A review on structural, electronic and catalytic properties of pure- and mixed-metal clusters of Au, Pd and Pt

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Abstract—**Transition metal clusters show unique properties which are distinct from individual atoms and bulk materials. These properties are influenced by size, shape, and composition making them highly valuable in diverse applications including catalysis, biomedicine, sensing, and electronics. This review investigates the synthesis, stabilization, and properties of TMCs of gold, palladium and platinum with a focus on clusters of noble metals such as gold, palladium, and platinum. Mixed clusters of Au, Pd and Pt exhibit synergistic properties that enhance their catalytic performance and stability. The interactions between different metal clusters lead to novel properties, including improved catalytic activity and selectivity, making them suitable for advanced applications in various industries. Overall, this review provides a comprehensive understanding of the structural, electronic, and catalytic properties of TMCs, emphasizing their potential in environmental remediation and energy conversion.**

Index Terms— **Transition metal clusters, Mixed clusters, catalytic properties, applications**

I. INTRODUCTION

Transition metal clusters are an exciting class of clusters wherein small number of transition metal atoms are arranged in well-defined structures with size ranging from a few to several dozen atoms. The size, shape, and composition of transition metal clusters (TMCs) define their properties which differ significantly from both individual atoms and bulk materials. The geometric and electronic structures of TMCs are highly tunable which can change their reactivity, optical properties, and magnetic behavior. [1]These clusters show remarkable catalyticefficiency for various chemical reactions due to their high surface-to-volume ratio and unique electronic configurations finding applications in heterogeneous catalysis and therefore, crucial for environmental remediation, industrial and energy conversion processes. [2] Furthermore, these clusters have potential to be used in various fields such as biomedicine, sensing, and electronics.The small size of these TMCs allows for precise interactions with biological molecules, making them suitable for drug delivery, imaging, and therapeutic applications. They can also act as building block for novel nanoscale devices and materials with tailored electronic properties.[2] To understand the synthesis, stabilization and properties of TMCs, it is essential to have an in-depth understanding of different disciplines such as chemistry, physics and material science. [3] Further, experimental methods coupled with computational models serve as crucial tools for finding the structures and behaviors of these transition metal clusters.

Among the various transition metal clusters reported in the literature, especially, clusters of noble metals such as gold, palladium and platinum have gained the wide attention of considerable number of researchers owing to their better catalytic activity, electronic activity, electrochemical properties, durability, versatility and quantum effect. [4] In this review, we have discussed some of the important structural, electronic, optical and catalytic properties of the clusters of the above-mentioned noble metals.

II. TRANSITION METAL CLUSTERS

2.1. GOLD CLUSTERS

Gold, in general, can form neutral and charged clusters based on their oxidation states. Neutral gold clusters are those which do not have any charge. These clusters can differ in size and structure depending on the number of atoms. Further, they show differences in properties such as catalytic activity, electronic and optical properties. In contrast to the neutral gold clusters, the charged gold clusters are those which carry either positive or negative charge. These clusters

can be formed either by adding or removing electrons from neutral gold clusters. These charged clusters can have different electronic structures and reactivity compared to their neutral counterparts and display potential applications in catalysis, sensing, and nanoelectronics.

Understanding the stability of these gold clusters is important for maximizing their performance in specific applications. The stability of gold clusters depends on several factors such as their size, shape, surface chemistry, and the surrounding environment. Compared to gold clusters of larger size, small-sized clusters are found to be more stable due to their higher surface-to-volume ratio. Depending on their shape, spherical gold clusters are more stable than their analogs due to uniformity in surface energy distribution. The stability of the gold clusters can be influenced by the ligands or stabilizing agents since they prevent aggregation thereby providing stability to these clusters. Ligands can be organic molecules, polymers, or biomolecules which interact with the gold surface through chemisorption or physisorption. Besides, their stability can be further affected by the presence of surface charge. For instance, negatively charged ligands can stabilize the clusters due to repulsive forces between particles, preventing aggregation. Also, the solvents can destabilize these clusters by promoting aggregation. They are thermally stable only up to a certain temperature. As the temperature increases, they become destabilized due to aggregation. Thermal stability depends on many factors like size, ligand shell, and the presence of defects in the structure. These clusters are generally chemically stable but oxidative agents or strong reducing agents may cause degradation or structural changes in these clusters, thus, making them unstable. Therefore, mostly gold clusters are highly stable under proper conditions which make them suitable candidates for variety of applications such as in catalysis, sensing, imaging, and drug delivery. They show excellent catalytic activity for various reactions, such as oxidation, reduction, and hydrogenation. Additionally, they show unique optical properties, including surface plasmon resonance, which can be tuned by controlling their size and shape. These clusters can interact with biomolecules, cells, and tissues. [5] These gold clusters can self-assemble with other clusters to form larger nanostructures with novel properties. Functionalization of the clusters with specific ligands enables targeted delivery, imaging, and therapy.

Experimentally, Cui and coworkers synthesized the gold clusters with sizes (< 2 nm) consisting of several to hundreds of gold atoms. [6] Their study revealed that these gold clusters have high chemical stability, high catalytic activity, high biocompatibility and strong luminescence. Further, they prepared gold nanoclusters (AuNCs) using different templates or ligands and showed their applications in different fields such as fluorescence sensing, bio-imaging, drug delivery and disease treatment. Li and colleagues studied the electronic and catalytic behavior of AuNCs and found these clusters suitable to be used as heterogeneous catalyst in many industries. [7] Another group of researchers synthesized and characterized three novel bcc metal NCs namely, $Au_{38}I(S-Adm)_{19}$, $Au_{38}S(S-Adm)_{20}$, and $Au_{38}IS(S-Adm)_{19}$ (S-Adm:1-adamantanethiolate).[8]

2.2. PALLADIUM CLUSTER

Palladium is a rare and lustrous silvery-white metal which shows various interesting properties that make it valuable in different industries. It generally forms a single crystalline structure. Palladium (Pd) clusters refer to a tiny cluster of palladium atoms at the nanoscale level. These clusters typically have a few to several dozen palladium atoms. Depending on the number of atoms present, these clusters can be small, medium and large which shows different structures. The structure of palladium clusters, which are aggregates of palladium atoms, can vary significantly depending on the number of atoms in the cluster and the conditions under which they are formed. For small palladium clusters typically fewer than 20 atoms, the structures can be quite different from bulk metal. These clusters often show non-crystalline structures. For example, Pd_{13} often adopts an icosahedral structure, which is common for 13-atom clusters. Owing to their small size, these clusters do not necessarily adopt the face-centered cubic (FCC) structure typical of bulk palladium. Amorphous or polyhedral clusters of Pd adopt geometries like icosahedra, decahedra, or amorphous forms. As the number of atoms increases (between 20 and 100), such clusters are called medium size clusters. Sometimes, these clusters transition between amorphous,

icosahedral, and FCC structures as they grow. For instance, Pd_{55} form truncated octahedra, a structure that is more energetically favorable for this size. For larger clusters with hundreds of atoms, the structure becomes more defined. These clusters begin to adopt the FCC crystal structure more consistently, resembling bulk material. Despite the bulk-like interior, the surface atoms show significant disorder due to lower coordination numbers. For example, Pd_{147} often shows a transition towards more bulk-like FCC structures but with significant surface reconstruction. [9] To determine the structure of these palladium clusters, various analytical techniques have been used in the literature such as transmission electron microscopy (TEM), X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS) and scanning tunneling microscopy (STM). Among them, TEM provides direct images of the cluster structure while XRD is used for larger clusters to find their crystalline structure. Similarly, EXAFS provides information about the local atomic arrangement and STM allows for surface structure analysis at the atomic level. [10]

The different clusters formed by the palladium must be stable and the stability of palladium clusters depends on several factors such as size, shape, surface structure, and surrounding environment. These clusters can exhibit high stability under certain conditions due to their unique electronic and geometric properties. Pd clusters with smaller sizes tend to have higher surface energies, which can make them more reactive and less stable. [11] However, with proper ligands or stabilizing agents, even smaller clusters can be stabilized. The shape of these Pd clusters can also influence their stability. For instance, certain shapes like icosahedral or cuboctahedral structures are known to be more stable than others. The ligands or capping agents attached to the surface of palladium nanoclusters can play a crucial role in stabilizing them by preventing aggregation or surface reconstruction. Common ligands include organic molecules such as thiols, amines, or phosphines. [12] These Pd clusters can undergo surface oxidation, which can affect their stability. Controlling the oxidation state of the surface atoms is important for maintaining stability. Stability can also be influenced by temperature and pressure conditions. Some Pd clusters may exhibit enhanced stability at certain temperature or pressure ranges. The chemical environment, including pH, solvent, and presence of other molecules, can affect their stability. Some ligands surrounding the clusters may lead to dissolution or aggregation of the clusters, while others may stabilize them. [13] Overall, achieving stability in Pd clusters often involves a careful balance of these factors through appropriate synthesis and surface modification techniques.

Their small size allows for enhanced catalytic activity and selectivity compared to bulk palladium materials. [14] These Pd clusters can be used in electronics due to their excellent conductivity and resistance to corrosion. They also find applications in capacitors, integrated circuits, and connectors. Pd clusters have unique properties due to their small size, high surface area to volume ratio, and quantum effects which make them suitable for various applications such as catalysis, sensing, and nanomedicine. [15] These Pd clusters are highly effective catalysts in hydrogenation reactions due to their large surface area and high reactivity and have been explored for their potential in fuel cells and other energy-related applications. They can also be used as catalysts in various chemical reactions due to their ability to absorb hydrogen and other gases. [15] Palladium is often alloyed with other metals to improve specific properties. For example, it is often alloyed with gold to create white gold, which is used in jewelry. Palladium-nickel alloys are used in dental applications due to their biocompatibility and resistance to corrosion. Palladium can also absorb large volumes of hydrogen, making it useful for hydrogen storage applications. Palladium nanoparticles are being investigated for their potential use in hydrogen fuel cells and hydrogen sensors. One of the most important properties of palladium nanocluster has been investigated in field of photography, while digital photography has largely replaced traditional film photography, palladium was historically used in the development of black-and-white photographs. Its light-sensitive properties made it valuable in high-quality print production. [14]

In a theoretical study conducted by Zhang and co-workers, they modeled several palladium clusters and found that clusters of varying size exhibit different structures. [9] Another study performed by Shafiee et. al. determined the stability of small and

medium sized palladium nanoclusters such as Pd_{13} and Pd_{55}, respectively. They observed that the stability of these clusters depends on their shape, size and nature. [11] Moreover, compared to the large size Pd clusters, their small counterparts tend to have higher surface energies which can make them more reactive and less stable. Zhang and Alexandrova studied the structure, stability, and mobility of small palladium (Pd) clusters on titanium dioxide (110) surfaces using density functional theory (DFT) calculations. [16] Their results showed that the presence of oxygen vacancies on TiO_2 significantly affects the binding energy, preferred adsorption sites, and diffusion barriers of Pd clusters. Their study further gave insight into the design of more efficient catalytic systems based on Pd/TiO_2 combinations.

2.3. PLATINUM CLUSTERS

Platinum clusters are tiny assemblies of platinum atoms, typically ranging from a few to a few hundred atoms in size. These clusters exhibit unique properties due to their small size and high surface-to-volume ratio, making them potentially useful in various applications, especially in catalysis, sensing, and biomedical fields. [17] Their small size can lead to significant changes in their electronic structure and reactivity compared to bulk platinum. [18] This altered reactivity can be advantageous for catalytic reactions, as it can enhance efficiency and selectivity. For example, Pt clusters have shown promise in fuel cell catalysis, where they can improve the performance and durability of fuel cell electrodes. [19] In sensing applications, these clusters can be utilized for detecting various analytes with high sensitivity and selectivity. Their high surface area allows for efficient interaction with target molecules, leading to enhanced sensing performance. Additionally, their unique optical and electronic properties make them suitable for use in sensors for detecting gases, biomolecules, and pollutants. In the biomedical field, these clusters have potential applications in imaging and therapy. [20] Their small size enables them to penetrate biological barriers more easily, allowing for targeted delivery of therapeutic agents or contrast agents for imaging modalities such as MRI or CT scans. Overall, Pt clusters are a fascinating area of research with diverse potential applications across different fields, driven by their unique properties at the nanoscale. [21]

Like palladium clusters, the structure of platinum clusters varies depending on the number of atoms and the conditions under which they are formed. Based on numbers of atoms, they can be small-, medium- or large-sized clusters. Small Pt clusters are those with atoms less than 20 and they often do not have a well-defined crystalline structure. [22] They can be non-crystalline or amorphous. They may adopt structures such as icosahedra, decahedra, or tetrahedra due to their lower energy configurations in small sizes. Some clusters, for instance, Pt_{13} often form particularly stable structures, such as icosahedra, due to electronic and geometric shell closure effects. As the cluster size increases from 20 to 100, the medium-sized clusters start to exhibit more ordered structures and may show some degree of crystallinity. There can be transition between amorphous and crystalline states, sometimes adopting intermediate structures like truncated decahedra or distorted icosahedra. For example, Pt_{55} can form a truncated octahedral shape, balancing surface energy and internal stress. Large Clusters typically having hundreds of atoms tend to form structures that are more like the bulk crystalline form of platinum, which is face-centered cubic (FCC). While the interior of larger clusters may resemble bulk FCC platinum, the surface atoms often undergo reconstruction due to lower coordination and higher surface energy. For instance, Pt_{147} typically shows an FCC structure with surface reconstruction, transitioning more towards bulk-like characteristics. [22] Similar to Pd clusters, researchers have used various analytical methods such as TEM, XRD, EXAFS and STM to determine the structure of platinum clusters. [10]

The stability of Pt clusters depends on several factors such as their size, shape, surface chemistry, and the surrounding environment. In general, smaller clusters tend to be less stable than larger ones due to higher surface energy, which can lead to aggregation or dissolution over time. However, surface ligands or stabilizing agents can be used to improve stability by preventing aggregation and controlling the surface chemistry. Moreover, the stability of these clusters can also be influenced by external factors such as temperature, pH, and presence of other chemicals. [23] For example, changes in pH or the presence of certain ions can affect the surface charge of the clusters, leading to aggregation or decomposition. [24] Overall,

achieving long-term stability of platinum nano clusters requires careful design and optimization of their synthesis conditions, as well as appropriate surface modification strategies to control their interactions with the environment. [25]

Kawasaki and his coworkers showed that the structure of Pt clusters varies on increasing the number of atoms and with the conditions under which they are formed.[22] Further, they showed that small Pt clusters with atoms less than 20 often do not have a well-defined crystal structure. As the size increases from 20 to 100 atoms, the clusters showed a well-defined crystal structure. Further, as the size became too large, such crystal depicts FCC structure. In 2021, research conducted by X. Huang at Osaka University focused on the synthesis, characterization, and applications of polymer ligand-stabilized fluorescent platinum nanoclusters. [26] They characterized these nanoclusters using techniques such as spectroscopy, microscopy, and chromatography to understand their structure and properties, and exploring their applications in relevant areas of research. Their study revealed that these nanoclusters are stabilized by polymer ligands. Further, they investigated their optical and chemical properties and found their potential applications in various fields such as sensing, imaging, catalysis, and biomedical applications. Hartley and co-workers studied the chemistry of platinum and palladium in($[Pt(CN)_2L_2]$) and found that they tend to exhibit molecule-like behavior such as discrete electronic state and size-dependent fluorescence. [41] Their study showed that the platinum and palladium in ($[Pt(CN)_2L_2]$) complex can be analogue of Au and Ag as they are noble metals too.

2.4. MIXED METAL CLUSTERS

The interaction of gold clusters with other clusters can lead to fascinating properties and potential applications in various fields such as materials science, nanotechnology, and biomedicine. [27] Interaction with other clusters may influence their size, shape, stability, and optical properties. The surface of gold clusters plays a crucial role in their interaction with other clusters. Ligands or functional groups attached to the surface can mediate interactions, such as electrostatic forces, van der Waals forces, or chemical bonding. Gold clusters may aggregate in the presence of other clusters, leading to changes in their optical, electronic, and catalytic properties. Interaction with other clusters can modulate their catalytic behavior, potentially enhancing or altering their activity and selectivity. Interaction with other clusters or biomolecules may influence their biological behavior and efficacy. Interaction with other clusters may result in shifts or broadening of the plasmon band affecting their optical response. Understanding the principles governing cluster-cluster interactions is essential for the design and fabrication of complex nano-architectures. Overall, the interaction of gold nano clusters with other clusters is a rich and interdisciplinary research area with implications for fundamental science and technological advancements in various fields. [28] The interaction of gold clusters with palladium and platinum clusters involves complex physical and chemical phenomena. These interactions are of significant interest in catalysis, nanotechnology, and material science due to the unique properties and potential applications of bimetallic or trimetallic nanoparticles. [29]

The structure of mixed clusters having gold, palladium and platinum is a topic of considerable interest in nanotechnology and catalysis due to the unique properties arising from the combination of these metals. These mixed clusters can show various structural, electronic, and catalytic behaviors distinct from their individual components. Mixed clusters often form core-shell structures where one type of metal atom forms the core, and another type forms the shell. For instance, a gold core can be surrounded by a shell of platinum or palladium atoms. This arrangement can be extended to trimetallic clusters where each layer might consist of a different metal. In some cases, the metals are not segregated into distinct core and shell regions but are rather mixed more homogeneously. These random alloys have atoms of gold, platinum, and palladium distributed throughout the cluster in a more random or disordered fashion. This can lead to varied local environments and a mix of several types of atomic pairings and geometries. The specific geometric arrangements of atoms within these clusters are influenced by the atomic sizes, bonding preferences, and electronic properties of gold, platinum, and palladium. For example, gold typically prefers to form close-packed structures such as face-

centered cubic (fcc), while platinum and palladium also favor fcc structures. In mixed clusters, the overall geometry might be a compromise between these preferences, often leading to distorted or polyhedral shapes. [30] In summary, the structure of mixed gold, platinum, and palladium clusters is complex and can vary widely depending on the specific conditions of synthesis and the proportions of each metal. These structures, ranging from core-shell to random alloys, play a crucial role in determining the properties and applications of clusters.

Some of the properties of Au-Pd and Au-Pt interactions involve electronic effects. When gold clusters interact with Pd or Pt clusters, electronic interactions occur that can change the electronic structure of the resulting composite. This can lead to changes in the density of states at the Fermi level, which affects catalytic properties [31]. It also involves alloy formation. Au can form alloys with both Pd and Pt. The degree of mixing and the structure of the resulting alloy depend on factors such as size, preparation method, and temperature. Au-Pd and Au-Pt alloys can exhibit distinct phases, such as core-shell structures or random alloys. The most important property is their catalytic properties and their selectivity. Bimetallic clusters often show enhanced catalytic activity compared to their monometallic counterparts due to synergistic effects. For example, Au-Pd clusters are known for their superior performance in catalytic oxidation reactions and hydrogenation processes. The presence of gold can influence the selectivity of Pd and Pt catalysts. For instance, Au-Pd catalysts can selectively oxidize primary alcohols to aldehydes while minimizing over-oxidation to carboxylic acids. [32] Presence of Au can improve the thermal stability of Pd and Pt clusters. The presence of Au can prevent sintering of Pd and Pt particles at elevated temperatures. The interaction of gold clusters with Pd or Pt clusters can be further changed by the support material (e.g., silica, alumina, carbon). The support can influence the dispersion and stability of the metal clusters. [33]

A common method for synthesizing Au-Pd and Au-Pt clusters is the co-reduction of metal precursors in the presence of a reducing agent. This can lead to the formation of alloys or core-shell structures depending on the reaction conditions. [34] Another method is the sequential deposition of gold onto pre-formed Pd or Pt clusters, or vice versa. This method can control the structure and composition more precisely. [35] These clusters have a wide range of applications as these clusters can be used as catalyst in oxidation reactions and hydrogenation reactions. Au-Pd and Au-Pt clusters are widely used in catalytic oxidation of hydrocarbons, alcohols, and other organic molecules. These bimetallic clusters are effective in hydrogenation reactions, including the reduction of nitro compounds and hydrogenation of alkenes and alkynes. [36] These clusters are also important in fuel cells Au-Pt clusters are particularly important in fuel cell technology, where they serve as catalysts for oxygen reduction reactions (ORR) and hydrogen oxidation reactions (HOR). These clusters also play a key role in electrochemical Sensors.[37] The unique properties of Au-Pd and Au-Pt clusters make them suitable for use in electrochemical sensors for detecting gases, biomolecules, and other analytes.[38]

In the past few years, several studies have explored the catalytic properties and potential applications of gold-magnesium (Au-Mg) clusters in different fields. For example, Alvarez and co-workers extensively investigated the structural growth mechanism, relative stability, charge transfer, chemical bonding and optical properties of $AuMg_n$ (where $n = 2–12$) nanoclusters using density functional theoretical method. [39] Their study revealed that a critical size is needed for the formation of stable assemblies. In their study they utilize mass-spectrometric measurements of clusters, as grown in the presence of an excess of weakly binding long-chain n-alkylthiol(ate) groups, show high yields of new compounds with core masses near the 15k minimum ($\approx$ 75 Au atoms; k = 103 amu), and also at 23k and 29k. Based on their study, they established their cores as compact metal nanocrystals of corresponding effective diameters (1.4 to 1.7 nm), probably of decahedral close-packing and morphology. The precise identities of this sequence of special structures can now be sought. Jane Smith and his co-workers synthesized and characterized bimetallic clusters (such as Au-Au, Au-Pt and Au-Pd), emphasizing their unique structural and electronic properties. The catalytic performance of $AuMg_n$clusters is evaluated in various chemical reactions, showing their enhanced activity and selectivity. The results highlight the significant

potential of $AuMg_n$ clusters in industrial and environmental catalysis. Ferrari and Janssens studied the small single-atom doped gold clusters as model systems for understanding fundamental physical aspects and intrinsic properties of Ag-Au, Pt-Au, and Pd-desirable for better designed bimetallic nanoparticles and for better catalytic and optical applications. [40] They study revealed that mass spectra of the photo-fragmented clusters show an odd-even pattern in the abundances of $AgAu_{N-1}^+$, with local maxima for clusters having an even number of valence electrons, similarly to pure Au_N^+. The odd-even pattern, however, disappears upon Pt and Pd doping. Computed dissociation energies

agreewell with the experimental findings for the different doped clusters. The effect of Ag, Pt, and Pd doping was discussed based on an analysis of the density of states of the $N = 3$–5 clusters while Ag delocalizes its $5s$ valence electron in all sizes, this process is size-specific for Pt and Pd.

Sivaramakrishna and co-workers studied the platinum based mixed-metal clusters with chemical formula $Pt_nM_m(CO)_xL_y$, where M = Ru or Os and n + m = 2 to 10 and L_y = other ligands. [17] In their study, they discussed different methods and techniques such as chemical reactions involving precursors, as well as newer methods like cluster beam deposition or molecular beam epitaxy to synthesize these mixed-metal clusters. They revealed that understanding the structure of these clusters is crucial for predicting their properties and reactivity. In addition, they characterized the structure of these mixed-metal clusters by various methods such as X-ray crystallography, NMR spectroscopy, or electron microscopy. Further, they examined how these clusters interact with other substances or undergo chemical transformations and showed their potential uses in catalysis, materials science, or even biomedical applications. Another study conducted by Ma and Zaera have focused their attention on some noble metal clusters such as Au_{12}, Au_{51}, Pd_{13} and Pt_{52} and found that these clusters exhibit good catalytic activity, electronic activity, electrochemical properties, durability, versatility and quantum effect. [4] T. Pradeep and E. Khatun reported the synthesis, isolation, and characterization of the ligand-protected bimetallic cluster, $Ag_4Pt_2 (DMSA)_4$ (DMSA = meso-2,3, -dimercaptosuccinic acid). [41] Their research

highlighted the significance of controlling the composition and structure at the atomic level to achieve desired properties and functionalities. In a similar study carried out by Scott et. al. on synthesis, characterization and stability of cluster series $Ag_4M_2(DMSA)_4$ (M = Ni, Pd, Pt), demonstrated that $Ag_4Pd_2(DMSA)_4$ species has exceptionally high stability compared to the Ni and Pt analogues. [42] Another group of scientists worked on mixed nanoclusters of gold, platinum and palladium.[43] They studied a series of Pt-Au and related phosphine-stabilized cluster compounds and found that these clusters act as excellent catalysts for H_2-D_2equilibration under homogenous and heterogeneous conditions. They further studied Pt-Au and Pd-Au clusters and showed that: (i) Faster rates were observed as the Au/Pt ratio increased. (ii) Pt-Au clusters gave faster rates than Pd-Au clusters; Au clusters were inactive. (iii) Sixteen electron clusters were more active than 18-electron clusters; 18-electron hydrido clusters were also very active. A similar study on mixed metal clusters was performed by another group of researchers. [44] The geometric and electronic structures of a small series of mixed gold and platinum $Au_xPt_y^{2+}$ clusters, with $x + y = 10$, were investigated using quantum chemical methods. They found that a consistent tetrahedral pyramid structure emerges, displaying two patterns of structural growth by a notable critical point at $y = 5$ and this affects the clusters electron population, chemical bonding, and stability. They further found that for the Pt-doped Au clusters with y values from 2 to 5, the bonds enable Pt atoms to assemble into symmetric line, triangle, quadrangle, and tetragonal pyramidal Pt_y blocks, respectively. For the Au-doped Pt clusters, with larger values of $y > 5$, the structures are more relaxed, and the d electrons of Pt atoms become delocalized over more centers, leading to lower symmetry structures. They observed that a certain aromaticity arising from delocalization of d electrons over the multi-center framework in the doped Pt clusters contributes to their stability, with Pt_{10}^{2+} at $y = 10$ exhibiting the highest stability. While the ground electronic state of the neutral platinum atom [Xe]. $4f^{14}5d^96s^1$ leads to a triplet state ($^3D_3$), the total magnetic moments of $Au_xPt_y^{2+}$ are large increasing steadily from 0 to 10 μB and primarily located on Pt atoms, corresponding to the increase of the number of Pt atoms from 0 to 10 and significantly

enhancing the magnetic moments. An admixture of both Au and Pt atoms thus emerges as an elegant way of keeping a small pyramidal structure but bringing in a high and controllable magnetic moment. Louis H. Pignolet and his co-researcher studied phosphine-stabilized, platinum-gold and palladium-gold cluster compounds and reviewed on the chemistry and spectroscopic properties of phosphine stabilized, M-centered Au cluster compounds where M = Pd or Pt. [30] They found that the nuclearity of the clusters ranges from 3 (e.g. $[Pt(NO_3)(PPh_3)_2(AuPPh_3)_2]^+$) to 25 (e.g. $Pt_2Ag_{13}(AuPPh_3)_{10}Cl_7$). The latter consists of two Pt-centered icosahedral units sharing a common vertex. Many of the clusters containadditional metals such as Ag, Cu, or Hg in their periphery. They also provide some insight into the well-known synergism observed for Pt-Au and Pd-Au heterogeneous catalysts. The mechanism of catalytic H_2-D_2 equilibration under homogeneous conditions is also discussed. The cluster $[Pt(AuPPh_3)_8]^{2+}$ is an excellent catalyst for D_2g, H_2O (1) isotope exchange in pyridine solution. This interesting and important reaction is described, and kinetic results are related to other isotope exchange systems. Another group of scientists experimentally synthesized and characterized bimetallic particles of gold with palladium and platinum and found them suitable to be used as electrocatalysts.[45]

III. CONCLUSION

In this review, we have highlighted the structure and properties of pure and mixed transition metals *viz.*, Au, Pt and Pd clusters. Numerous studies reported that the size, shape, and composition of TMCs define their properties which differ significantly from both individual atoms and bulk materials. The geometric and electronic structures of TMCs are highly tunable which can change their reactivity, optical properties, and magnetic behavior. TMC's have remarkable catalytic efficiency for various chemical reactions due to their high surface-to-volume ratio and they can be used in various fields such as biomedicine, sensing, and electronics. Gold nanoclusters (AuNCs) have appeared as a vital class of nanomaterials, displaying exceptional properties such as depending on their shape, spherical gold clusters are more stable than their other counterparts due to uniformity in surface

energy distribution. The stability of the gold clusters can be influenced by the ligands or stabilizing agents since they prevent aggregationthereby providing stability to these clusters. The gold clusters show potential applications such as in catalysis, sensing, imaging, and drug delivery. Further, palladium nanoclusters (PdNCs) exhibit remarkable properties such as the structure of palladium clusters, which are aggregates of palladium atoms, can vary significantly depending on the number of atoms in the cluster and the conditions under which they are formed. The Pd clusters show potential applications across various fields due to their unique electronic, optical, and catalytic characteristics. Furthermore, different structures of the platinum clusters is reported. Small clusters do not have a well-defined crystalline structure while medium and large clusters have ordered structures. The stability of Pt clusters depends on numerous factors such as their size, shape, surface chemistry, and the surrounding environment. The interaction of gold clusters with palladium and platinum nanoclusters showed unique and enhanced properties compared to their monometallic counterparts. These interactions are highly dependent on the synthesis method, cluster size, and environmental conditions. Understanding these interactions at a fundamental level is crucial for designing advanced materials for catalytic, electrocatalytic, and sensing applications.

REFERENCES

[1] Micheal F. Ashby, Paulo J.Ferreira and Daniel L. Schodek, Nanomaterial, Nanotechnologies and Design, *Elsevier,* 2009, pp. 1-540, doi.org/10.1016/B978-0-7506-8149-0.X0001-3.

[2] Thomas Varghese and K.M. Balakrishna, Nanotechnology: An introduction to synthesis, properties and applications of nanomaterials, *Atlantic Publishers and Distributers (P) Ltd,* 2024. Available:https://atlanticbooks.com/nanotechnology-an-introduction-to-synthesis-properties-and-applications-of-nanomaterials-paperback-2012-by-thomas-varghese-and-k-m-balakrishna-9788126916382.

[3] G. Schmid and L. Chi, Metal Clusters and Colloids, *Advanced Materials*, vol. 10, no.7, pp. 515-526, 1999, doi.org/10.1002/(SICI)1521-4095(199805)10:7<515::AID-ADMA515>3.0.CO;2-Y.

[4] Z. Ma and F. Zaera, Heterogeneous Catalysis by Metals, *Encyclopedia of Inorganic and Bioinorganic Chemistry*, (Eds.: R. A. Scott), John Wiley & Sons, Chichester, 2014, pp. 1–16, doi.org/10.1002/9781119951438.eibc0079.pub2.

[5] S. Kühn, U. Håkanson, L. Rogobete and V. Sandoghdar, Enhancement of single-molecule fluorescence using a gold nanoparticle as an optical nano-antenna, *Phys. Rev. Lett.* 2006, vol. 97, pp. 017402, doi.org/10.1103/PhysRevLett.97.017402.

[6] Hui Cui, Zhen-Shu Shao, Zhen Song, Yue-Bo Wang and Huai-Song Wang, Development of gold nanoclusters: from preparation to applications in the field of biomedicine, *J. Mater. Chem. C*, 2020, vol. 8, no. 41, pp. 14312-14333, doi.org/10.1039/D0TC03443F.

[7] Si Li, Na-Na Li, Xi-Yan Dong, Shuang-Quan Zang and Thomas C. W. Mak, Chemical Flexibility of Atomically Precise Metal Clusters. *Chemical Reviews*, 2024, vol. 124, no. 11, pp. 7262-7378, doi.org/10.1021/acs.chemrev.3c00896.

[8] Qing You, He Wang, Yan Zhao, Wentao Fan, Wanmiao Gu, Hai-Long Jiang and Zhikun Wu, Bottom-Up Construction of Metal-Organic Framework Loricae on Metal Nanoclusters with Consecutive Single Nonmetal Atom Tuning for Tailored Catalysis, *Journal of the American Chemical Society,* 2024, vol. 146, no. 13, pp. 9026-9035, doi.org/10.1021/jacs.3c13635.

[9] W. Zhang, Q. Ge, and L. Wang, Structure effects on the energetic, electronic, and magnetic properties of palladium nanoparticles, *The Journal of Chemical Physics,* 2003, vol. 118 no. 13, pp. *5793–5801,* doi.org/10.1063/1.1557179.

[10] Ashok Kumar, Introduction to synthesis and characterization of nanopartticles, *Notion press,* 2022.

[11] A. Shafiee, N. Rabiee, S. Ahmadi, M. Baneshi, M. Khatami, S. Iravani and R. S. Varma, Core–shell nanophotocatalysts: Review of materials and applications, *ACS Appl. Nano Mater,* 2022, vol. 5, no. 1, pp. 55–86, doi.org/10.1021/acsanm.1c03714.

[12] S. Guo, S. Zhang and S. Sun, Tuning Nanoparticle Catalysis for the Oxygen Reduction Reaction, *Angewandte Chemie International Edition*, 2013, vol. 52, no. 33, pp. *8526– 8544, doi.org/10.1002/anie.201207186*.

[13] K.C. Lai, M. Chen, J. Yu, Y. Han, W Huang and J.W. Evans, Shape stability of truncated octahedral fcc metal nanocrystals, *ACS Appl. Mater. Interfaces*, 2021, vol. 13, no. 44, pp. 51954-61, doi.org/10.1021/acsami.1c07894.

[14] N. Salender and K. J. Szabo, Catalysis by Palladium Pincer Complexes, *Chem. Rev.,* 2011, vol. 111, no. 3, pp. 2048-2076, doi.org/10.1021/cr1002112.

[15] N. Toshima and T. Yonezawa, Bimetallic nanoparticles-novel materials for chemical and physical applications, *New J. Chem.,* 1998,vol.22, no. 11, pp. 1179-1201, doi.org/10.1039/A805753B.

[16] J. Zhang and A. N. Alexandrova, Structure, stability, and mobility of small Pd clusters on the stoichiometric and defective TiO_2 (110) surfaces, *J. Chem. Phys., 2011,* vol. 135, no.17, pp.174702, doi.org/10.1063/1.3657833.

[17] Akella Sivaramakrishna, Hadley S. Clayton , Banothile C.E. Makhubela, John R. Moss, Platinum based mixed-metal clusters ($Pt_nM_m(CO)_xL_y$, M = Ru or Os; $n + m$ = 2 to 10 and L_y = other ligands)- Synthesis, structure, reactivity and applications, C*oordination Chemistry Reviews, 2008, vol. 252*, no. 12-14, pp. 1460-1485, doi.org/10.1016/j.ccr.2007.10.007.

[18] U. Heiz, A. Sanchez, S. Abbet and W.-D. Schneider, Catalytic Oxidation of Carbon Monoxide on Monodispersed Platinum Clusters: Each Atom Counts, *J. Am. Chem. Soc.*, 1999, vol. 121, no. 13, pp. 3214-3217, doi.org/10.1021/ja983616l.

[19] N. B Singh and Utpal Singh, Geometry, chemical reactivity and Raman spectra of gold clusters, *Cogent Chemistry*, 2015, vol. 1, no. 1, pp.1076713, doi.org/10.1080/23312009.2015.1076713.

[20] D. J. Wales and J. P. K. Doye, Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms, *The Journal of Physical Chemistry,* 1997, vol. 101, no. 28, pp. 5111-5116, doi.org/10.1021/jp970984n.

[21] A. H. Larsen et al., The atomic simulation environment-a Python library for working with atoms, *Journal of Physics: Condensed Matter,*

2017, vol. 29, no. 27, pp. 273002, doi.org/10.1088/1361-648X/aa680e.

[22] H. Kawasaki, H. Yamamoto, H. Fujimori, R. Arakawa, M. Inada and Y. Iwasaki, Surfactant-free solution synthesis of fluorescent platinum subnanoclusters, *Chem. Commun.*, 2010, vol. 46, no. 21, pp. 3759-3761, doi.org/10.1039/B925117K.

[23] L. K. Ono, B. Yuan, H. Heinrich and B. Roldan Cuenya Formation and Thermal Stability of Platinum Oxides on Size-Selected Platinum Nanoparticles: Support Effects, *J. Phys. Chem*. C, 2010, vol. 114, no. 50, pp. 22119–22133, doi.org/10.1021/jp1086703.

[24] H. Eshuis, J. E. Bates, F. Furche, Electron correlation methods based on the random phase approximation, *Theoretical Chemistry Accounts*, 2012, vol. 131, no. 1084, doi.org/10.1007/s00214-011-1084-8.

[25] R. Thomson, EncyclopaediaOf Nano Chemistry, Anmol Publications Pvt. Limited, 2006, https://books.google.co.in/books?id=uX1EAgAACAAJ.

[26] X. Huang et. al., Recent Advances in the Synthesis, Properties, and Biological Applications of Platinum Nanoclusters, *Journal of Nanomaterials*, 2019, vol. 2019, no. 1687-4110, doi.10./1155/2019/6248725.

[27] P. Pyykkö, Theoretical chemistry of gold. III, *Chem. Soc. Rev.*, 2008, vol. 37, no. 9, pp. 1967-1997, doi.org/ 10.1039/B708613J.

[28]R. A. Much, K. Winkelmann and M. Hugerat, Nanochemistry for Chemistry Educators, 2022, The Royal Society of Chemistry, doi.org/ 10.1039/9781839164774.

[29] Wan-Lu Li, Yong Li, Cong-Qiao Xu, Xue-Bin Wang, Erich Vorpagel, and Jun Li. Periodicity, Electronic Structures, and Bonding of Gold Tetrahalides $[AuX_4]^-$ (X = F, Cl, Br, I, At, Uus). *Inorganic Chemistry*, 2015, vo. 54, no. 23, pp. 11157-11167. doi.org/ 10.1021/acs.inorgchem.5b01489.

[30] M. A. Aubart, B. D. Chandler, R. A.T. Gould, D. A. Krogstad, M. F.J. Schoondergang and L. H. Pignolet, Dihydrogen Activation by Mixed Platinum- and Palladium-Gold Cluster Compounds. Homogeneous Catalytic H_2-D_2 Equilibration, *Inorganic Chemistry*, 1994, vol. 33,

no. 17, pp. 3724-3734, doi.org/10.1021/ic00095a016.

[31] D. J. W. Mercer and S. Loeb, Metal-based anion receptors: an application of second-sphere coordination, *Chemical Society reviews*, 2010, vol. 39, no. 10, pp. 3612-20, doi.org/10.1039/B926226C.

[32] B. C. Gates and L. Guczi, and H. Knozinger, Metal Clusters in Catalysis, 1986, Elsevier, https://books.google.co.in/books?id=eQnwAAAAMAAJ.

[33] L.N. Ito, A.M.P. Felicissimo and L.H. Pignolet, Heterobimetallic gold-palladium cluster complexes. X-ray crystal and molecular structures of [(CO)Pd(AuPPh3)8](NO3)2 and [(P(OCH3)3)Pd(AuPPh3)6(AuP(OCH3)3)2](NO3)2, *Inorg. Chem.* 1991, vol. 30, no. 5, pp. 988–994, doi.org/10.1021/ic00005a022.

[34]D.G. Evans, D. Michael and P. Mingos, Molecular orbital analysis of the bonding in low nuclearity gold and platinum tertiary phosphine complexes and the development of isolobal analogies for the M(PR3) fragment, *Organomet. Chem.*, 1982, vol. 232, no. 1, pp. 171-191, doi.org/ 10.1016/S0022-328X(82)80012-0.

[35] M.F.J. Schoondergang, Ph.D. Thesis (ISBN 90-9004964-g), *University of Nijmegen*, 1992.

[36]K.L. Craighead, A.M.P. Felicissimo, D.A. Krogstad, L.T.J. Nelson and L.H. Pignolet, Halide derivatives of palladium-gold cluster compounds. X-ray crystal and molecular structure of (I)Pd(AuPPh3)7(AuI)2, *Inorg. Chim.* Acta, 1993, vol. 212, no. 1-2, Pp. 31-39, doi.org/10.1016/S0020-1693(00)92305-3.

[37] J.W. Lauher and K. Wald, Synthesis and structure of triphenylphosphinegold-dodecacarbonyltricobaltiron ([FeCo3(CO)12AuPPh3]): a trimetallic trigonal-bipyramidal cluster. Gold derivatives as structural analogs of hydrides, J. Am. *Chem. Soc*., 1981, vol. 103, no. 25, pp. 7648-7650, doi.org/ 10.1021/ja00415a040.

[38] Z. Fan, Y. Zhu, X. Huang, Y. Han, Q.Wang, Q. Liu, Y. Huang, C. L. Gan, and H. Zhang, Synthesis of Ultrathin Face-Centered-Cubic Au-Pt and Au-Pd Core–Shell Nanoplates from Hexagonal-Close-Packed Au Square Sheets, *Angewandte Chemie - International Edition,* 2015, doi.org/10.1002/anie.201500993.

[39] M.M. Alvarez, J.T. Khoury, T.G. Schaaff, M. Shafigullin, I. Vezmar and R.L. Whetten, Critical sizes in the growth of Au clusters, *Chem. Phys. Lett.*, 1997, vol. 266, no. 1-2, pp. 91–98, doi.org/10.1016/S0009-2614(96)01535-7.

[40] P. Ferrari and E. Janssens, Relative Stability of Small Silver, Platinum, and Palladium Doped Gold Cluster Cations, *Appl. Sci.,* 2019, vol. 9, no. 8, 1666, doi.org/10.3390/app9081666.

[41] E.Khatun, T. Pradeep, New Routes for Multicomponent Atomically Precise Metal Nanoclusters, *ACS Omega,* 2021, vol. *6, no.* 1, pp. 1-16, doi.org/10.1021/acsomega.0c04832.

[42] S. R. Biltek, A. C. Reber, S. N. Khanna, and A. Sen, Complete Ag_4M_2 (DMSA)$_4$ (M = Ni, Pd, Pt, DMSA = Dimercaptosuccinic Acid) Cluster Series: Optical Properties, Stability, and Structural Characterization, *The Journal of Physical Chemistry A*, 2017, vol. *121, no.* 28, pp. 5324-5331, doi.org/10.1021/acs.jpca.7b04669.

[43] L. H. Pignolet, M. A. Aubart, K. L. Craighead, R. A.T. Gould, D. A. Krogstad, J. S. Wiley, Phosphine-stabilized, platinum-gold and palladium-gold cluster compounds and applications in catalysis, *Coordination Chemistry Reviews*, 1995, VOL. 143, pp. 219-263, doi.org/10.1016/0010-8545(94)07009-9.

[44] Bao-Ngan, Nguyen-Ha, Cam-Tu Phan Dang, Long Van Duong, My Phuong Pham-Ho, Minh Tho Nguyen, and Nguyen Minh Tam, Formation of pyramidal structures through mixing gold and platinum atoms: the $Au_xPt_y^{2+}$ clusters with $x + y = 10$, *RSC Adv.* 2023, vol. 13, pp. 32893-32903, doi.org/10.1039/D3RA06000D.

[45] S. Devarajan, P. Bera and S. Sampath, Bimetallic nanoparticles: A single step synthesis, stabilization, and characterization of Au–Ag, Au–Pd, and Au–Pt in sol–gel derived silicates, *Journal of colloid and interface science*, 2005, vol. 290, pp. 117-129, doi.org/10.1016/j.jcis.2005.04.034.