deformed in Rh₅B. For Rh_nAl clusters electron densities are highly deformed in Rh_nAl (n = 3, 4, 7) whereas, more electron density deformation is seen in Rh₄Ga. More deformed electron density suggests that electrons are more deformed on bonds as well as on atoms. Clusters where electron density is deformed mainly on atoms are less stable than the clusters where electrons are deformed on both the bonds and atoms. Little contribution of electron density from boron is seen in the formation of boron doped rhodium clusters whereas no contribution of electron density from aluminium and gallium is noticed in the formation aluminium or gallium doped rhodium clusters (Figure 13). More deformed electron density along the bonds signifies higher ionic character and lesser covalent character. Therefore, larger deformed electron density along the bonds shows higher stability because of the higher ionic character Figure 13 shows that deformed electron density is more for Rh₅B, Rh₄Al, Rh₇Al and Rh₄Ga clusters which suggests higher stability of these clusters in comparison to their neighbour. It is observed that in the case of boron-doped rhodium clusters, electrons are more deformed along all bonds and atoms than other Al and Ga doped clusters. Therefore, it can be inferred that Rh_nB clusters are more stable than Rh_nAl and Rh_nGa. Electron density diagrams of some Rh_nX clusters evaluated B3LYP/DNP level are given in Figure 14. It is noticed from Figure 14 that electron densities are more deformed in B doped

A

Figure 12. (A) DFT-computed DOS pictorial diagrams of Rh_nB ($n = 1-7$) clusters. (B) DFT-computed DOS pictorial diagrams of Rh_nAl ($n = 1-7$) clusters. (C) DFT-computed DOS pictorial diagrams of Rh_nGa ($n = 1-7$) clusters.

clusters than Al and Ga doped clusters. These results correlate well with results obtained using BLYP functional. However, the electron density is found to be more deformed on Rh_4B , Rh_5B , Rh_4Al and Rh_4Ga clusters. Figures 13 and 14 show higher electron on Rh_nB in comparison to Rh_nAl and Rh_nGa .

3.9 Spin density analysis

Figure 15 shows spin density analysis of Rh_nX ($n = 1-7$ and $\text{X} = \text{B}, \text{Al}$ or Ga) clusters. Rh_1B , Rh_3B , Rh_5B and Rh_7B clusters are found to be non-magnetic because spin up density is almost equivalent to spin down

B

Figure 12. continued

density. (Blue colour represents spin up density and brown represents spin down density). While, Rh_2B , Rh_4B and Rh_6B clusters possess non zero magnetic moment because spin up density is non-equivalent to spin down density i.e., full cancellation of spin up and spin down density is not occurred. Rh_1Al , Rh_5Al and Rh_7Al

clusters possesses zero magnetic moment because of the cancellation of spin up and spin down density (Blue colour = spin up and green colour = spin down density). Whereas, Rh_2Al , Rh_3Al , Rh_4Al and Rh_6Al clusters possesses non-zero magnetic moment due to the non-equivalence of spin up and spin down density. For Rh_3Al , Rh_4Al and Rh_6Al clusters, almost one type of

C

Figure 12. continued

spin density is noticed. Resultant spin density of Rh_1Ga , Rh_5Ga and Rh_7Ga is zero because of the total cancellation of spin-up and spin-down density (Red colour = spin-up and brown = spin-down density). Rh_2Ga , Rh_3Ga , Rh_4Ga and Rh_6Ga clusters possess non-zero magnetic moment because of some net resultant spin density values.

3.10 QTAIM analysis

To understand the topology of electron density, Bader's quantum theory of atoms in molecules (QTAIM) is being used. This theory is based on three-dimensional electron density functions. Electron density ρ , and the Laplacian of electron density $\nabla^2\rho$, at the bond critical

point (BCP) are constraint which are usually employed to determine the nature and level of bonding between two atoms. A large value of ρ (>0.2 a.u.) and larger

Figure 13. DFT-computed electron density diagrams of Rh_nX clusters ($n = 1-7$) [$X = B, Al$ or Ga] using BLYP functional.

as well as negative value of $\nabla^2\rho$ signifies a covalent interaction, while a small value of ρ (<0.10 a.u.) and a positive value of $\nabla^2\rho$ denote an ionic or closed-shell interaction. But this vision is not comprehensive for transition metal complexes due to diffuse electron circulation of these elements. So, in transition metal complexes, it is observed that ρ has a small value and $\nabla^2\rho$ has a small and positive value for a covalent interaction. QTAIM analysis for ρ and $\nabla^2\rho$ are mentioned in Table 7. It is noticed that average density ρ values for doped clusters are observed to be higher than bare atomic clusters which suggest some ionic nature on doped clusters. Laplacian of electron density $\nabla^2\rho$ are also found to be large (negative) for doped clusters which makes them ionic. Bader charge analysis for few clusters bare and doped clusters are presented in Table 8. Table 8 shows that for doped clusters, Bader charge separation among rhodium atoms are higher than bare ones. More charge separation among atoms signifies ionic character. It is also noticed that Rh₄Al and Rh₄Ga have higher average charge separation in comparison to Rh₄B which suggests higher ionic character at the bonds in Rh₄Al and Rh₄Ga. That is, Rh₄Al and Rh₄Ga bear higher ionicity among bonds. Electron density is found to be more deformed in Rh₄Al than Rh₃Al which is further confirmed from denser contour circle at Rh₄Al (Figure 16).

3.11 COOP analysis

A combination with the analysis of atom and orbital projected density of states (COOP) technique was

Figure 14. DFT-computed electron density diagrams of Rh_nX clusters $n = 4, 5$ [$X = B, Al$ or Ga] using B3LYP functional.

Figure 15. Spin density diagrams of DFT-computed Rh_nX clusters ($n = 1-7$) [$\text{X} = \text{B}, \text{Al}$ or Ga].

applied to evaluate the bonding features of clusters.^{52,53} COOP gives a quantitative explanation of the bonding, non-bonding and anti-bonding interaction between two atoms. Positive, negative and zero COOP scales signify bonding, anti-bonding and non-anti-bonding characteristics, respectively (Figure 17). Figure 16 shows that all the d electrons of Rh–Rh bonds are in bonding region in the doped clusters. Rh–B and Rh–Ga bond electrons are also noticed to be present in bonding COOP region. Some of p and s electrons involved in the Rh–Rh bond formations are in antibonding region. While, in the case of RhAl clusters, all the electrons of Rh–Rh bonds are in bonding and s electrons of Rh–Al bonds are in anti-bonding region. It can be concluded that all d electrons are in the bonding region and some s and p electrons are present in the antibonding region. Similar phenomenon is also noticed in DOS study.

3.12 Catalytic activity of Rh_5B , Rh_4Al and Rh_4Ga clusters

Rh_5B , Rh_4Al and Rh_4Ga clusters are chosen for the investigation of activation of methanol molecule to compare their activity towards methanol activation with pure Rh_5 . Recently it was noticed that some Mg-doped rhodium clusters activated methanol *via* O–H and C–H dissociation.⁵⁴ In this study, in contrast to Rh_5 , Rh_4Al and Rh_4Ga clusters are found to be more favorable for

Table 7. Calculated electron density ρ and Laplacian of electron density, $\nabla^2\rho$ at the bond critical points (BCP) for some selected clusters in a.u.

Clusters	Average density among all bonds (ρ)	Laplacian of electron density ($\nabla^2\rho$)
Rh_4	0.05	0.11
Rh_5	0.04	0.14
Rh_6	0.04	0.09
Rh_4Al	0.15	0.26
Rh_4Ga	0.18	0.39
Rh_4B	0.05	0.10
Rh_5B	0.21	0.42

Table 8. Bader charge difference among bonds in doped clusters.

Cluster	Bader Charge difference among Rh atoms	Bader Charge difference among Rh and doped atoms
Rh_4	0.08	
Rh_5	0.09	
Rh_4B	0.11	0.12
Rh_4Al	0.31	0.89
Rh_4Ga	0.29	0.67

Figure 16. Calculated deformed charge density diagram by Bader analysis.

methanol activation, while Rh_5B shows least activity (observed from the energy profile). Variation of selected geometrical parameters for the activation of methanol are shown in Table 9 and relative free energies of the reactants, transition states and products are given in Figure 18. Coordinates of some structures are mentioned in Table S3 (Supplementary Information). Figure 18 shows that methanol is adsorbed on different atoms like Rh atom for Rh_5B and Rh_4Ga , and on Al atom for Rh_4Al cluster. Due to the adsorption of CH_3OH on Rh_5B , Rh_4Al and Rh_4Ga clusters, C–O and O–H bond lengths of methanol got slightly elongated in comparison to pure methanol molecule. Adsorption energy of methanol on Rh_5B , Rh_4Al and Rh_4Ga clusters are 2.39, 2.49 and 2.51 eV, whereas adsorption energy of methanol on Rh_5 is evaluated to be 2.46 eV. BSSE-corrected energy values for methanol adsorbed on Rh_5B , Rh_4Al and Rh_4Ga clusters are found to be 0.09, -0.06 and -0.08 eV, respectively. Calculated adsorption energy values suggest that adsorption of methanol molecule on Rh_4Al and Rh_4Ga are more favourable in comparison to pure Rh_5 clusters. Whereas, less possibility of methanol adsorption on Rh_5B is noticed due to small adsorption energy in comparison to pure Rh_5 -methanol adsorption. In this study, we have investigated the O–H activation of methanol catalyzed by boron, aluminum or gallium-doped rhodium clusters and compared with pure rhodium finite sized cluster. Activation free energy barrier for methanol activation catalyzed by pure Rh_5 is found to be 0.61 eV. Geometry of the O–H dissociated product is seen to be bridged (adsorbed) hydrogen on two rhodium atoms stabilized by 0.22 eV with respect to the reactant (Figure 18). Activation free energy calcu-

lated for O–H bond dissociation of methanol catalyzed by Rh_5B is found to be 0.73 eV and the product formed after complete O–H dissociation is stabilized by 0.41 eV. The dissociated hydrogen atom is adsorbed on the doped boron atom ($\text{B–H} = 1.23 \text{ \AA}$). Only one imaginary frequency of -269 cm^{-1} is obtained for the transition state which corresponds to the movement of proton to the nearby boron atom. Again, O–H bond dissociation catalyzed by Rh_4Al has the activation barrier height of 0.34 eV. Imaginary frequency found for this transition state is -211 cm^{-1} . Dissociated hydrogen atom is found to be bonded with two rhodium atoms *via* bridge coordination (average bond length of Rh–H is $1.391 \text{ \AA}$) and product thus formed is stabilized by 0.28 eV with respect to its reactant. Transition state corresponding to the O–H bond dissociation of CH_3OH catalyzed by Rh_4Ga involves the breaking of the O–H bond and subsequent transfer of hydrogen atom to nearby rhodium atom where methanol molecule was adsorbed. Activation free energy barrier (relative energy) for O–H bond dissociation is found to be 0.29 eV. Only one imaginary frequency of -228 cm^{-1} is obtained for the transition state which corresponds to the movement of hydrogen to one of the rhodium atoms. Product thus formed on complete rupture of O–H bond is bridge coordinated hydrogen to two rhodium atoms (average bond length of Rh–H is $1.372 \text{ \AA}$) which is stabilized by 0.31 eV (Figure 18). Transition states obtained for the activation of methanol on Rh_5 , Rh_4B and Rh_4Al and Rh_4Ga have the activation barrier height of 0.61, 0.72, 0.34 and 0.29 eV, respectively, suggesting that Rh_4Ga and Rh_4Al clusters are more promising catalysts for methanol activation.

Figure 17. DFT-computed COOP structures of bare and doped clusters.

4. Conclusions

Based on DFT study of non-metal (B, Al or Ga) doped Rh_n (n = 2–8) clusters it is concluded that the stability of boron doped clusters is higher than aluminium and gallium-doped rhodium clusters. Calculated reactivity and electron density parameters suggest that photostability of Rh₅B, Rh₄Al and Rh₄Ga clusters is higher than their corresponding neighbours. Even atomic boron-

doped rhodium clusters are more stable than odd ones whereas both even and odd atomic clusters are stable in Al and Ga-doped clusters. Mulliken population analysis suggests that the charge is transferred from non-metal atoms to Rh atom. Dipole moment values are observed to be increased in the order as, Ga < Al < B doped rhodium clusters which suggests the higher polarity of Rh_nB. Non-zero magnetic moment is noticed in all odd atomic doped clusters, but among the even atomic doped

Table 9. DFT-computed O–H and C–O bond lengths (Å) of CH₃OH molecule adsorbed on bare and doped clusters in the case of reactants and transition states.

Bond with cluster	Reactant Bond length	Transition state Bond length
O–H (Rh ₅)	0.973	1.593
O–H (Rh ₅ B)	0.976	1.602
O–H (Rh ₄ Al)	0.979	1.671
O–H (Rh ₄ Ga)	0.978	1.662
C–O (Rh ₅)	1.443	1.448
C–O (Rh ₅ B)	1.465	1.487
C–O (Rh ₄ Al)	1.479	1.492
C–O (Rh ₄ Ga)	1.462	1.480

Figure 18. DFT-computed relative energies of reactant, transition state (T.S.) and product.

clusters only Rh₃Al and Rh₃Ga have non-zero moment. DOS and COOP studies reveals that d orbitals of Rh are responsible for bonding and for the formation of doped clusters. Orbitals of the doped atoms are not participating in the overall bonding in HOMO. Overlapping among orbitals is more in LUMO than in HOMO. Sideways orbitals overlapping (π type) are primarily responsible for bonding among metal d orbitals. QTAIM and Bader charge analysis suggest more ionic character in the case of doped clusters than bare variant. Relative free energy barrier height is smaller for Rh₄Ga and Rh₄Al than Rh₅ towards O–H dissociation. So, Rh₄Ga and Rh₄Al clusters are more catalytically active for CH₃OH activation than pure Rh₅ cluster, whereas Rh₅B is least active.

Supplementary Information (SI)

BSSE-corrected energies of doped clusters, magnetic and dipole moment variations with cluster size, and coordinates of doped clusters involved in methanol activation are presented in Table S1, Figure S2 and Table S3 respectively. Supplementary Information is available at www.ias.ac.in/chemsci.

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References

- Johnston R L 2002 In *Atomic and Molecular Clusters* St. Edmundsbury press (London: Taylor and Francis) p. 256
- Connerade J P and Solovyov A V 2004 In *Latest Advances in Atomic Cluster Collisions: Fission, Fusion, Electron, Ion and Photon Impact* (London: Imperial College Press) p. 398
- Reinhard P G and Suraud E 2004 In *Introduction to Cluster Dynamics* (Weinheim: Wiley-VCH) p. 315
- Baletto F and Ferrando F 2005 Structural properties of nanoclusters: Energetic, thermodynamic, and kinetic effects *Rev. Mod. Phys.* **77** 371
- Knickerbein M B 2001 Experimental Observation of Superparamagnetism in Manganese Clusters *Phys. Rev. Lett.* **86** 5255
- Reddy B V, Khanna S N and Dunlap B I 1993 Giant magnetic moments in 4d clusters *Phys. Rev. Lett.* **70** 3323
- Moseler M, Hakkinen H, Barnett R N and Landman U 2001 Structure and magnetism of neutral and anionic palladium clusters *Phys. Rev. Lett.* **86** 2545
- Jortner J 1992 Cluster size effects *Z. Phys. D* **24** 247
- Johnston R L 1998 The development of metallic behaviour of clusters *Philos. Trans. R. Soc. London, Ser. A* **356** 211
- Pearson W B 1972 *The Crystal Chemistry and Physics of Metals and Alloys* (New York: Wiley) p. 515
- Ruban A V, Skriver H L and Norskov J K 1999 Surface segregation energies in transition-metal alloys *Phys. Rev. B* **59** 15990
- Bozzolo G, Ferrante J, Noebe R D, Good B, Honey F S and Abel P 1999 Surface segregation in multicomponent systems: Modeling of surface alloys and alloy surfaces *Comput. Mater. Sci.* **15** 169
- Molenbroek A M, Haukka S and Clausen B S 1998 Alloying in Cu/Pd Nanoparticle Catalysts *J. Phys. Chem. B* **102** 10680
- Braunstein P, Oroand L A, Raithby P R and Schmid G 1999 In *Metal Clusters in Chemistry* (Weinheim: Wiley-VCH) **3** 1325
- Kalita B and Deka R C 2007 Stability of small Pd_n (n = 1 – 7) clusters on the basis of structural and electronic properties: A density functional approach *J. Chem. Phys.* **127** 244306
- Galicía R 1985 *Rev. Mex. Fís.* **32** 51
- Cox A J, Louderback J G and Bloomfield L A 1993 Experimental observation of magnetism in rhodium clusters *Phys. Rev. Lett.* **71** 923
- Cox A J, Louderback J G, Apsel S E and Bloomfield L A 1994 Magnetism in 4d-transition metal clusters *Phys. Rev. B* **49** 12295
- Mendes F M and Schmal M 1997 The Cyclohexanol dehydrogenation on Rh-Cu/Al₂O₃ Catalysts: 2 Chemisorption and reaction *Appl. Catal. A* **163** 153
- Trunschke A, Ewald H, Gutschick D, Miessner H, Skupin M, Walther B and Bottcher H C 1989 New bimetallic Rh-Mo and Rh-W clusters as precursors for selective heterogeneous co hydrogenation *J. Mol. Catal.* **56** 95
- Fromen M C, Serres A, Zitoun D, Respaud M, Amiens C, Chaudret B, Lecante P and Casanove M J 2002 Structural and magnetic study of bimetallic CO_{1-x}Rh_x *J. Magn. Magn. Mater.* **242** 610
- Parsons R and Vandernoot T 1988 The oxidation of small organic molecules: A survey of recent fuel cell related research *J. Electroanal. Chem.* **257** 9
- Agrell J, Germany G, Jaras S G and Boutonnet M 2003 Production of hydrogen by partial oxidation of methanol over ZnO-supported palladium catalysts prepared by microemulsion technique *Appl. Catal. A: Gen.* **242** 233
- Liu S, Takahashi K, Eguchi H and Uematsu K 2007 Hydrogen production by oxidative methanol reforming on Pd/ZnO: Catalyst preparation and supporting materials *Catal. Today* **129** 287
- Ghatak K, Sengupta T and Pal S 2015 Computational investigation on the catalytic activity of Rh₆ and Rh₄Ru₂ clusters towards methanol activation *Theor. Chem. Accounts* **134** 1597
- Behr A, Brunsch Y and Lux A 2012 Rhodium nanoparticles as catalysts in the hydroformylation of 1-dodecene and their recycling in thermomorphic solvent systems *Tetrahedron Lett.* **53** 2680
- Yoon T J, Kim J I and Lee J K 2003 Rh-based olefin hydroformylation catalysts and the change of their catalytic activity depending on the size of immobilizing supporters *Inorg. Chim. Acta* **345** 228

28. Li K, Wang Y, Jiang J and Jin Z 2010 Hydroformylation of higher olefins by thermoregulated phase-transfer catalysis with rhodium nano particles *Chin. J. Catal.* **31** 1191
29. Vu T V, Kosslick H, Sculz A, Harloff J, Paetzold E, Ranik J, Kragl U, Fulda G, Janiak C and Tuyen N D 2013 Hydroformylation of olefins over rhodium supported metal-organic framework catalysts of different structure *Microporous Mesoporous Mater.* **177** 135
30. Sidhpuria K B, Patel H A, Parikh P A, Bahadur P, Bajaj H C and Jasra R V 2009 Rhodium nanoparticles intercalated into montmorillonite for hydrogenation of aromatic compounds in the presence of thiophene *Appl. Clay Sci.* **42** 386
31. Sanchez A, Fang M, Ahmed A and Sanchez-Dolgado R A 2014 Hydrogenation of arenes, N-heteroaromatic compounds, and alkenes catalyzed by rhodium nanoparticles supported on magnesium oxide *Appl. Appl. Catal. A* **477** 117
32. Chung Y M and Rhee H K 2003 Partial hydrogenation of 1,3-cyclooctadiene using dendrimer-encapsulated Pd–Rh bimetallic nanoparticles *J. Mol. Catal. A* **206** 291
33. Srivastava A K and Misra N 2014 Structures, stabilities, electronic and magnetic properties of small Rh_xMn_y ($x + y = -4$) clusters *Comput. Theory Chem.* **1047** 1
34. Mekkath J H and Pastor G M 2012 First-principles study of structural, magnetic, and electronic properties of small Fe–Rh alloy clusters *Phys. Rev. B* **85** 054407
35. Dennler S, Morillo J and Pastor G M 2003 Calculation of magnetic and structural properties of small Co–Rh clusters *Surf. Sci.* **532** 334
36. Lu J, Bai X, Jia J F, Xu X H and Wu H S 2012 Structural, electronic and magnetic properties of Co_nRh ($n = 1 - 8$) clusters from density functional calculations *Phys. B* **407** 14
37. Yang J X, Wei C F and Guo J J 2010 Density functional study of Au_nRh ($n = 1 - 8$) clusters *Phys. B* **405** 4892
38. Soltani A, Boudjahem A G and Bettahar M 2016 Electronic and magnetic properties of small Rh_nCa ($n = 1 - 9$) clusters: A DFT study *Int. J. Quantum. Chem.* **116** 346
39. Lecours M J, Chow W C T and Hopkins W S 2014 Density Functional Theory Study of $\text{Rh}_n\text{S}^{0,\pm}$ and $\text{Rh}_{n+1}^{0,\pm}$ ($n = 1 - 9$) *J. Phys. Chem. A* **118** 4278
40. Zhang S, Zhang Y, Yang X, Lu C, Li G and Lu Z 2015 Systematic theoretical investigation of structures, stabilities, and electronic properties of rhodium-doped silicon clusters: Rh_2Si_n^q ($n = 1 - 10$; $q = 0, \pm 1$) *J. Mater. Sci.* **50** 6180
41. Jia L C, Zhao R N, Han J G, Sheng L S and Cai W P 2008 Geometries and Stabilities of the Carbon Clusters with the Rhodium Impurity: A Computational Investigation *J. Phys. Chem. A* **112** 4375
42. Dutta A and Mondal P 2016 Structural evolution, electronic and magnetic manners of small rhodium $\text{Rh}_n^{+/-}$ ($n = 2 - 8$) clusters: a detailed density functional theory study *RSC Adv.* **6** 6946
43. Delley B 2000 From molecules to solids with the DMOL³ approach *J. Chem. Phys.* **113** 7756
44. Delley B 1990 An all-electron numerical method for solving the local density functional for polyatomic molecules *J. Chem. Phys.* **92** 508
45. Becke A D 1988 Density-functional exchange-energy approximation with correct asymptotic behavior *Phys. Rev. A* **38** 3098
46. Lee C, Yang W and Parr R G 1988 Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density *Phys. Rev. B* **37** 785
47. Delly B and Ellis D E 1982 Efficient and accurate expansion methods for molecules in local density models *J. Chem. Phys.* **76** 1949
48. Bader R F W 1990 In *Atoms in Molecules: A Quantum Theory* (Oxford, U.K.: Oxford University Press)
49. Bader R F W 1998 A Bond Path: A Universal Indicator of Bonded Interactions *J. Phys. Chem. A* **102** 7314
50. Bader R F W 1991 A Quantum Theory of Molecular Structure and Its Applications *Chem. Rev.* **91** 893
51. Keith T A 2013 *AIMAll (Version 13.02.26)*, ed. TK Gristmill Software, Overland Park KS, USA. (<http://aim.tkgristmill.com>)
52. Matar S F, Pöttgen R, Al Alam A F and Ouaini N 2012 *Chem. Phys. Lett.* **5** 75
53. Hughbanks T and Hoffmann R 1983 Chains of trans-edge-sharing molybdenum octahedra: metal-metal bonding in extended systems *J. Am. Chem. Soc.* **105** 3528
54. Dutta A and Mondal P 2017 Structural, electronic and catalytic properties of single magnesium atom doped small neutral Rh_n ($n = 2 - 8$) clusters: Density functional study *Comput. Comput. Theory Chem.* **1115** 284