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Introductory Chapter: Salient Features of Nanocatalysis

Alkadevi Verma, Madhulata Shukla and Indrajit Sinha

1. Introduction

Drawbacks in homogeneous and heterogeneous catalysts necessitate new catalytic paradigms for overcoming the limitations associated with both types. The model catalyst should combine the advantages of homogeneous with heterogeneous catalysis. Thus, the catalyst for a particular reaction should exhibit good activity, selectivity, and product yield. At the same time, it should be separable (recoverable) from the reaction medium, stable and reusable. Tailored nanostructures have displayed the potential to meet these stringent requirements.

Transition metals, specifically precious noble metals such as Pt, Pd, Rh, Ru, Au, Ag, and Cu, are commonly used as homogeneous and heterogeneous catalysts in majority of chemical transformations [1, 2]. The primary reason for this is the variable oxidation states offered by them. They also possess good adsorption properties essential for heterogeneous catalysis. Combination of these two properties enables the transition metal nanoparticles to act as electron conduits for the reactants adsorbed on the surface of the catalyst. Initial examples of nanoparticles in catalysis were Ag nanoparticles in photography and Pt utilized in the decomposition of hydrogen peroxide (H_2O_2). Thereafter, noble metal nanoparticles have been used extensively as catalysts for many organic reactions such as carbon-carbon coupling in Suzuki, Stille and Heck reactions, hydrogenation, dehydrogenation reaction, oxidation, etc. [3].

Nanoparticles, owing to high surface energies, tend to get agglomerated resulting in enhanced particle sizes with lower surface area. The latter implies lesser number of surface active sites in the catalyst. Stabilizers such as surfactants or polymers, that may also act functionalizing agents, are frequently used to protect nanoparticles surfaces against aggregation. Such surface altering processes also cause change in the electronic structure of the nanoparticle and because of that in their catalytic activity as well [4]. The other approach to circumvent this problem is by implanting these NPs on large surface area but low density insoluble solids supports like zeolites, carbon based materials etc. The support material may be relatively inert. Alternatively, the support could modify the chemical and adsorption properties of the catalyst. Active supports like these may enhance or impede the performance of the catalyst for a specific reaction by tuning the electron density of NPs. Another possible scenario is that the support is a better adsorbent for one of the reactants and thereby improves the performance of the catalyst.

Currently, nanoparticles are increasingly substituting conventional heterogeneous catalysts [5]. Due to smaller sizes, nanoparticles have higher surface area and increased exposed active sites. In that way nanoparticles have larger contact areas with reactants and are catalytically more active than conventional heterogeneous catalysts. Variations in shape and composition of nanocatalysts give access to

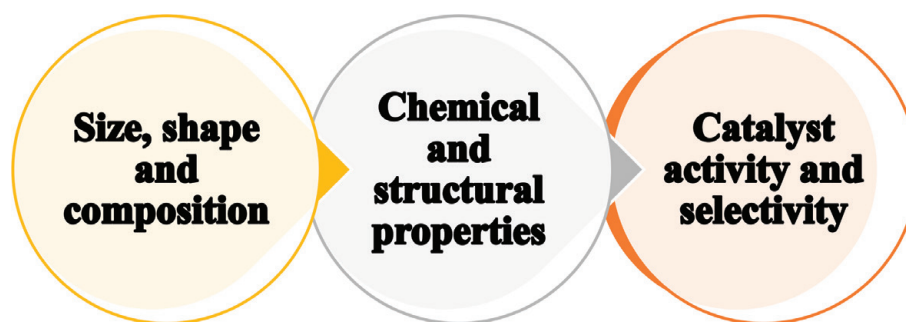


Figure 1.
Dependence of catalytic activity on size, shape and composition.

different types of catalytic sites. A particular type of site displays better selectivity towards a particular reaction pathway. Thus, from the point of view of increased activity and selectivity nanocatalysts have properties which tend to those of homogeneous catalysts. On the other hand, nanocatalysts are relatively easier to separate from the reaction mixtures and therefore, in that sense, are heterogeneous catalysts. Furthermore, adsorption of reactant(s) on to the nanocatalyst is a necessary precondition for any nanocatalyzed reaction. This is again characteristic of a heterogeneous catalytic process. Therefore, nanocatalysts with better activity, stability, and selectivity can be designed and synthesized by controlling their size, shape, and composition of nanomaterials [6–8]. **Figure 1** illustrates the typical cause and effect relation followed.

To study the size effect of catalyst, metal nanoparticles with the same shape but different sizes are applied in a reaction. The influence of nanoparticle size on catalytic activity and selectivity can thus be determined.

2. Effect of size

2.1 On catalytic properties

Nanocatalysts as compared to their bulk counterparts, commonly offers much higher surface-to-volume ratio. Prominent changes in the electronic states and coordination environment of the surface atoms of a catalyst nanoparticle might be possible when its size decreases typically to a certain nanoregime. Therefore, change in size of nanoparticles affects coordination environment, electronic state, and adsorption energy of the reactant molecules.

2.2 Size-dependent coordination environment

The effect of atoms at corners and edges of nanoparticles becomes dominant with decreasing the size of nanoparticles [9, 10]. Cao et al. summarized a relation between surface metal atoms with different coordination numbers of cuboctahedral and cubic geometry of nanoparticles with overall size of the nanoparticles [11]. They concluded that the coordination numbers 9, 7, and 4 of a cuboctahedral nanoparticle and 8, 6, and 3 in a cubic nanoparticle exhibits strong dependence on the size of the nanoparticle. Such strong correlation of size-dependent catalytic performance (for a particular nanocatalyst shape) was also reported by Tao et al. for room temperature CO oxidation reaction. For instance, in Pt nanoparticles with a size of about 2.2 nm, the Pt atoms (CN = 7) at the edge of triangular nanoclusters are active for CO oxidation even at room temperature. However, Pt atoms with CN of 9 on the terrace of Pt (111) are not active for CO oxidation at room temperature [12].

2.3 Size-dependent electronic state

The electronic structure of metal nanoparticles of 1–2 nm (in the quantum regime) is like that of a molecule. Thus, Au nanoparticles smaller than 1 nm, are more molecular than metallic. Thus, molecule-like electronic states of metal nanoparticles of 1–2 nm exhibits inherently different catalytic performance in contrast to a nanoparticle with a larger size [11]. This was experimentally demonstrated for the first time by Goodman et al., in CO oxidation on Au nanocluster with thickness of three atomic layers supported on TiO₂ [13, 14]. Analysis of Au LIII XANES white lines by these authors revealed that supported Au nanoparticles with different sizes have different average coordination numbers. Thus Au nanoparticle of 3 nm has average CN = 9.5. Similarly the nanoparticles of 1 nm have average CN = 6, while nanoparticles of 0.5–1 nm have CN = 3.6. This shows that smaller Au nanoparticles have a size-dependent electronic environment [15–17].

2.4 Size-dependent adsorption energy

Adsorption is a primary step in heterogeneous catalysis. Size-dependent adsorption energies of reactants on catalyst surfaces with different coordination numbers have also been suggested in literature. References [18, 19] assert that the adsorption energy is dependent on the coordination environment of metal nanoparticles. Usually, catalyst atom(s) with low coordination number (CN) exhibits stronger adsorption for a given molecule than those catalyst atoms with higher coordination number [20, 21]. For example, adsorption energy of adsorbates including $\bullet\text{O}_2$, $\bullet\text{OH}$, $\bullet\text{OOH}$, $\bullet\text{O}$, $\bullet\text{H}_2\text{O}$, and $\bullet\text{H}_2\text{O}_2$ on Pt nanocatalyst decrease linearly with increase in coordination number from 3 to 9 [20]. Similar linear relationships between adsorption energy and coordination number have been reported for other transition metal catalysts such as Co, Ni, Cu, Rh, Pd, Ag, Ir, and Au [20].

3. Effect of shape on catalytic properties

The representative shapes of metal nanoparticles based on dimensionality are shown in **Figure 2**. Spherical, pseudo-spherical, dodecahedral, tetrahedral, octahedral, cubic shape represents 0D nanoparticles. 1D morphology of nanoparticles includes nanotubes, nanorods or nanowires, nanocapsules, etc. [21, 22]. Hexagonal, triangular, quadrangular plates or sheets, belts, rings, etc. fit in to the 2D shape NPs [23]. 3D morphologies of nanoparticles are complex such as nanoflowers, nanostars, polygonal nanoframes, etc. [24, 25]. Compared to simple

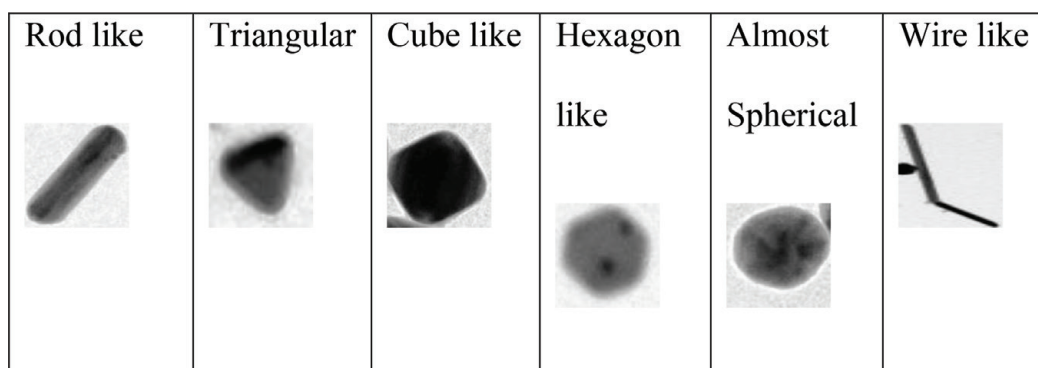


Figure 2.
Different types of anisotropic nanoparticles.

isotropic morphologies of nanoparticles, novel anisotropic morphologies have unique physicochemical properties due to the different numbers of steps, edges, and kink sites present on to the surface of catalyst in nanoscale regime. For example, polyhedral Au NPs with high-indexed facets are found to exhibit excellent optical and catalytic properties, [26, 27] Au rods with different ratios of length and width display different transverse and longitudinal plasmon bands. Preicel et al. have recently published a review on different types of anisotropic gold nanoparticles used in catalysis [28]. Branched Au NPs with multiple tips adopting structures like stars and flowers are increasingly being used for catalysis, surface-enhanced Raman scattering, and sensing [29].

4. Composition effect

The section introduces the effect of composition on catalytic activity from the perspective of alloy and bimetallic nanoparticles only. Commonly, bimetallic nanoparticles can be categorized into alloy (ordered or random), Janus and core-shell (core shell or cluster-in-cluster) structure types. The type of bimetallic or alloy nanostructure formed depends on the synthesis methodology utilized (**Figure 3**).

Catalytic activity of bimetallic nanomaterials is different from of its component metals. Instead of being an average of the catalytic activities of its components, bimetallic nanoparticles may also exhibit synergistic catalytic properties [30, 31]. One such example of composition effect was studied by Lim and co-workers in catalytic activity of Pt-Y alloy for electrocatalytic oxygen reduction [32]. The addition of various amounts of Y changes the electronic structure of Pt and thus modifies the binding energy of the oxygen-containing species. The optimum catalytic performance was achieved at a particular composition of Pt-Y alloy. Thus, the catalytic activity of Pt-Y alloy catalysts follows the trend of $\text{Pt}_{70}\text{Y}_{30} > \text{Pt}_{78}\text{Y}_{22} > \text{Pt}_{64}\text{Y}_{36} > \text{Pt}_{86}\text{Y}_{14} > \text{Pt}_{91}\text{Y}_9 > \text{Pt}$. Sun and co-workers also demonstrated such composition-dependent catalytic activity of monodisperse CoPd nanoparticles for formic acid oxidation [33].

The effect of composition also exists in core-shell bimetallic nanoparticles. Jiang et al. established the composition-dependent activity of core-shell Cu@M (M = Co, Fe, Ni) catalyst nanoparticles for hydrolytic dehydrogenation of ammonia borane [34]. In core-shell Cu@M structures, collaboration of Cu with M can change the width of surface d band, which is beneficial for catalytic enhancement. Only an optimum Cu/M ratio in all three cases shows the best catalytic activity.

Extensive use of BNPs have been reported in catalytic oxidation of dyes [35], glucose [29], CO [36], benzyl alcohol [37], and methanol [38] oxygen reduction [39] propane dehydrogenation [36] hydrogenation of nitro-aromatic compounds [40], electro-catalytic oxidation of methanol [28] as well as in desulfurization of thiophene [41].

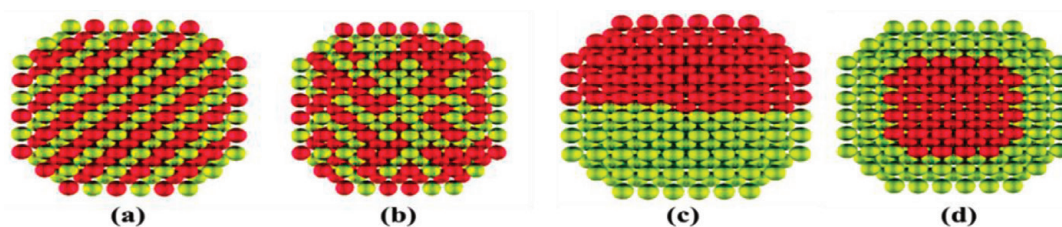


Figure 3. Different possibilities of bimetallic nanostructures observed: (a) ordered alloy; (b) random alloy; (c) Janus-like; and (d) core shell.

5. Conclusions

High surface area and consequently, enhanced surface active sites have led to extensive use of nanoparticles (NPs) as catalysts. Altering the nature and density of active sites can improve their catalytic activity. Change in nanoparticle size, shape, and composition affects the active site catalytic properties. The three listed aspects may also affect the electronic structure of the nanostructures. Moreover, appropriate functionalization of the nanostructures, not improve their stability against aggregation, but also impact their electronic structures and adsorption properties. Low density support materials also influence the nanostructure electronic state and the resultant properties.

Anisotropic shapes offer different densities of surface, edge, and corners in nanoparticles. Atoms in corners and edges possess low coordination and can lead to better interaction with the substrate and other reacting species for catalysis. On the other hand, possible variations in composition offered by bimetallic nanoparticles can not only reduce the cost of nanomaterial but may also show synergistic properties.

Author details

Alkadevi Verma¹, Madhulata Shukla² and Indrajit Sinha^{3*}


¹ Department of Chemistry, Rewa Engineering College, Rewa, India

² Department of Chemistry, G.B. College, Veer Kunwar Singh University, Ramgarh, India

³ Department of Chemistry, Indian Institute of Technology (Banaras Hindu University) Varanasi, India

*Address all correspondence to: isinha.apc@iitbhu.ac.in

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