



Understanding CO oxidation mechanism over pristine Pt and 4d & 5d elements doped 4-atom nanoclusters

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Introduction

Study of the adsorption of gases on metal surface has gained renewed importance in the last decade due to the advent sophisticated surface technique. CO oxidation on metal surface is one of the most important catalytic reactions due primarily to two reasons. Technologically, it is a very important reaction in car-exhaust emission control, CO lasers, air purification and sensors. Scientifically, it is one of the simplest catalytic reactions and thus is widely used as a model system to understand heterogeneous catalysis.

Carbon monoxide or CO is colorless, odorless but poisonous and even deadly gas. It is produced from the incomplete burning or partial oxidation of various fuels like coal, gasoline and natural gas. It is very necessary to remove CO from enclosed atmosphere and various residue gases. In addition, even trace CO is harmful to Pt catalyst with application such as in fuel cells. The purification of feed gases for these applications is of course mandatory. CO oxidation is an excellent reaction for the evolution of catalysts with easy operation and low cost. CO oxidation to CO₂ is essential automotive exhaust and low temperature fuel cell for environmental and health friendly emission.

Catalyst for CO oxidation can be grouped into two main categories: non-noble metal catalysts and supported noble metal catalyst. Supported noble metal catalysts mainly include Pt, Pd, Ag, Au and Rh and their bimetallic structure (Pt₃M) (M= Pd, Ag, Au, Rh). And maybe Non noble metal catalysts include iridium and their (Pt₃Ir) structure. Supported noble metal catalysts, especially Pt-Pd-Au-Ag have been extensively used studied for CO oxidation. Among them, Au catalyst always exhibits excellent activity at lower temperature, while Pd and Pt catalyst have higher turnover frequencies at relatively high temperature. Platinum among these has shown the most remarkable catalytic efficiency. Platinum nanoclusters have become a fundamental topic of investigation for CO oxidation pertaining to their catalytic surface area and molecular level insights they provide for reaction on metal surface. Challenges associated with Pt-based catalyst are the high cost, low abundance, and rapid deactivation of the catalyst by CO poisoning. This is a certain extent can be overcome by replacing Platinum with transition metals, Which improve catalytic nature of parent clusters. Alloying the platinum cluster with Rh, Pd, Ag, Au and Ir manipulate the geometrical and electronic structure of the cluster and enhanced catalytic properties.

Although various studies have shown that Pt bimetallic systems to exhibit better catalytic activities and lower CO poisoning effect, complete elimination of Pt poisoning is still unresolved. Here we report the effect of transition metal (Rh, Pd, Ag, Au, and Ir) doping in the pure Pt₄ clusters for CO oxidation and explore the mechanism of CO oxidation catalytic activity at an atomic level.

Density Functional Theory

Density functional theory is a computational quantum mechanical modeling method used in material science to investigate the electronic structure of many body system, in particular atoms, and molecules and condensed phases. Using this theory the properties of a many electron system can be determined by using functional, i.e. functions of another function. In the case of DFT, these are functional of the spatially dependent electron density. The density in density functional theory (DFT) refers to electron density, which is the object of all DFT calculations. DFT differ from various other wave function-based method which focuses on determining the ground-state 3N dimensional wave function such as the Hartree-fock (HF) method. Electron density, often denoted as ρ or n° , refers to the 3-dimensional function of 3 spatial coordinates describing the distribution of electrons in a given system. It is of interest in DFT as it allows us to determine all observable properties of the system without knowing the exact ground state wave function, hence providing great computational ease. A functional is a function of a function. A commonly used functional would be definite integral. In Kohn-Sham DFT, notably the most widely used version of DFT, the functional can be seen as comprising of three main contributions:

- (1) Kinetic energy
- (2) Columbic interaction between pairs of electrons.
- (3) Columbic interaction between electrons and nuclei

For example when we consider columbic interaction of each electron with the electron density, we also include a non physical self interaction particles in the system can also undergo exchange interaction and their motions are also correlated (i.e. they are not independent). Hence, another term called the XC (exchange-correlation) functional is also include into the overall density functional expression to account for all these additional effects that have not already been accounted for.

The following is an expression of the kohn-Sham DFT

$$\mathbf{E}[\rho] = \mathbf{T}_s[\rho] + \int dr V_{ext}(r)\rho(r) + \mathbf{E}_H[\rho] + \mathbf{E}_{xc}[\rho]$$

The first term is the electron kinetic energies; the second represents the electron-nuclei interaction energy, the third represent the hartree (or coulomb) energy and E_{xc} is the exchange – correlation energy. Classical DFT allow the calculation of the equilibrium particle density and prediction of thermodynamics properties and behavior of a many body system on the basis of model interactions between particles. The spatially dependent determine the local structure and

composition of the material. In DFT techniques the electronic structure is evaluated using a potential acting on the systems electrons. This DFT potential is constructed as the sum of external potential V_{ext} , which is determined solely by the structure and the elemental composition of the system, and an effective potential V_{eff} , which represents interelectronic interactions. Thus, a problem for a representative supercell of a material with n electron can be studied as a set of n electron can be studied as a set of n electron Schrodinger like equation, which are also known as Kohn-Sham equation.

The intractable many bodies problem of interacting electron in static external potential is reduced to traceable problem of noninteracting problem of noninteracting electrons moving in effective potential. The effective potential includes the external potential between and coulomb interaction between the electrons i.e., exchange and correlation interaction. Modeling the latter two interactions becomes the difficulty within KS DFT. The simplest approximation is local density approximation which is based upon exact exchange energy for uniform electron gas, which can be obtained from Thomas Fermi model and from fits to correlation energy for uniform electron gas.

However, one of the simplest density approximations (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated:

$$\sum_{XC}^{LDA}(n) = \int \epsilon_{xc}(n)n(r) d^3r.$$

The local spin density approximation (LSDA) is a straight forward generalization of the LDA to include electron spin:

$$\sum_{XC}^{LSDA}(n \uparrow, n \downarrow) = \int \epsilon_{xc}(n \uparrow, n \downarrow) n(r) d^3r.$$

In LDA, the exchange-correlation energy is typically separated into the exchange part and the correlation part: $\epsilon_{xc} = \epsilon_x + \epsilon_c$.

Later, (GGA) generalized gradient approximation gave very good result for molecular geometries and ground state energies have been achieved. GGA have the following form:

$$\sum_{XC}^{GGA}(n \uparrow, n \downarrow) = \int \epsilon_{xc}(n \uparrow, n \downarrow, \nabla n \uparrow, \nabla n \downarrow)$$

Local density approximation

Local density approximations are class of approximation to exchange-correlation (XC) energy functional in density functional theory that depend upon the value of the electronic density at each point in space. Successful local approximations are those that have been derived from the homogenous electron gas model.

In general, for a spin-unpolarized system, local density approximation for the exchange correlation energy written as

$$\Sigma_{XC}^{LDA}(\rho) = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r},$$

Where, ρ is the electronic density and ϵ_{xc} is the exchange-correlation energy per particle of homogenous electron gas of charge density ρ . The exchange correlation energy is decomposed into exchange and correlation into exchange and correlation terms linearly,

$$\mathbf{E}_{xc} = \mathbf{E}_x + \mathbf{E}_c$$

LDA are important in the construction of more sophisticated approximation to exchange correlation energy, such as generalized correlation or hybrid functional, as a desirable property of any approximate exchange-correlation is that it reproduce the exact results of HEG for non varying densities.

Generalized gradient approximation

In LDA in DFT has been successfully to calculate the structural properties of solid, including the calculations of stability, lattice constant, bulk module, and phonon spectra. Since the LDA replaces the inhomogeneous density of the system of the system with a locally homogenous electron gas, the amount of error introduced by LDA will be larger for highly localized or inhomogeneous system than for delocalized system. To generate more accurate XC functional, the generalized gradient approximations capture both the local and semi local information the electron density and gradient at a given point.

A generalized gradient approximation (GGA) for the exchange correlation functional with explicit dependence on the gradient of charge density in DFT extends the practical implementation of DFT to inhomogeneous systems. Computationally it is simple to extend the LDA functional to the GGA functional with simple gradient calculation of density at minimal cost. Here we use GGA functional by Perdew, Burke, and Ernzerhof (PBE), which satisfies many exact properties of DFT. Typical form of a GGA functional is:

$$\mathbf{E}_{xc} = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho, \nabla\rho) d\mathbf{r}$$

PBE present a simplified and improved GGA version with no empirical element. It includes feature such as local electron density and its gradient and second-order gradient in the enhancement factor, $F(x)$ and $F(c)$. This functional has been proven to be highly accurate and computationally efficient, and now the most used functional.

Van Der Waals correlation to DFT

In Kohn sham DFT calculation, van der Waals correlation are often implemented in the structure optimization calculations because the typical functional such as LDA, GGA are not found to treat long range dispersion force faithfully. But even in the context of van der Waals correlation DFT-D and DFT-D3 schemes higher accuracy methods are available but these are limited to smaller system sizes. Dispersion corrected DFT are not new functional but a mix of conventional functional plus D3 dispersion correction energy term. The dispersion correction energy terms is relatively simply function of interatomic distance and contain adjustable parameters that are fitted to interaction energies. DFT-D and DFT-D2 energy correction consider all pair of atoms (all electrons all paired) while DFT-D3 also consider triplet (its maybe called excited state of atom) of atom (two unpaired electron are present in Different orbital have parallel spin).

Dispersion correction can lead to significant can lead to significant improvement in accuracy and the computational cost associated with dispersion correction are negligible. (Google molecular modeling basics)

Now, the total energy in case of VdW correction is given by,

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}}$$

Where $E_{\text{DFT-D}}$ is general KS self-consistency energy and E_{disp} is the correction to the correction functional.

Spin-polarized DFT

We have Neglected the spin degree of freedom up to this point, assuming $\rho\uparrow(r) = \rho\downarrow(r) = \rho(r)/2$, which is generally the case in many solids. But in the case of open- shell systems with an odd number of electrons or magnetic solid, spin polarization should be considered. The calculation adds spin variable to electron density and XC potential so that the energy functional depends on both the electron density on both the electron density, $\rho(r) = \rho\uparrow(r) + \rho\downarrow(r)$ and spin density $s(r) = s\uparrow(r) - s\downarrow(r)$. Then the calculation consider the total number of electron as $n = n\uparrow + n\downarrow$ and XC potential for example, as $U_{\text{xc}}(r) = U_{\text{xc}}\uparrow(r) + U_{\text{xc}}\downarrow(r)$. The spin polarized DFT with GGA works the same way. Thus dealing with spin straight-forward only if we accept the doubled calculation time due to the two simultaneous iterative loops for each spin variable.

D band Model

The D band model of Hammer and Norskov is widely used in understanding and predicting catalytic on transition metal surface. Here we demonstrate that this model is inadequate for capturing the complete catalytic activity of the magnetically polarized TM surface and propose its generalization. Here comparison of adsorption energies of CO molecule on the surface of 4d

and 5d TMs (Pt, Ag, Au, Rh, Ir, and Pd) determined with spin polarized DFT based method with the prediction of our model. Due to low abundance, toxicity- related and high cost of 4d and 5d metals, in recent years researchers have turned to developing catalyst using cheap and abundant 3d transition metals (TMs) and their alloy or oxides. The catalytic reaction in these materials can be operate using spin. Theoretical studies are focused on the understanding the nature of interaction between the adsorbate and the d-electron of the TM surface. To understand the role of d-electron is the called d band center model. In the D band model, band of d states participating in the interaction is approximated with single state at energy ϵ_d known as the center of the d band.

According to this model, the variation in the adsorption energy from one TM surface to another correlates the upward shift of this d band center with respect to Fermi energy. A stronger upward shift indicates the possibility of the formation of larger number of empty antibonding states, leading to stronger binding energy. The upward shift indicates the possibility of formation of larger number of empty antibonding states, leading to a stronger binding energy. The upward shift of d band center can therefore be treated as a descriptor of catalysis. The d band center model predicts a uniform decrease (increase) of adsorption energy of a given molecule from one TM surface to another where the number of d electron increases (decrease). We show here that for better comparison with results obtained from the spin based DFT based methods, the conventional d band center model has to be extended by considering two band center, one each for spin majority and the spin minority electron of the system.

To understand the trend in catalytic activity across TMs one should consider the spin polarization of metal surface in addition to number of electrons. We schematically compare the d band center of metallic surface with and without spin polarization. When spin polarization is considered in calculation, it is appropriate to consider two d band center, one for the spin up state $\epsilon_d\uparrow$ and the other for spin down state $\epsilon_d\downarrow$. These are shifted in opposite direction in energy relative to the unpolarized d band center; ϵ_d . $\epsilon_d\uparrow$ is shifted downward, while the $\epsilon_d\downarrow$ is shifted upward with respect to ϵ_d . If we consider that these two center interact with adsorbate level, we should obtain two set of bonding and antibonding levels. Naturally when the degree of spin polarization is smaller, the two d band center is close to each other, and their activity is similar. However, when the spin polarization is higher two band center are shifted significantly in opposite direction. If we consider the interaction with adsorbate possessing multiple levels, there are more unoccupied metal adsorbate antibonding state giving rise to strong attractive interaction, while there are more occupied state for majority spin electrons, resulting in strong repulsion. Therefore the minority spin d band binds more strongly to the adsorbate, while the binding with majority spin states is weaker.

The adsorption energy can be expressed as follow

$$\Delta E_d = -\sum_{\sigma,\sigma'} \frac{f_{\sigma} V_{\sigma,\sigma'}^{dai^2}}{\epsilon_{ai\sigma'}^* - \epsilon_{d\sigma}} - \sum_{\sigma,\sigma',j} (1 - f_{\sigma}) \frac{f_{\sigma} V_{\sigma,\sigma'}^{dai^2}}{\epsilon_{d\sigma}^* - \epsilon_{aj\sigma'}} + \sum_{\sigma,\sigma',j} f_{\sigma} \alpha V_{\sigma,\sigma',j}^{da} i^2 + \sum_{\sigma,\sigma',j} (1 + f_{\sigma}) \alpha V_{\sigma,\sigma',j}^{da} i^2$$

$V_{\sigma,\sigma',j}^{da^k}$ are the matrix elements of the coupling between the TM d state with K^{th} adsorbate state $\sum_{ai\sigma'}^*$ is the energy of i^{th} unoccupied adsorbate state with spin σ' and $\epsilon_{ai\sigma'}$ is the energy of the j^{th} occupied adsorbate state. Two d band center for majority and minority spin are respectively $\epsilon_{d\uparrow}$ and $\epsilon_{d\downarrow}$. The first term in above equation is energy gain due to the interaction of the unfilled adsorbate state with metal states. The first term always describes an attractive interaction, while second term has both attractive and repulsive component. Here f_{σ} is the fractional filling of metal state with spin σ . The last two terms in above equation are due to orthogonalization of adsorbate state and TM d state and are always repulsive. The parameter α is adjustable and has unit of eV^{-1} . The third term is due to orthogonalization of empty adsorbate state on the metal d states, while the fourth term represents the orthogonalization of filled adsorbate states on the metal states.

Quantum espresso simulation package

The combination of methodology and algorithmic innovation and ever-increasing computer power is delivering a simulation revolution in material modeling, starting from the nanoscale up to bulk material and devices. Electronic Structure Simulation based on Density Functional Theory (DFT) have been instrumental to this revolution, and their application has now spread out a restricted core of researchers in condensed matter physics and quantum chemistry, involving a vast community of end users with very diverse scientific background and research interests.

Over the past few decades, Innovation in material simulation and modeling has resulted from the concerted efforts of many individual and group worldwide, often of small size. Their success has been made possible by combination of competences, ranging from the ability to address meaningful and challenging problems, to rigorous insight into theoretical methods, ending with a marked sensibility to matters of numerical accuracy and algorithmic efficiency.

We present an algorithm and implementation for the computation of exact exchange in Quantum espresso (QE) that exhibits greatly improved strong scaling. Quantum espresso is an integrated suite of open source computed codes for quantum simulation of material using state of art electronic structure techniques, based on DFT, DF perturbation Theory, within the plane wave pseudo potential and projector augmented wave approach. QE is an open source software package for electronic structure calculation using plane wave density functional theory, and support the use of local, semi local and hybrid DFT functional. Wider application of hybrid functional is desirable for the improved simulation of electronic band energy alignments and thermodynamics properties, but the computational complexity of evaluating the exact exchange potential limits the practical application of hybrid functional to large systems and requires efficient implementation. Quantum Espresso owes its popularity to the wide variety of properties

and process it allow to stimulate, to its performance on an increasingly broad array of hardware architecture, and to a community of researchers that rely on its capabilities as a core open source development platform to implement their ideas. The Increasing use of high throughout density functional theory (DFT) calculation in the computational design and optimization of material require the availability of a comprehensive pseudo potential. Density functional Theory calculation with plane wave and pseudopotentials represent one of the most important simulation techniques in high performance computing.

Quantum espresso (QE) is a full initio package implementing all feature of DFT

- Electronic and ionic minimization (or relaxations) for total energies, band structure, density of states, etc. using ultrasoft, norm-conserving, PAW pseudopotentials.
- Linear response methods to calculate phonon spectra, dielectric constants and born effective charges.

Although QE can deal with any level of electronic structure calculation, it is most suited for beginners to quantum world in three respects. First it is free and open code.

Computational Method

We use Quantum espresso (1) which is a compute package to study the electronic structure and optimization using molecular dynamics simulation. All self consistent total energy calculation was based on spin polarized density functional theory as implemented in the quantum espresso (QE) package. Electron-ion interactions were described using all electron projected-augmented wave (PAW) pseudopotentials. Electronic exchange correlation interaction were evaluated by the local density approximation (LDA) proposed by Perdew-Zunger and generalized gradient approximation (GGA) formulated by Perdew-Burke-Ernzerhof (PBE). The standard DFT (with LDA and PBE functional) framework cannot provide an accurate description of the long-range dispersion force, i.e., very much required for the accurate prediction of the adsorption properties of molecule over TM systems. For the treatment of the long-range dispersion forces, the semiempirical van der Waals correction D2 and D3 proposed by grimme were employed. The sum of the total energy of self-consistent DFT ($E_{\text{KS-DFT}}$) with vdW correction (E_{disp}) is given by

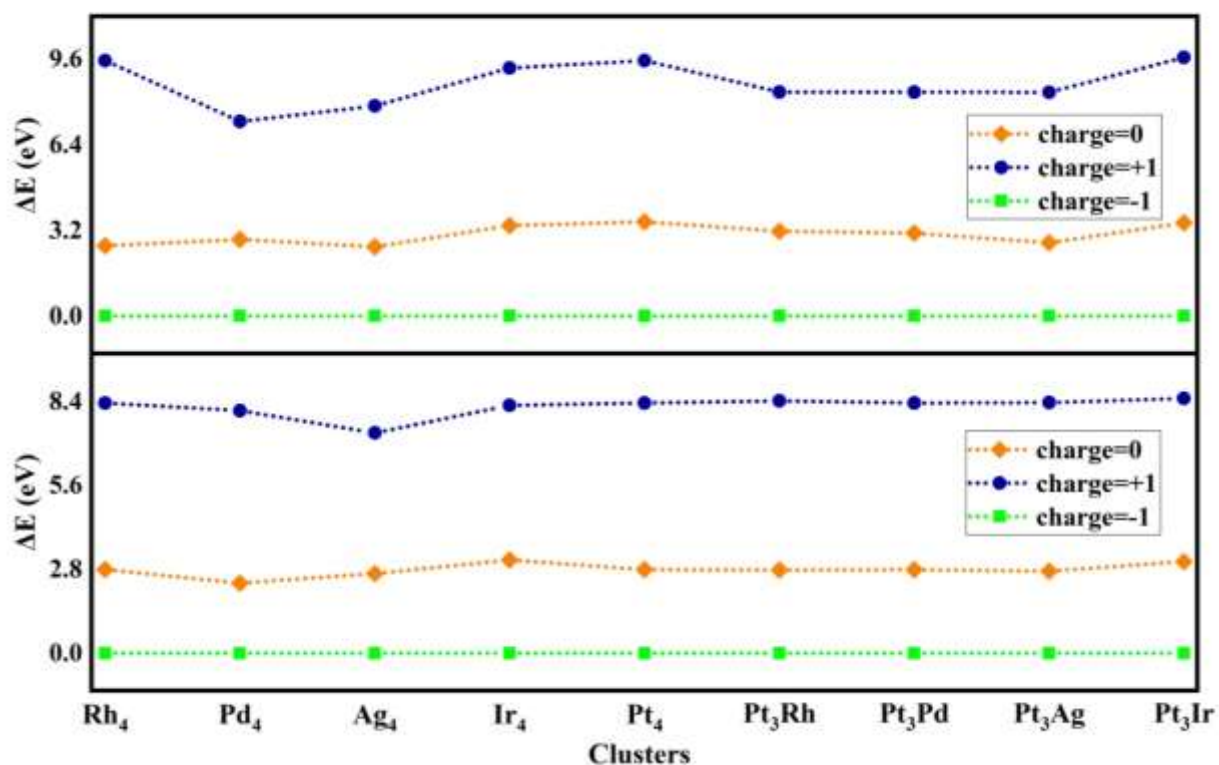
$$E_{\text{DFT+D2/D3}} = E_{\text{KS-DFT}} + E_{\text{disp}}$$

We have also used XCrysden which is a molecular-structure visualization program based on the crystalline structure. It facilitates a display of iso-surface and contour, which can be seen crystalline structure and for better visualization, interactive rotation too is provided as a part of the same program.

Result and discussion

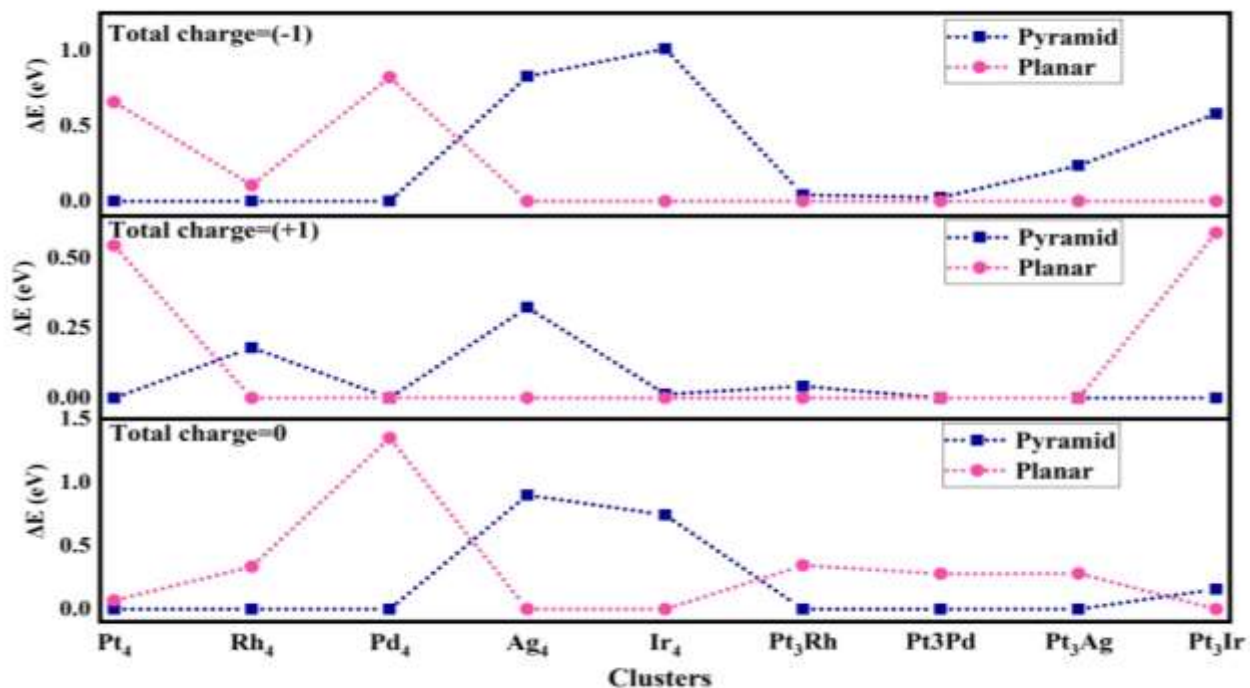
Structure Stability

Stability occurs when a system is in its lowest energy state, or in chemical equilibrium with its environment. This may be a dynamic equilibrium in which individual atoms or molecules change form is conserved. To establish the structure stability we define stability in two ways by charge (0, +1, -1) & by geometry (Pyramid (Td) & Planar (C_{2v})). To differentiate stability of clusters with respect to each other for each charge of clusters, we computed relative energy of clusters and we got that clusters with -ve charge is more stable compared to Neutral and positive charge clusters respectively. It can be seen from Graph



GRAPH – I

Now define stability of structure by geometry which is planar and pyramid with respect to each other for each configuration of clusters calculate binding energy of all clusters. The least binding energy of clusters which gave the highest binding energy for CO among the bimetallic clusters. Going from 4d to 5d transition metal there is decrease in binding energy. From binding energy calculation, we can say that when clusters are neutral Pt₄, Rh₄, and Pd₄ more stable in pyramid geometry than planar geometry by energy range of 0.0 to 1.4 eV. Also results of binding energy suggest that Rh, Pd, Ag doped Pt clusters are the more stable structure in pyramid geometry compared to planar geometry. It can be seen from graph - II



GRAPH - II

In positively charged clusters pristine and doped Rh, Pd, and Ag more stable in planar geometry as compared to pyramid geometry. Now, negatively charged clusters pristine and doped Rh, Pd, Ir platinum clusters more stable in planar geometry as compared to pyramid geometry. From all this comparison we conclude that planar geometry and negatively charged clusters is more stable in their respective species.

CO adsorption over Pt₃M and M₄ clusters

In order to gain insight into the effect of subtract on the catalytic efficiency of the Pt₄/bimetallic clusters (Pt₄ and Pt₃M) (M= Pt, Rh, Pd, Ir, Ag) we begin our study with a complete analysis of CO oxidation on free standing clusters. The pyramid geometry has been reported as the lowest energy structure of Pt₄. The pyramid (tetragonal) geometry of M₄ and Pt₃M is shown in below figure - III



Parent (M₄)

Dopant (Pt₃M)

The planar geometry of M₄ and Pt₃M is shown in below figure - III

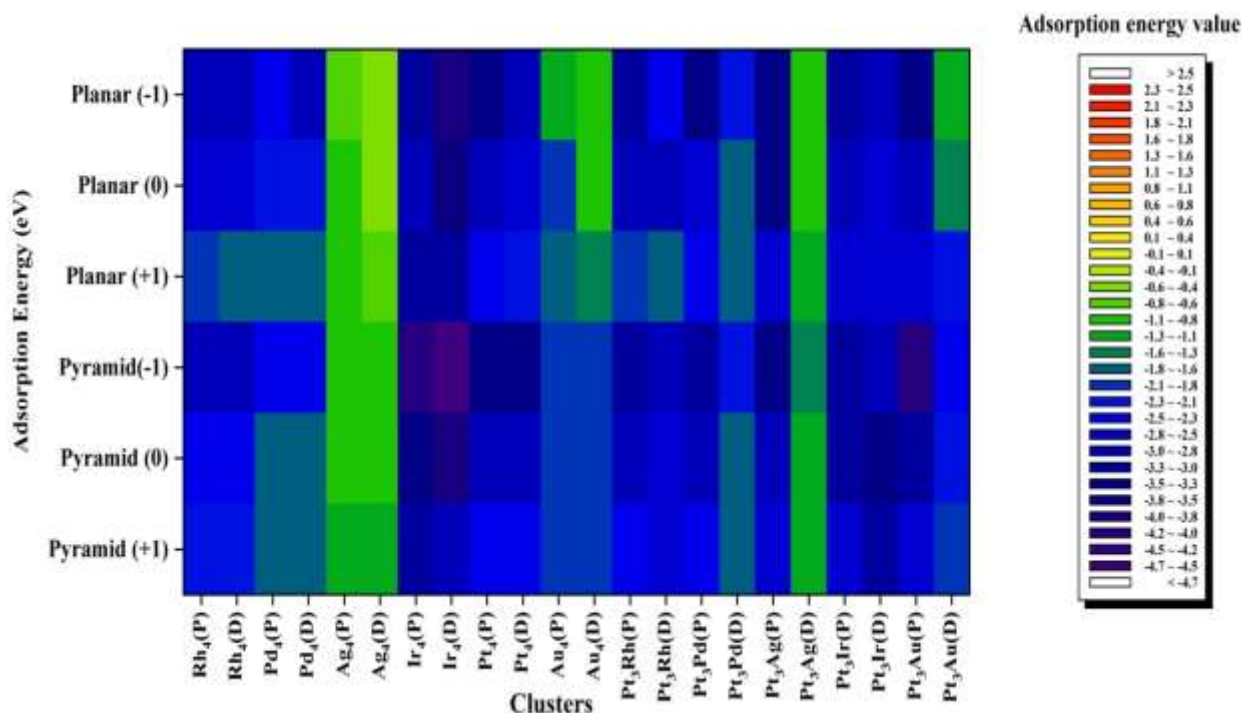


Figure – III Relaxed geometries of M₄ and Pt₃M

Next, CO adsorption was done each cluster followed by geometrical relaxation. The fully relaxed systems adsorb on the clusters end mode taking a slightly geometry with respect to clusters. The adsorption energy of CO onto M₄ and Pt₃M clusters define as

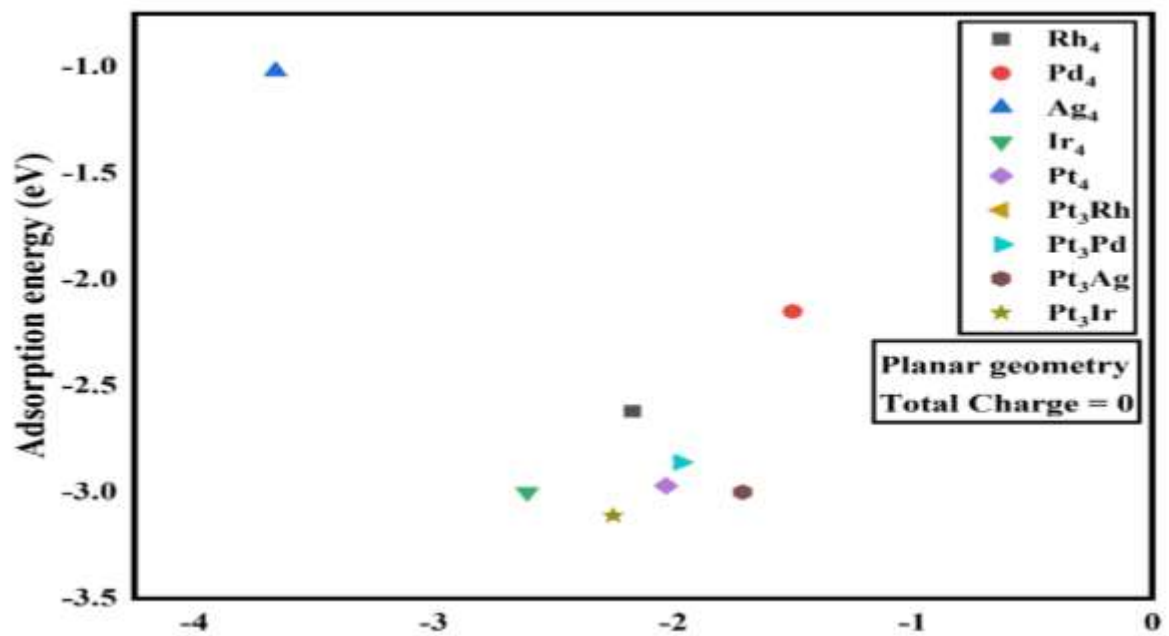
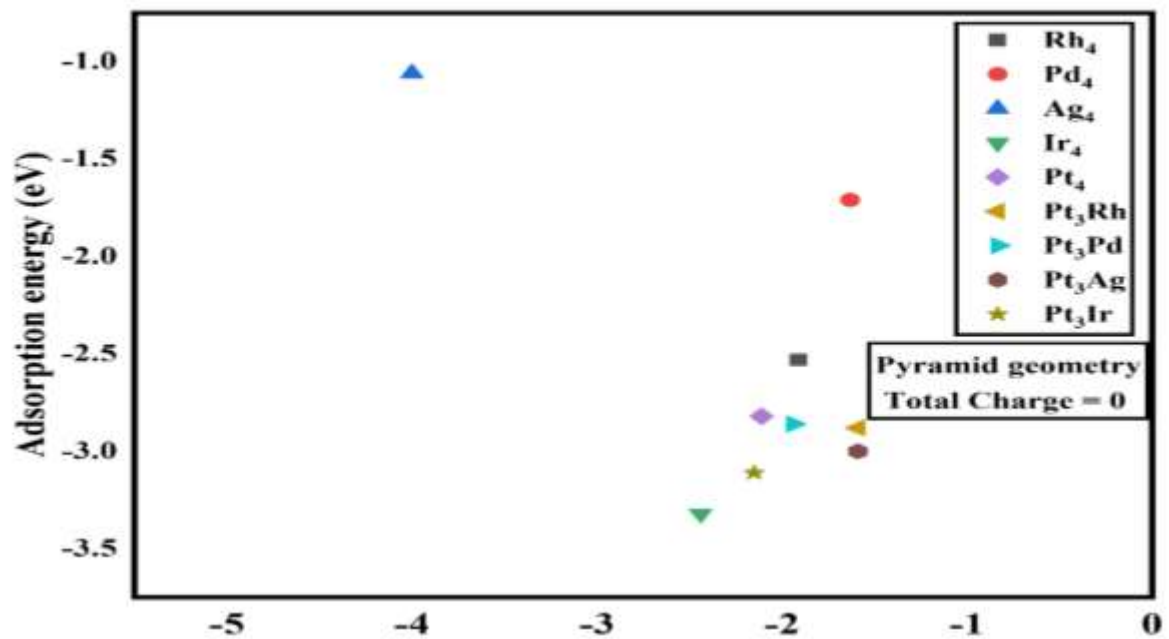
$$E_{(\text{CO-ads})} = E_{(\text{clusters} + \text{CO})} - E_{(\text{clusters})} - E_{(\text{CO})}$$

Where $E_{(\text{clusters} + \text{CO})}$, $E_{(\text{clusters})}$, $E_{(\text{CO})}$ are energies of the cluster adsorbed with CO, the bare cluster, and the CO molecule respectively. The variation examined in the CO adsorption energy can be seen from heat map

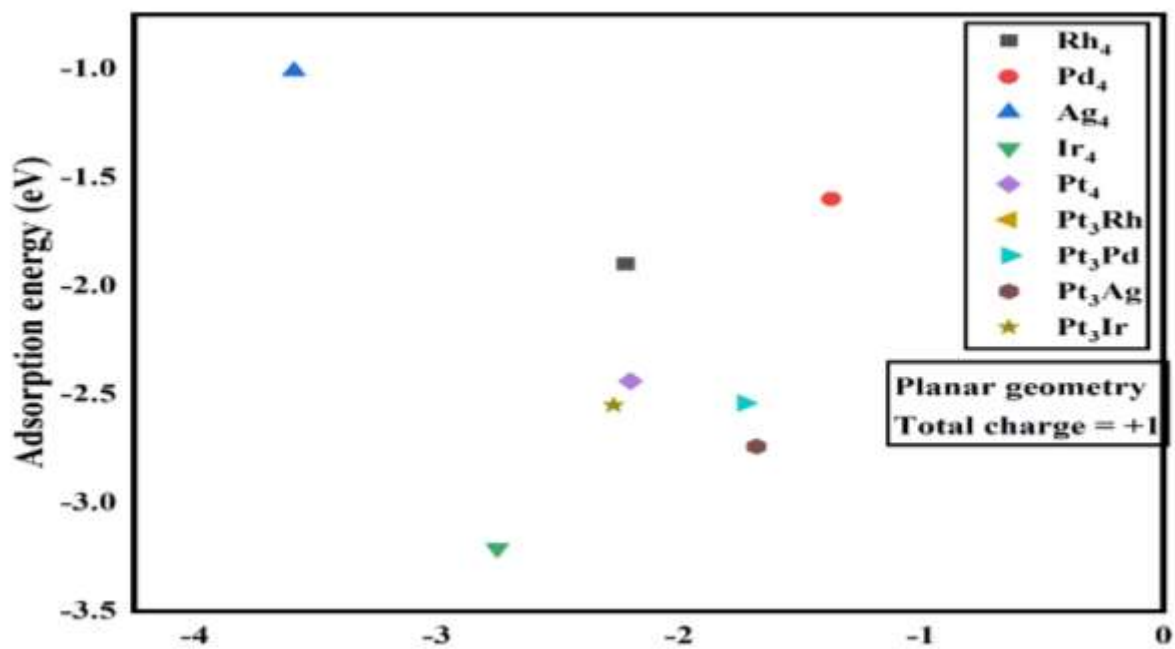
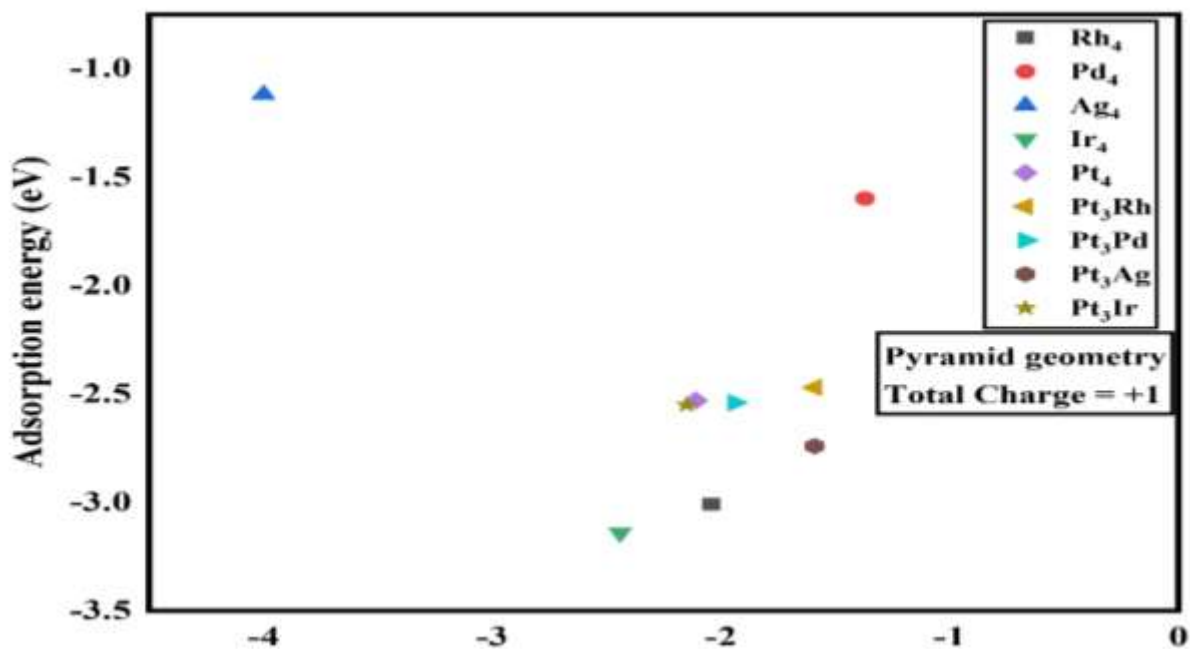


Heatmap of CO adsorption energy ($E_{\text{CO-ads}}$) over Pt_3M and M_4 with respect to different geometries and different charge

The adsorption energy of CO on Pt atom of Pt_4 , Pt_3Rh , Pt_3Pd , Pt_3Ag , Pt_3Ir clusters are -2.82, -2.88, -2.86, -3, and -3.11 respectively. Going from left to right of the periodic table, the adsorption energy decreases with increasing number of d-electron of the M. Going from 4d to 5d transition metal there is increase in adsorption energy of respective clusters. It is observed that CO adsorption energy on the Pt atom is higher on the bimetallic free-standing clusters than on a pure Pt_4 clusters. This is expected as charge has been transferred from Pt atoms to the transition metal in the clusters, making Pt more deficient of charge and more reactive towards CO. CO also get adsorbed on the Pd & Ir atom with only 0.16 and 0.33 higher energy than that for Pt atom. But in the case of Pt_3Rh & Pt_3Ag atom CO get adsorbed Rh & Ag atom with 0.2 and 1.67 eV lower than for Pt atom. We can define relation between adsorption energy vs d band center for different systems in different geometry & different charges from Graphs.



$E \rightarrow \epsilon_d$ (Total Charge = 0)



$E \rightarrow \epsilon d$ (Total Charge = +1)

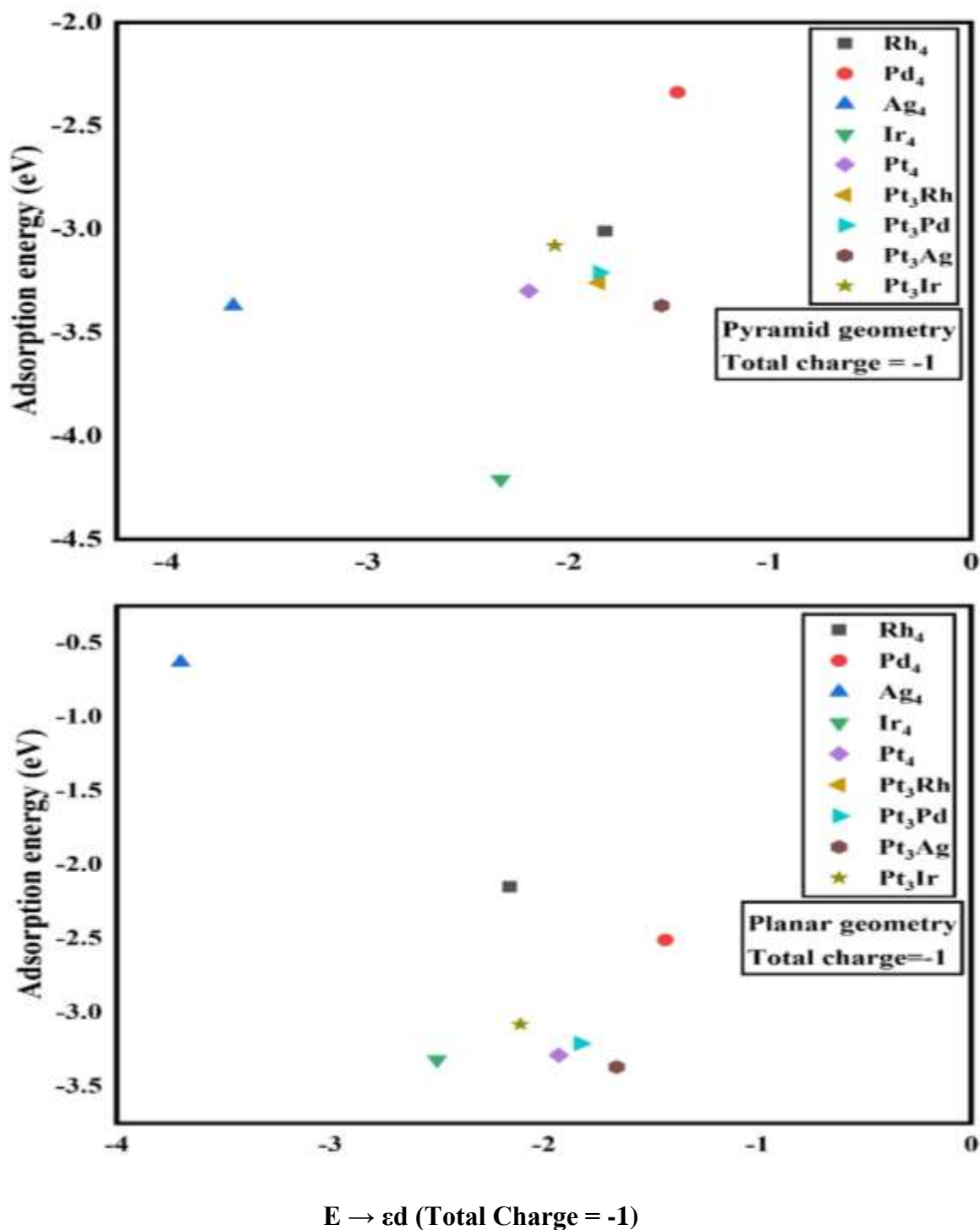
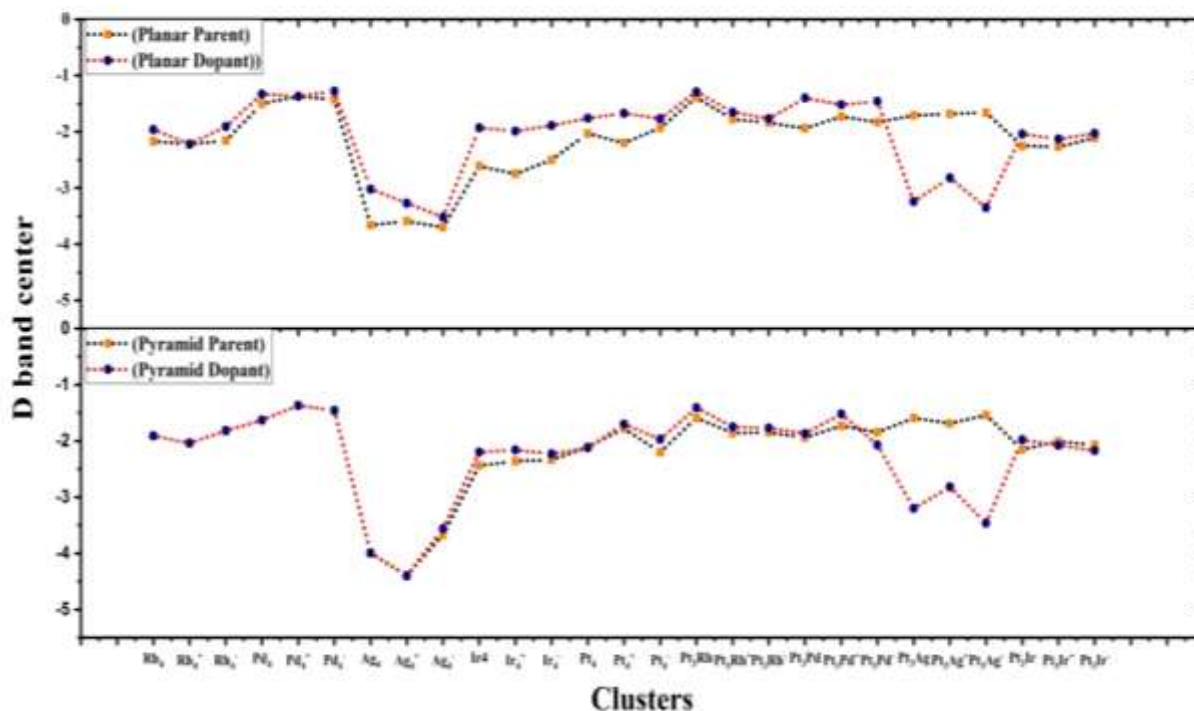


Figure – IV Relation between Adsorption energy vs d band center for different clusters (Pt₃M & M₄) (M = Rh, Pd, Ag, Ir)

Hence for free standing Pt₃Pd & Pt₃Ir there is a stactical probability for CO to adsorbed on the Ir and Pd rather than Pt in the bimetallic clusters, the problem of Pt poisoning can be solved. The

binding energies were -2.78, -2.79, -2.74, -3.06 eV. For Pt₃Rh, Pt₃Pd, Pt₃Ag, Pt₃Ir. The binding energy is greatest in the case of Pt₃Ir. Interestingly CO adsorbs with a weaker binding energy on these clusters. The charge in the catalytic properties of the clusters due to the support can be understood better by looking into the electronic structure of the systems. The d band model is very useful in the explaining the adsorption strength of adsorbents on the transition metals. Graph - V is the representation of the distance of the d band center from the Fermi energy. The lower the d band center from the Fermi energy, fewer empty antibonding states are available for CO-adsorption.



GRAPH - V

In graph-V for Pt₃Rh, the d band center of Pt and Rh atoms lie very close to each other, explaining the competitive adsorption of CO on this clusters. The d band center of Rh, Ir is closer to the Fermi level than that for Pt. Hence for CO adsorption, the Rh & Ir atom is the preferred site by energy difference 0.2 & 0.33 the d band center of the Pd, closer to the Fermi level than that for Pt. Hence Pd atom is the preferred site for CO adsorption. The d band centers of the Pt atom in Pt₃Ag are closer to the Fermi level than that of Ag in their cluster eliminating the chance of adsorption Of CO on Ag sites. Hence, CO prefers the Pt atom sites in Pt₃Ag clusters. And In Pt₃Pd, Pt₃Rh & Pt₃Ir clusters CO prefer the Rh, Pd & Ir sites.

In the case of Pt₃Ag case highest number of antibonding state available for Pt as compared to Ag atom and as shown in graph-V for Pt₃Rh, Pt₃Pd & Pt₃Ir antibonding state are more available for

Rh, Pd & Ir as compared to Pt. These cause the up and downshift of d band center with respect to Fermi level.

Therefore, the d band center position relative to Fermi energy is good indicator of the favorable adsorption site in a system and can be effective tool to design catalyst with no Pt poisoning

Even though Pt₃Pd emerges as our best options to avoid Pt poisoning.

Conclusion

We studied the Pt₄, M & Pt₃M as CO oxidation catalyst. The presence of M(Rh, Pd, Ag, Ir) on platinum solving the critical problem of Pt degradation by CO. The relative position of d-band center from the Fermi level efficiently indicates the favorable adsorption site in a respective cluster. Most remarkably, Pt₃Pd has Pd as preferable site with energy difference of 0.16 eV for CO adsorption rather than Pt, solving the critical problem of Pt poisoning. Also Pt₃Ir & Pt₃Rh cluster has Ir as preferable site with energy difference 0.33 & 0.2 eV.

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