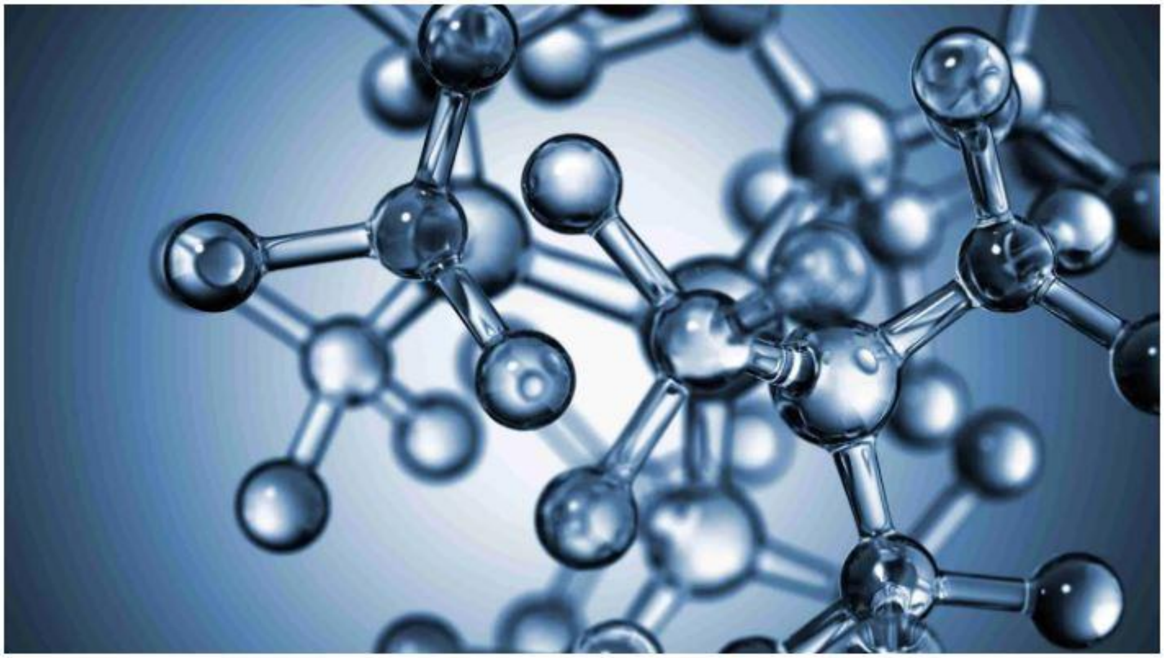
Chapter 1: Introduction of present work



“There's plenty of room at the bottom”

- Prof. Richard Feynman

(Father of modern nanotechnology)

Picture courtesy: *https://industrywired.com/nano-technology-and-its-applications-in-medicine-energy-and-transportation/*

1.1 Nanoscience: Definition and Origins

Nanoscience is the science of studying and exploring molecules (or objects) ranging between 1 and 100 nanometer (nm) and the technology that utilizes the unique properties of these materials into practical applications is called nanotechnology [1]. Nanoscience and nanotechnology are rapidly increasing scientific fields that encompass tailoring and tuning of materials at 1-100 nm scale which results in structures, technologies, and systems with novel features and functionalities [2]. One of the most exciting new technologies of the twenty-first century is nanotechnology. It is the ability to apply the theory of nanoscience to practical situations by monitoring, quantifying, assembling, regulating, and producing matter at the nanoscale. The word nano is derived from the Greek word 'νάνος', which means 'dwarf'. Nanoparticles differ from microparticles (1-1000 μm), "fine particles" (100-2500 nm), and "coarse particles" (2500-10,000 nm). Because of their smaller size, nanoparticles often possess significantly distinct physical or chemical properties than larger fragments of the same substance.

Nanoparticles can be found in natural sources such as forest fires, volcanic ash, weathering of metal containing rock etc. [3] as well as anthropogenic sources like internal combustion engines, power plants, incinerators, jet engines, metal fumes (smelting, welding), etc [4]. Nanomaterials found naturally on Earth have long been linked to the emergence of life, from the first cells to humans. Nanomaterials and their derivatives have been created and used by mankind since prehistoric times. The cave paintings found in Sulawesi, Indonesia, are the oldest recorded examples of art expression by humans. They were created approximately 40,000 BCE using fat, charcoal, and plant pigments [5]. Similarly, cave paintings from the Chauvet-Pont-d'Arc cave in France (dating from 34,000 BCE) also suggests that people in prehistoric times may have unknowingly used nanomaterials like graphene [6]. Carbon nanotubes have been identified in pottery from Keeladi, India, dating back to between 600 and 300 BC. The inner black covering of the Keeladi pottery shards displayed a variety of carbon nanostructures, including sheets-like structures that resemble graphene oxide and bundles of single-walled and multi-walled carbon nanotubes [7]. However, it is unknown how carbon nanotubes originated or whether the material that contains them was intentionally used.

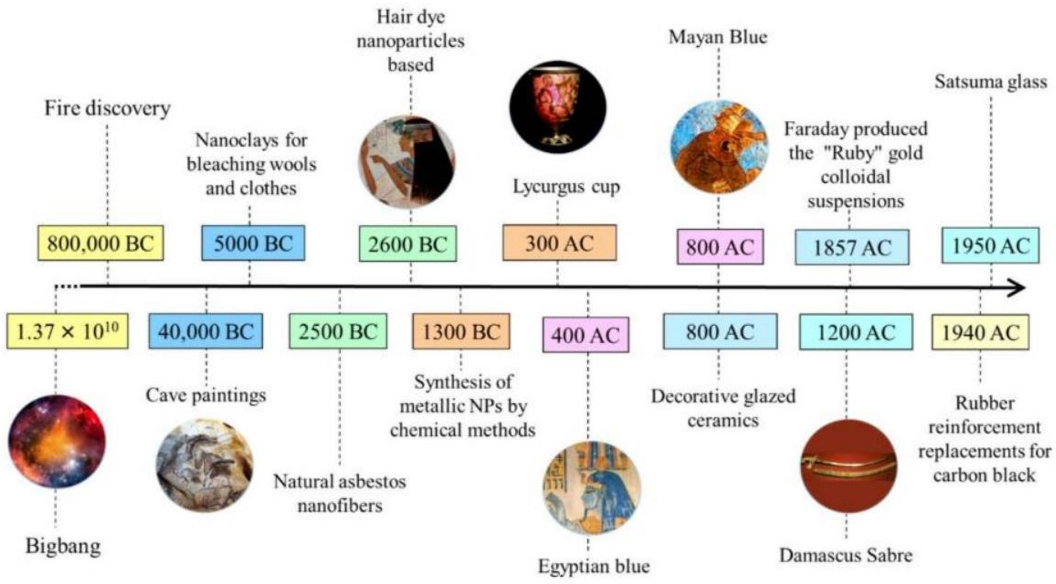


Figure 1.1: Timeline summarizing nanomaterials used in ancient civilizations [6].

Figure 1.2: Lycurgus cup showing two different phenomenons *(Figure source:https://www.amusingplanet.com/2016/12/lycurgus-cup-piece-of-ancient-roman.html).*

One of the most interesting examples of nanotechnology found in the medieval period is the Lycurgus cup which is also the oldest known dichroic glass. In direct light, the dichroic glass appears green; in indirect light, it appears purple-red. The team of scientists found that the cup had nanoparticles ranging in size from 50 to 100 nm when they examined it in 1990 [8] using a transmission electron microscope (TEM). According to X-ray studies, these nanoparticles are an alloy of gold and silver (Ag-Au), with a roughly 7:3 Ag:Au ratio distributed within a glass matrix. In addition, there is also 10% copper (Cu) dispersed throughout the same material [9]. The green color is produced by light scattering by colloidal dispersions of Ag nanoparticles bigger than 40 nm, whereas the red color is produced by the light absorption of the Au nanoparticles (~520 nm).

In 1857, Michael Faraday examined the characteristics of "Ruby" gold colloidal suspensions and demonstrated how, in specific lighting scenarios, Au NPs may change the color of the solution [10]. In 1952, Radushkevich and Lukyanovich identified carbon nanotubes using electron microscopy [11]. Long before the term "nanotechnology" was coined, the American physicist and Nobel laureate Richard Feynman (Figure 1.3) introduced the significance of this much-hyped field in his widely quoted lecture titled "There's plenty of room at the bottom" at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959 [12].

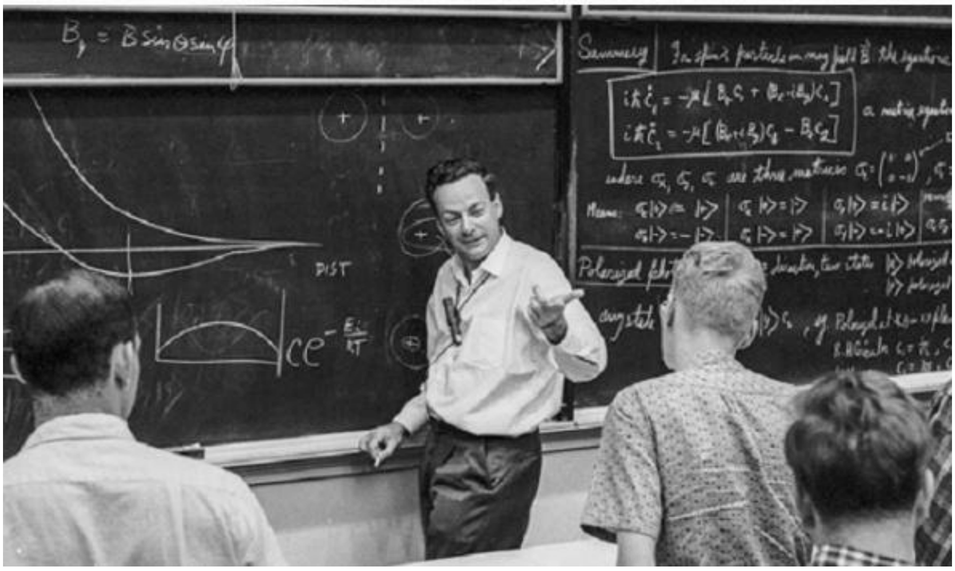


Figure 1.3: Nobel laureate Richard Feynman speaking at one of his classrooms *(Figure source: https://speakola.com/ideas/richard-feynman-nanotechnology-lecture-1959).*

"Why can't we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin?" was the question put up by Feynman and added, not merely "There is room at the bottom," "There is plenty of room at the bottom." Additionally, he described his idea of using machines to construct smaller machines, all the way down to the molecular level [13]. Feynman is considered the father of modern nanotechnology since this new idea supported his views. More than a decade later, Japanese researcher Norio Taniguchi, who was studying ultra-precision machining, coined the term "nanotechnology" [14]. In 1986, Erick Drexler promoted the concept of nanotechnology with his publication "Engines of Creation: The Coming Era of Nanotechnology" [15]. Real progress in nanotechnology happened when physicists Gerd Binnig and Heinrich Rohrer invented Scanning Tunneling Microscope (STM) at IBM Zurich Research [16]. In 1986, they were awarded the "Nobel Prize in Physics" for their development of the "STM." This discovery led to the creation of the scanning probe microscopy (SPM) and atomic force microscope (AFM), which are now the preferred instruments for researchers studying nanotechnology.

In recent times, nanotechnology plays a huge role in diagnosis and therapy of many human diseases [17]. Additionally, it has been used to produce more economical and efficient energy and to enhance environmental conditions. Examples includes reducing pollution coming from automobile exhaust and power plants, producing solar cells at much lower cost. However, the application of computational tools in nanotechnology is still in its early stages, requiring additional research. The rise of the field of nanoinformatics has occurred to address computational needs at the nanoscale.

1.2 Synthesis of nanomaterials

Generally, there are two types of synthesis method for nanomaterials. Currently, independent of the nanoparticle origin, the methods are divided into “top-down” and “bottom-up” approaches.

(i) Top down approach includes segmentation of solid materials into small fractions to form nanoparticles. This method is appropriate for manufacturing thin films and nanoparticles larger than 100 nm in size that display distinct traits from their bulk counterparts. The advantage of top down approach is cost effective large scale production of nanoparticles [2]. The environmental impact of this method is quite low. The major disadvantages are broad size distribution and varied particle shape obtained during the process.

(ii) Bottom up approach include assembling of individual atoms or molecules into forming nanoparticles. This approach exploits the physical and chemical properties of atoms, ions or molecules to gather into nanoparticles [18]. Coprecipitation, sol-gel and micro emulsion are some of the examples of bottom up approaches. The advantages of this technique are ability to control the shape and composition of particles to form nanostructures with fewer defects. However, the main disadvantages include a lack of instruments for effective molecular and atomic handling, as well as a high production cost.

1.3 Reactivity of nanoparticles

The origin of reactivity of materials at the nanoscale level are based on "quantum confinement effects" and having a larger surface-to-volume ratio than bulk materials, which has significant effects for all processes that occur at a material surface, such as catalysis, adsorption, surface diffusion, and so on. Nanoparticles have distinct electronic energy levels due to the confinement of the electronic wave function to the particle's physical size, as opposed to continuous levels in bulk. This phenomenon is termed as quantum confinement effect [19]. When nanoparticles are reduced to a given size, the quantum confinement effect in nanomaterials can be interpreted in terms of electron wavelength. The term “confinement” refers to the confinement of an electron's mobility to a specific energy level. Increasing confinement causes major changes in the particle's energy band diagram, affecting its electrical and optical properties. One of the significant example is gold whose melting point decreases and a color shift occurs from brilliant yellow to red as it transform itself from bulk to nano-size [20].

In contrast to bulk materials, nanomaterials have a higher surface-to-volume ratio. This implies that if a material is composed of an ensemble of nanomaterial subunits rather than bulk material, its outer surface will be greater for a given total volume of material. Reactivity is affected by the amount of a substance that comes into touch with surrounding materials, which increases with a material's surface area per mass. Surface phenomena such as catalysis, adsorption, desorption and detection have been affected positively due to increased exterior surface of the nanomaterials. Hence, increased surface-to-volume ratio of nanomaterials affects its chemical reactivity at the surface.

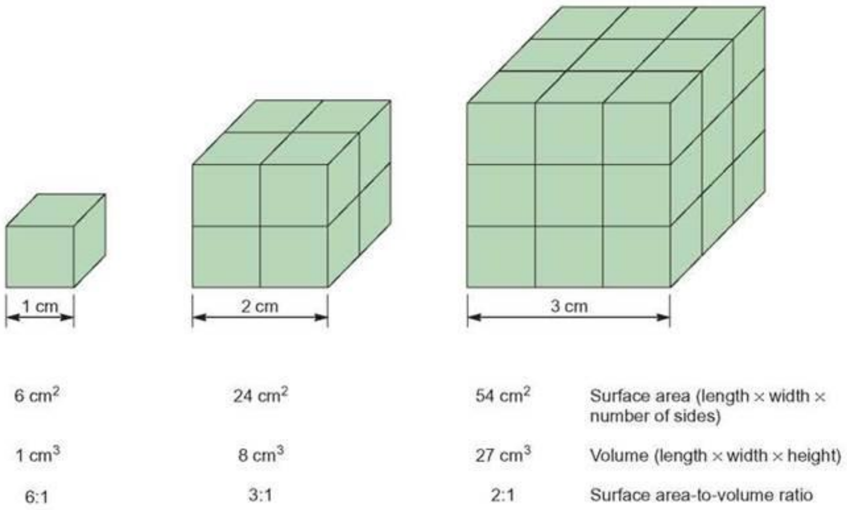


Figure 1.4: Changes in the surface to volume ratio as particle size changes. *(Figure source: https://schoolbag.info/biology/concepts/20.html)*

1.4 Nanoclusters and subnanometre clusters

When a single atom is altered, the characteristics of clusters—particles with a diameter of a few nanometers or less—change. A small number of atoms can form clusters that exhibit unique and frequently surprising properties. Because they can behave as independent active sites and because a small alteration in size or composition, like the addition or removal of a single atom, can significantly affect a reaction's activity and selectivity, they are highly valued in the catalysis field [21]. Clusters exhibit a range of fascinating electronic and magnetic properties due to a variety of factors such as high ratio of surface-to-bulk atoms, electronic shell closings [22], geometric shell closings [23] and quantum confinement. Robert Boyle initially hypothesized the prominence of clusters 350 years ago in his book "The Skeptical Chymist" [24]. However, F.A. Cotton first used the term "cluster" in the early 1960s [25]. Particles with diameters more than 2.0 nm (less than 100 nm) are now commonly referred to as nanoparticles, particles smaller than 2.0 nm as nanoclusters, and microscopic particles with core dimensions less than 1.0 nm as subnanometer clusters [26]. Nanoclusters and subnanometre clusters, in particular, have significantly greater difficulties during synthesis than metal nanoparticles due to their small size. Furthermore, the size effect causes sub-nanometer-sized metal clusters to have different properties than larger nanoparticles.

1.4.1 Preparation and characterization of small clusters

A highly flexible technique for producing clusters is called laser vaporization, in which a laser interacts with a revolving metal rod to produce plasma at the site of contact [27]. A gas, such oxygen or methane, can be seeded into the carrier gas during laser vaporization to create oxides and carbides, which can also result in mixed-composition clusters. Another widely used technique that sputters a target using plasma is magnetron sputtering [28]. Using this method, a voltage is applied to the target, causing it to erode. Atoms are then propelled into rare gas, where they cluster together. Electrospray ionization is an additional technique for ionizing the gas phase while introducing clusters into it [29]. The electrospray ionization technique has several benefits, including being reasonably priced, producing strong beams, and requiring minimum operator maintenance.

To characterize deposited clusters as well as to find more about their distinctive characteristics and interactions with support materials, a variety of techniques are available. These include scanning tunnelling microscopy (STM) [30, 31], (scanning) transmission electron microscopy ((S)TEM) [28], X-ray photoelectron spectroscopy (XPS) [32] and atomic force microscopy (AFM) [33].

1.4.2 Types of clusters

Clusters are classified into two groups based on the constituents present in the cluster.

Homo-atomic/homo-molecular clusters: Clusters formed with the same constituents of atoms/molecules. Examples are molecular cluster (e.g., H_2O), metallic cluster (e.g., Pt_n), carbon cluster (e.g., C_{60}) etc.

Hetero-atomic/hetero-molecular clusters: Clusters formed with the different constituents of atoms/molecules. Examples are metal oxide clusters (e.g., $(SnO_2)_n$), heterometallic clusters (e.g., Au_nAg_m), metal sulphides (e.g., PbS) etc.

Furthermore, as Table 1.1 illustrates, clusters are further divided into a various categories based on the type of chemical bonding.

Table 1.1: Sub classification of clusters based on chemical bonding.

Class	Examples	Nature of chemical bonding	Binding energy range (in kcal/mol)
Ionic clusters	$(NaCl)_n$	Strong ionic bonds	~50-100
Covalent clusters	$(ZnO)_n$, $(TiO_2)_n$	Strong covalent bonds	~20-100
Metal clusters	Pt_n, Au_n Pd_n	Moderate to strong metallic bonding	~10-50
Molecular clusters	$(H_2O)_n$	Molecular interactions, Hydrogen bonding	<10
van der Waals clusters	Xe_n, I_n	Weak binding due to polarization effects	<5

But metal clusters—more specifically, transition metal clusters—are the cluster in which we are most interested and want to discuss in details.

1.4.3 Importance of transition metal clusters in catalysis

Transition metal clusters exhibit distinctive structural, electronic, optical, and magnetic properties [34] which make their study particularly interesting. The incomplete d-subshell helps to the bonding in transition metal clusters. Due to the presence of localized and empty d-orbitals, the majority of characteristics of transition metal clusters differ significantly from those of simple metal clusters. Moreover, interaction occurs between the s and d electrons of the metals as a result of the extremely small energy difference between the (n+1)s and nd levels which determines the chemical composition and electrical structure of these clusters. In materials science, cluster characteristics can be modified not only by varying their size, but also by alloying it with different elements to form heteroatom clusters and alloys.

Cluster formation on a support material serves as a link between the conventional field of heterogeneous catalysis research and basic gas-phase investigations [35]. A new chemical reaction pathway with lower activation barriers is produced by the clusters' high surface-to-bulk atom ratio. Because clusters reduce the amount of precious metal needed for a catalytic process, they can have a significant economic impact. This is because the majority of active catalysts are made of precious metals. It has been demonstrated that altering the size of a cluster is a useful strategy for increasing activity and changing selectivity in a catalytic process. Support materials can have a significant impact on the traits of a cluster because charge transfer occurs from support to cluster and vice versa [36]. The most sophisticated density functional theory (DFT) techniques can be used to well-defined metal clusters, offering a molecular-level comprehension of catalytic active sites and potentially serving as a guide for upcoming theoretical and experimental investigations.

1.5 Catalytic oxidation of Nitric oxide (NO)

Nitric oxide or nitrogen monoxide (NO) is a colorless, free radical gas that is used as an intermediate in the chemical industry, whereas NO_2 is a reddish-brown poisonous, highly reactive gas with a stinging odor that is formed when NO is oxidized. The phrase “Nitrogen oxides (NO_x)” refers to both nitrogen monoxide (NO) and nitrogen dioxide (NO_2). NO_x are produced via three sources: Natural sources (lightning and forest fires), biogenic sources (nitrogen fixation by microorganisms) and anthropogenic sources (Power plants, automobile exhausts). NO_x obtained from natural sources are usually found in troposphere or stratosphere layer of atmosphere. However, NO_x obtained from man-made emissions such as industrial and automobile sources are near to the surface and cause several environmental as well as human health hazards. NO_x contribute greatly to a series of environmental problems such as smog and acid rain [37]. Additionally, NO_x emissions promote the formation of PM2.5 and other fine particles and secondary aerosols. The health effects of NO_x on humans include breathing difficulties, nausea, low blood pressure and other respiratory issues [38]. Hence, much efforts have been made to control and minimize NO_x emissions, particularly from anthropogenic sources.

Some notable modern approaches for controlling NOx emissions are three way catalysis, continuously regenerating traps (CRT), NO_x storage-reduction (NSR) and selective catalytic reduction (SCR). In CRT, NO is converted to NO_2, which then oxidizes the soot (also known as unburned hydrocarbons) that is present on a diesel particulate filter [39]. In NSR approach, NO is first oxidized to NO_2 using noble metals and then stored on the basic component in the form of nitrates [40, 41]. Nitrogen oxides are routinely eliminated and converted to nitrogen via selective catalytic reduction at high temperatures (300-400 °C) using ammonia or other reducing agents. NH_3-SCR is currently the most efficient technique for reducing NO_x emissions in the presence of excess oxygen [42]. Converting a fraction of NO to NO_2 can significantly increase the rate of NH_3-SCR reactions. The "fast" SCR reaction ($4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$) is approximately ten times faster than the normal NO and NH_3 reaction ($4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$) [37]. The selective catalytic reduction process is a well-established technology, but it demands a high temperature and presents difficulties when using and handling ammonia or other reducing chemicals. Hence, the oxidation pathway, in which NO is oxidized to NO_2 in the presence of a catalyst and then wet absorption by conventional alkaline solution or SCR system to form nitrates, is another interesting approach for NO_x abatement [43].

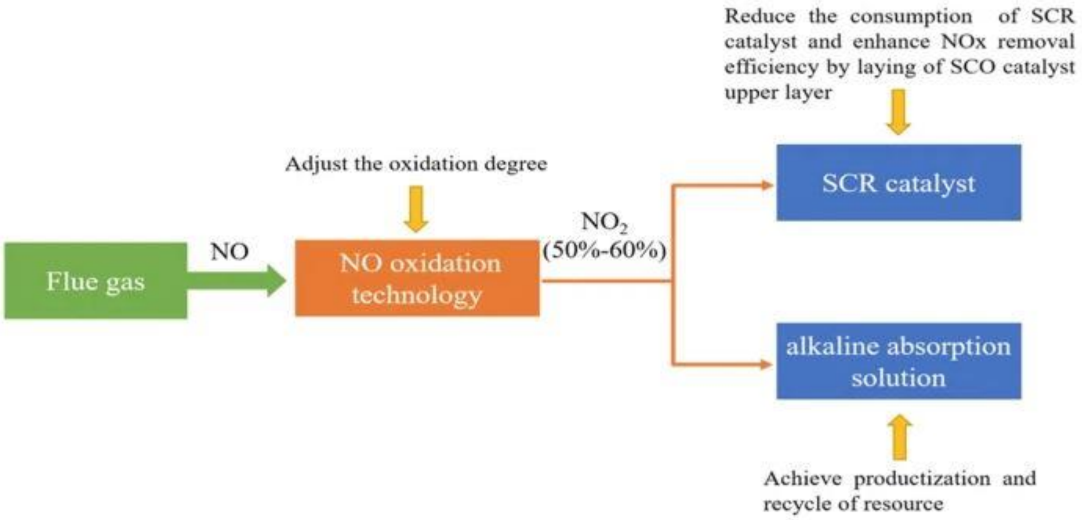


Figure 1.5: Combined system of gaseous pollutant removal with NO oxidation apparatus [43]

Because NO oxidation is more thermodynamically favorable at lower temperatures, it is possible to oxidize NO to NO_2 at room temperature. Compared with other methods, catalytic oxidation of NO to NO_2 using O_2 has its advantages due to the absence of undesirable oxidants, minimal secondary pollution, low cost, and ease of modification for existing SCR systems [43].

1.5.1 Importance of small transition metal clusters for catalytic oxidation of NO

Platinum's strong catalytic activity makes it a popular choice for catalytic oxidation of NO in all of these present-day techniques. Platinum (Pt) metal is extremely valuable when used in fuel cells and vehicle catalytic converters. Its exceptional qualities in three crucial areas, that is, activity, selectivity, and stability have allowed it to surpass all other catalysts. Platinum is considered as an ideal prototypical model catalyst for NO oxidation that has undergone substantial research in the past years [44-46]. In their investigation of the NO oxidation rate on Pt/SiO_2 and Pt/Al_2O_3, Denton *et al.* [47] discovered that Pt particle size played a major role in regulating the reaction rate, while the influence of the support was very less. Rønning and coworkers [48] studied NO oxidation using Pt/Al_2O_3 under two different concentrations of NO in which they found out that the catalyst is highly efficient in oxidizing NO with high oxidation rate. Since Pt catalysts are expensive, optimizing precious metal atomic efficiency can have a large economic impact as it lowers the amount of precious metal required for a catalytic reaction. Recently, a number of theoretical and experimental investigations have been performed on the reactivity of gas-phase Pt clusters, especially in the area of oxidation catalysis. Fernandez *et al.* [49] used a combination of IR spectroscopy and electronic structure computations to study catalytic NO reduction with CO by subnanometric Pt clusters in which they discovered that the Pt clusters are more reactive than singly distributed Pt atoms. Theoretical research by Schneider and coworkers [50] on the impact of Pt cluster size on CO and NO oxidation revealed that oxidation by molecular oxygen is thermodynamically more advantageous than atomic oxygen oxidation in Pt clusters. Hamad *et al.* [51] investigated the durability of platinum clusters and the adsorption of NO over it. Their findings indicate that Pt surfaces and small Pt clusters can exhibit comparable NO adsorption behaviors, which indicates in favor of the use of Pt clusters.

Similarly, Palladium (Pd) attracts great deal of attention in catalytic applications due to its high activity and stability in three way catalysis approach. Various experimental as well as theoretical studies have been performed to study the NO interaction on bare and supported Pd catalysts. The kinetics of the CO+NO and CO+O_2 reaction over single crystal and model planar Al_2O_3 supported Pd catalysts was reported recently using varieties of experimental methodologies [52]. Hao *et al.* [53] have studied the effect of NO on CO oxidation for pure and doped Pd catalysts using NO pulse experiment. They also performed theoretical calculations in which they found that NO binding energy is stronger than that of CO on Pd and Pt surfaces which resulted in NO inhibiting the CO oxidation process. The adsorption phenomenon of NO on various Pd surfaces has also been studied using ultraviolet photoelectric emission spectra and X-ray photoemission spectra [54, 55]. The adsorption and dissociation of NO on Pd_n (n=1-4) clusters was performed by Lacaze-Dufaure and co-workers [56] using theoretical calculations in which they revealed that NO dissociation is not possible on Pd_4 cluster. Gao *et al.* [57] did DFT calculations for NO adsorption and dissociation on neutral and charged Pd_{13} clusters in which they found out that anionic Pd_{13} cluster has lowest energy barrier and highest catalytic activity. Liu *et al.* [58] studied interaction of NO on subnanometer Pd_n (n = 8, 13, 19, 25) clusters ~~in~~ which provided an understanding into structure-sensitive Pd-based subnanometer catalysts to mitigate NO.

The automotive industry has historically employed noble metal catalysts, specifically platinum (Pt) and palladium (Pd), to regulate harmful emissions. However, on the other hand, gold (Au) was not thought to be an efficient catalyst until the middle of the 1980s. Due to their superior performance over platinum group metals at low temperatures, gold-based catalysts have the potential to address the "cold-start" issue in automobiles [59, 60]. Some even speculate that platinum group catalysts may eventually be replaced by gold catalysts [61, 62]. Active catalysis has been shown by unsupported nanosized Au particles [63, 64] for various chemical reactions suggesting that nano- or sub-nanogold particles may naturally possess catalytic activity. Moreover, the electronic structure of free anionic gold clusters is expected to mimic that of active supported gold catalysts as a result of charge transfer from supports to deposited gold clusters [65]. Several investigations have been done on the interactions between gold clusters, O_2 and NO as activation of both the reactants is important for NO oxidation. Huang *et al.* [66] used photoelectron spectroscopy to conduct an organized examination of the interactions between O_2 and Au_n^- (n = 1−7) and discovered that molecular chemisorption of O_2 occurs on Au_n^- for n = 2, 4, 6 and physisorption of O_2 occurs for odd sized Au_n^- (n = 3, 5, 7) clusters. Using infrared multiphoton desorption spectroscopy, Fielicke and coworkers [67] examined geometrical configurations and collected the vibrational spectra of $Au_nO_2^-$ (n = 4, 6, 8, 10, 12, 14, 18, and 20). After conducting multiple NO adsorption studies on Au_{1-12}^-, it was shown that for sizes with n = 4, 6, and 8, disproportionate reaction products $Au_nNO_2^-$ were produced [68]. The same group continued to study the adsorption and reaction of NO on anionic Au clusters up to 1 nm in size [69] and came to the conclusion that the spins of the clusters governed the adsorption of NO, and most even sizes with open electron shells were reactive.

1.6 Catalytic reactions over zeolite supported metal clusters

Recently, researchers seem to be interested in using catalytic metal particles smaller than 1 nm or even individual metal atoms because of their advantageous characteristics when compared to their bulk. Synthesizing those small metal subnanoparticles is challenging as they exhibits less thermodynamic stability than that of its bulk counterpart. Hence, a brilliant host is required which not act as a support but also participate in the reaction by providing charges, adsorption sites etc. Zeolite is an excellent host material with well-defined cavities and channels, as well as excellent shape and size selectivity. The molecular size of the holes and channels in zeolites causes shape selectivity; in other words, the degree to which the reactants or products accommodate inside the pores determines whether the reaction will occur inside the zeolite [70, 71]. In zeolites, isomorphous substitution produces Lewis or Brønsted acid sites that are suitable for coordinating widely dispersed transition metal centers. The presence of small pores in zeolites allows for the creation of unique nanoparticles and sub-nanoparticles containing catalytically efficient transition metals. Moreover, zeolites have a comparatively high thermal stability, which makes it possible to carry out reactions in both the gas and liquid phases under harsh conditions [72, 73]. Hence, all these unique characteristics make zeolites as preferred catalytic materials for numerous industrially applications.

Zeolites are aluminosilicate minerals that are crystalline and microporous. They consist of tetrahedral elementary building units of SiO_4 and AlO_4^-. Tetrahedra are linked by a common oxygen atom to form three-dimensional zeolites. This results in the net formula for tetrahedra being SiO_2 and AlO_2^-, where the AlO_4 atom has a negative charge. As a result, the zeolite's chemical formula is given by

$$A^{m+}_{y/m}[(SiO_2)_x.(AlO_2^-)_y].zH_2O$$

where x and y stand for number of Al and Si tetrahedra, M is the cation, and n is the cation's valency [74]. Löwenstein's rule [75] states that the aluminosilicate framework cannot have continuous Al-O-Al connection. The Si/Al ratio ranges from 1 to infinity depending upon the zeolite structure. The term "zeolite" was first used in 1756 by Swedish mineralogist Axel Predrik Cronstedt. It is taken from the Greek word meaning "boiling stone" as zeolites lose water when heated. The combinations of the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra in various ways result in the formation of secondary building units (SBU). When these SBU units are linked together, zeolites with cavities, channels, and cages of varying sizes are formed. Sodalite and pentasil units are two common secondary building units. Zeolite A and faujasite zeolites X and Y consist of building blocks of sodalite cages while pentasil unit is the building unit for ZSM-5, ZSM-11 and mordenite. The internal structure of the zeolites belonging to the faujasite family is comprised of large spherical cavities or supercages that are interconnected via a 12 membered ring opening where 12 denotes the number of bridging oxygen atoms. Faujasite has a large pore diameter of 7.4 Å and the diameter of supercages is approximately 13 Å [76]. Zeolites made up of pentasil units contain a network of two intersecting channels, in contrast to the faujasites' interconnecting cavity structure. These channels are elliptical or spherical in shape and might have a straight or sinusoidal intersection. These medium pore zeolites have pore openings consisting 10 member rings of TO_4 tetrahedra. ZSM-5 and ZSM-11 consist of intersecting channels with diameters of approximately 5 Å [76]. The Database of Zeolite Structures now has documented around 230 zeolite topologies [77].

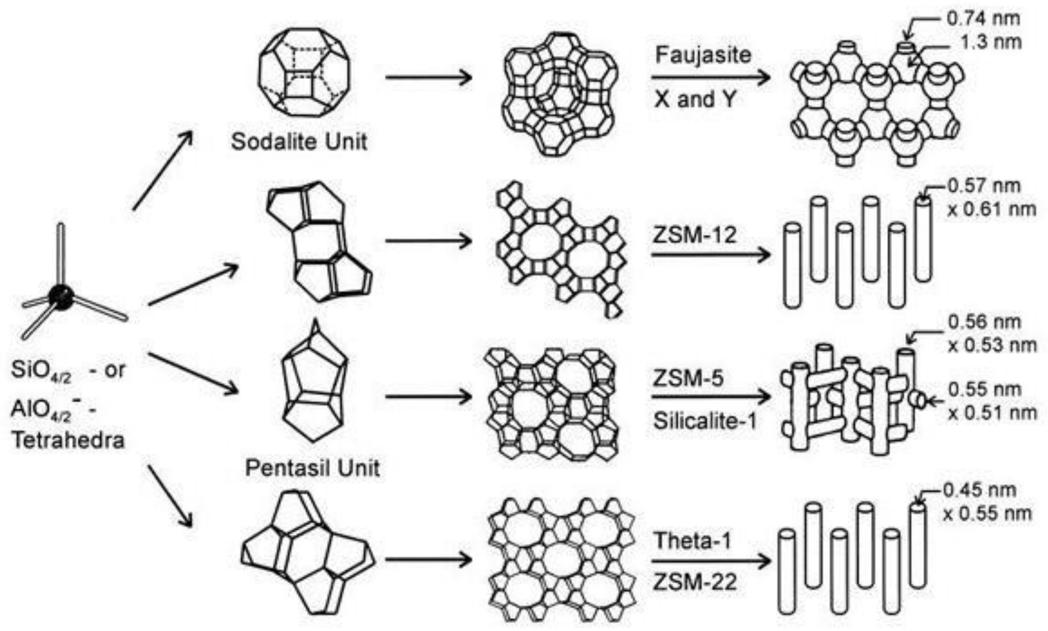


Figure 1.6: Examples of zeolites structures with their micropore dimensions [74].

Three distinct transition metal–zeolite combinations exist:

(i) Isolated metal nanoparticles: Transition metal clusters and subnanoparticles are incorporated directly into the pores of zeolites. Zeolites stabilizes the metal centers by encapsulating them.

(ii) Ion-exchanged cations sustained on $[AlO_4]^-$ tetrahedra: The zeolite framework's net neutrality is disrupted when an Al atom replaces a Si atom, resulting in an overall negative charge. The insertion of H^+ or extraframework cations like Li^+, Na^+ and Ca^{2+} balances this negative charge.

(iii) Zeolite framework with replaced single heteroatoms: Unlike other metal-zeolite arrangements, which simply produce extraframework species, the isomorphous replacement approach allows for the formation of genuinely single framework metal sites. Ti-containing MFI zeolite, frequently referred to as TS-1, is a well-known catalyst for isomorphically substituted zeolites.

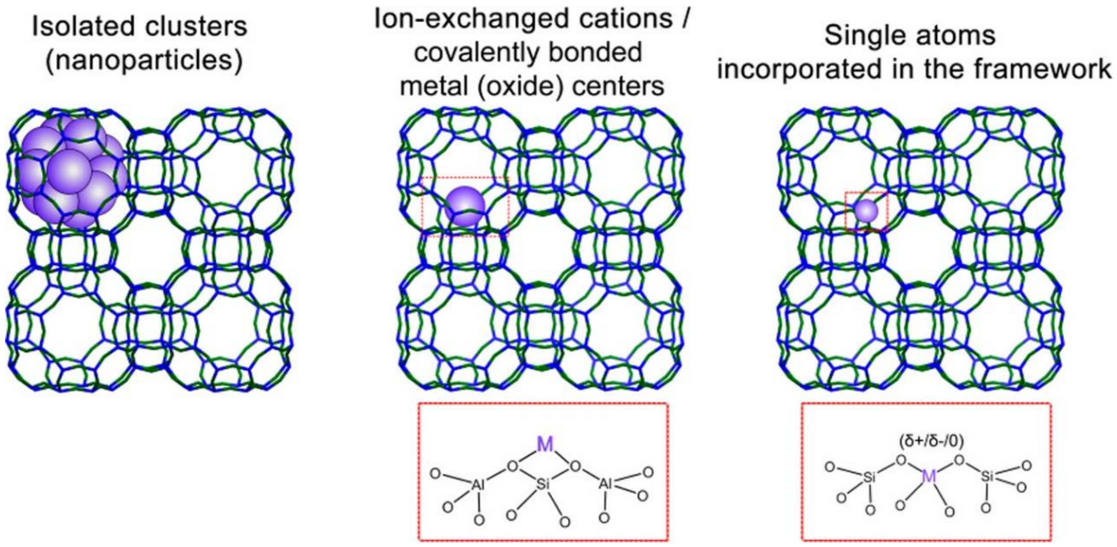


Figure 1.7: Various possible configurations of metal-zeolite composite [78]

The use of zeolites in catalytic processes such as biomass conversion [79, 80], conversion of natural gas into value added products [81], methanol-to-hydrocarbon conversion [82, 83] selective catalytic reduction of nitrogen oxides [84, 85] etc have been extensively studied. NO adsorption as well as desorption on Pd/ZSM-5 was investigated by Gu *et al.* [86]. They used Pd based zeolites as passive NO_x adsorbers (PNAs) since it can store NO_x at low temperatures which helps in diesel engine cold start NO_x mitigation. They also studied temperature effects on NO adsorption and proposed a mechanism via which NO adsorption and formation of different surface intermediates took place. Mechanistic traits of NO adsorption/desorption were investigated over Pd/SSZ-13 using FT-IR spectroscopy [87] in which it was found out that even in the presence of exhaust species like propylene and CO, Pd/SSZ-13 can store NO effectively. Grybos *et al.* [88] studied NO adsorption on Pd_n (n=1-6) clusters using density-functional calculations under periodic boundary conditions. A detailed investigation on adsorption characteristics and the cluster-support interactions were done and it was found that cluster-support interactions induces more blueshift on NO-stretching modes compared to NO adsorbed on a free cluster. The effects of the Al isomorphic substitution by B and Ga on the geometries, adsorption energies, and vibrational frequencies of NO and N_2O on a model for Au(I)/ZSM-5 catalysts was examined using density functional calculations [89] in which it was found that the electronic properties of Au(I) was altered by isomorphous substitution in ZSM-5, helping in promoting NO adsorption. Sobczak and co-workers [90] have investigated adsorption and co-adsorption of NO SCR-HC

(NO, C_3H_6 and O_2) on different zeolites (Non-acidic NaY, acidic H-Beta and H-ZSM-5) modified with gold. They proposed that the most appealing catalysts for SCR of NO with propene are Au/H-Beta and Au/H-ZSM-5 zeolites, which have high Si/Al ratios and strong acid sites. Na-ZSM-5 with a high SiO_2/Al_2O_3 ratio was chosen for NO oxidation by O_2 at ambient temperature using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and temperature-programmed surface reaction (TPSR) [91]. The outcomes demonstrate a dynamic equilibrium between NO_2 adsorption and the reaction of NO, and additionally indicate that the NO catalytic oxidation process is accompanied by a considerable adsorption of NO_2. NO and NH_3 oxidation was studied by Akter *et al.* [92] over chabazite (H-CHA), beta (H-BEA) and mordenite (H-MOR) at high temperature range (100-450^{0}C). They observed that H-CHA have shown greater conversion for NO oxidation and NH_3 oxidation due to its smaller pore size than that of BEA and MOR types, which aid in stabilizing activated transition complexes.

Studies on zeolites in NO oxidation are somewhat limited. Although some of these investigations on zeolites demonstrate the reaction mechanism of NO oxidation to some extent, further investigation is still required to explore different kinds of reaction pathway across various catalysts and the impact of different potential intermediates on the NO oxidation reaction process.

1.7 Mechanisms for NO oxidation

In general, the traditional bimolecular Eley-Rideal (E-R) [93, 94] or Langmuir-Hinshelwood (L-H) [95] mechanisms are followed for NO oxidation on various catalysts based on adsorption properties. Recently, two new mechanisms that represent trimolecular chemical reactions have been proposed: the termolecular Eley-Rideal (TER) [96, 97] and termolecular Langmuir-Hinshelwood (TLH) [98]. Different mechanisms are followed on different catalysts based on the adsorption and co-adsorption energies of the reactants (NO and O_2).

In order to occur E-R mechanism, adsorption energy (E_{ads}) of O_2 has to be higher or comparable with respect to E_{ads} of NO. First, O_2 is adsorbed onto the catalytic surface. Then NO comes from gas phase and attacks the free O atom of O_2, which eventually results in the formation of first NO_2. Then another NO enters the catalytic cycle, attacks the remaining O atom in the gas phase, forming second NO_2.

For L-H mechanism, co-adsorption energy (Co-E_{ads}) of NO and O_2 has to be higher than that of E_{ads} of O_2. At the start of the cycle, both NO and O_2 are co-adsorbed on the catalytic surface. N atom of NO interacts with one of the O atom of O_2, resulting in the elongation of O_2 molecule and formation of O-N-O-O bond. Reaction proceeds further when O-O bond breaks, resulting in the formation of first NO_2, leaving behind O atom. Another NO comes and gets adsorbed onto the surface, alongside O atom. These two species interact with each other to form second NO_2 molecule, thus completing the cycle.

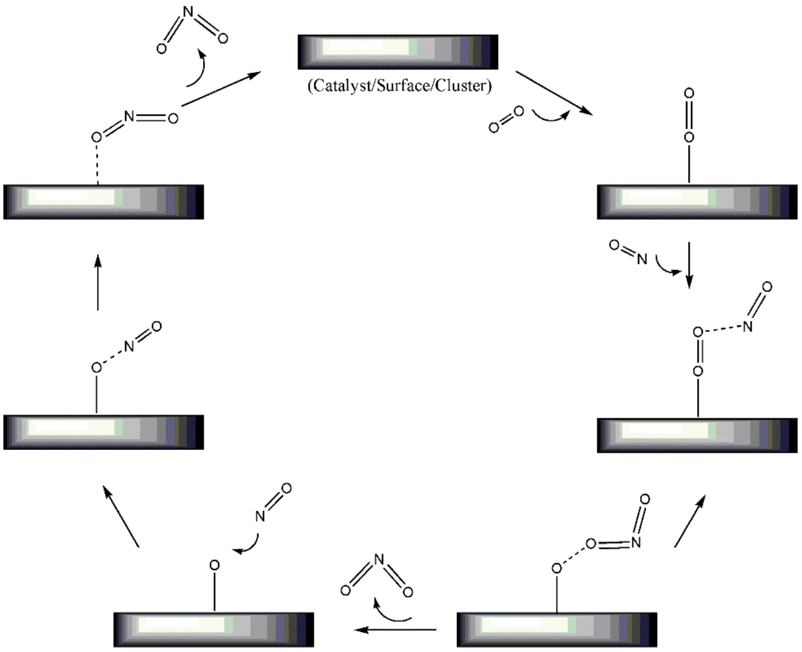


Figure 1.8: Schematic representation of Eley-Rideal (E-R) mechanism for catalyzing two NO molecules to two NO_2 molecules using O_2.

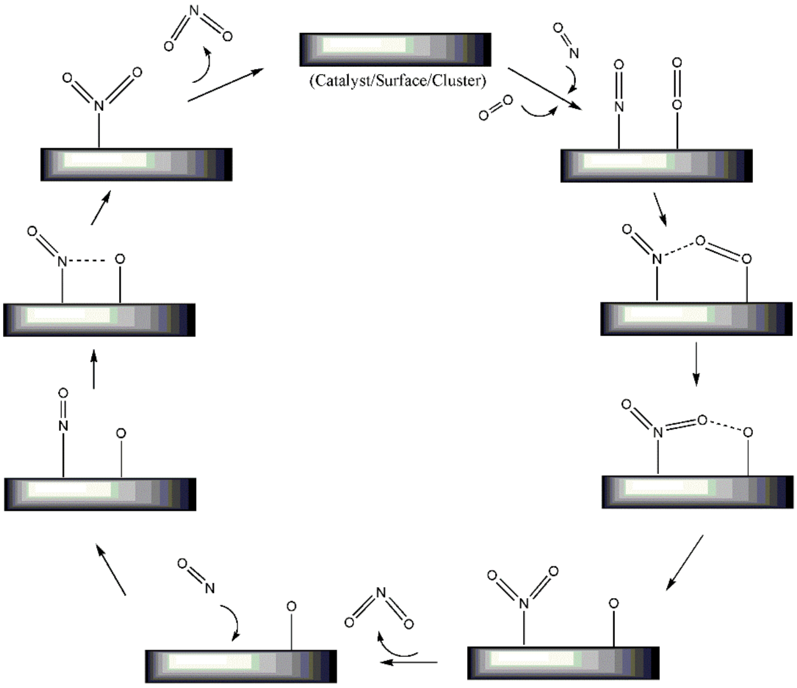


Figure 1.9: Schematic representation of Langmuir-Hinshelwood (L-H) mechanism for catalyzing two NO molecules to two NO_2 molecules using O_2.

The TER mechanism is a three-molecule reaction process wherein two pre-adsorbed NO molecules activate the gaseous O_2 molecule. The co-adsorption energy of two NO molecules has to be higher than that of co-adsorption of O_2 and NO as well as single adsorption of O_2 and NO. First, two NO molecules are co-adsorbed on the active site adjacently. Then O_2 molecule interacts with two NO molecules while remaining in the gas phase, forming O-N-O-O-N-O species. O-O bond of O_2 breaks which results in the formation of two NO_2 molecules simultaneously.

Similar mechanism occurs in TLH where O_2 molecule is activated using two NO molecules. In contrast to the TER process, here, O_2 is adsorbed to the catalytic surface. O_2 molecule interacts with its adjacent NO molecules to generate O-N-O-O-N-O species, which eventually results in the formation of two NO_2 molecules once O-O bond is broken.

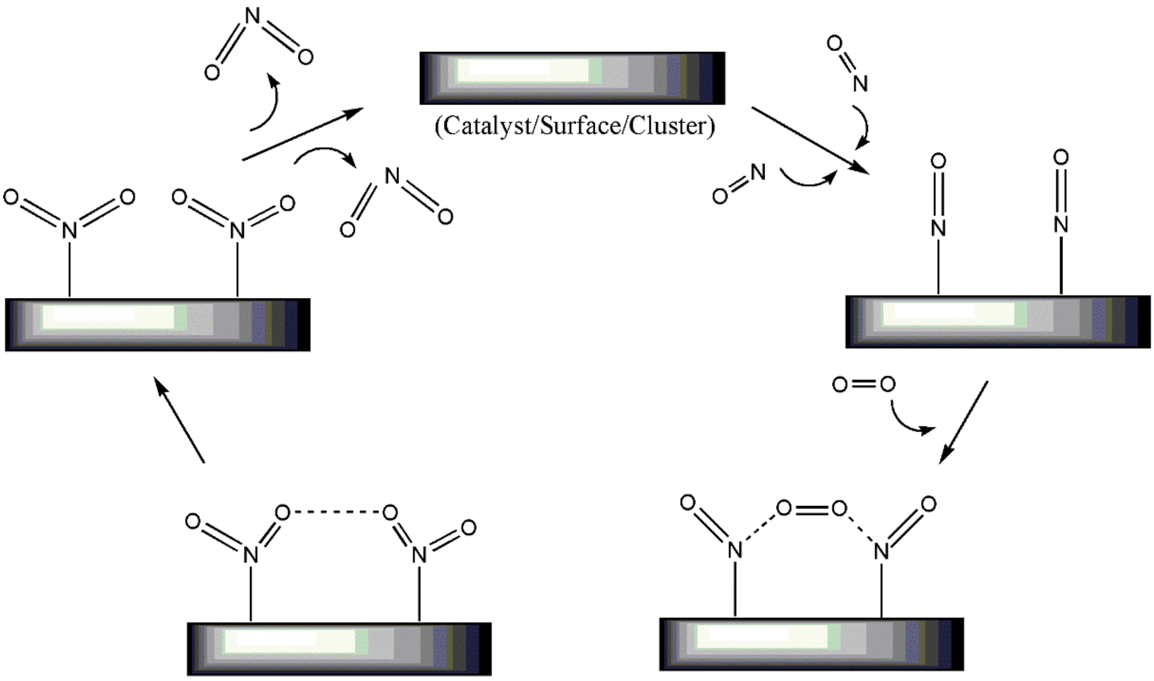


Figure 1.10: Schematic representation of termolecular Eley-Rideal (TER) mechanism for catalyzing two NO molecules to two NO_2 molecules using O_2.

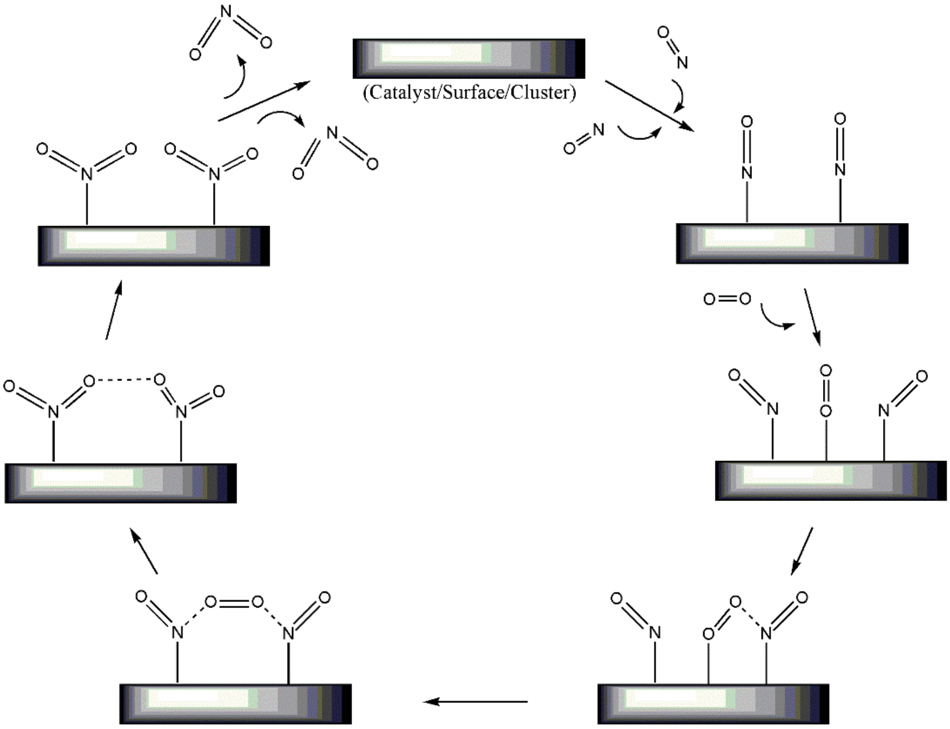


Figure 1.11: Schematic representation of termolecular Langmuir-Hinshelwood (TLH) mechanism for catalyzing two NO molecules to two NO_2 molecules using O_2.

1.8 Objectives of the present work

The thesis is carried out with the following goals in mind: to understand the mechanism of NO oxidation and to model the NO oxidation catalyst for improved comprehension at the atomistic level. The following objectives are-

1. To investigate the mechanistic pathway of catalytic oxidation of NO to NO_2 *on* $[Pt_2]^{0,\pm}$ *monometallic dimers using* O_2 *as the oxidant.*

2. To evaluate the synergistic effects in catalytic oxidation of NO on $[Au\text{-}M]^-$*(M=Pd & Pt) bimetallic dimers, in comparison with their monometallic counterparts.*

3. To test the hypothesis that the catalytic efficiency of pristine and doped $[Au_nPd_{3-n}]^-$ *(n=0-3) trimer clusters for catalytic oxidation of NO is higher than that of the dimers.*

4. To study the adsorption and activation of nitric oxide (NO) and oxygen (O_2) *on bare and supported* M_n*/ZSM-5[M=Au, Pd, Pt] (n=1-2) using ONIOM method.*

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