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TRANSITION-METAL CATALYSTS FOR OXIDATION REACTIONS

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ABSTRACT:
Oxidation reactions are essential processes in both natural and commercial contexts, and transition metal catalysts are essential in promoting these reactions. The importance of oxidation reactions/processes, and applications of transition metals for catalyzing oxidation reactions are covered in detail in this review. The review begins with an overview of the special qualities and catalytic capacities of transition metals, then explores the different kinds of oxidation processes and their commercial significance. It addresses common metals utilized in these processes and examines the electronic structures of transition metals that permit their catalytic activity. A review is conducted on the different kinds of transition metal catalysts, such as enzyme-inspired catalysts, heterogeneous, homogeneous, and nanocatalysts. The review ends with a discussion of the field's present problems, including selectivity and catalyst deactivation, as well as potential future developments with respect to green chemistry and sustainable catalysis.

Keywords: Transition Metal Oxides, Catalysis, Catalytic Mechanism, Green Chemistry, Catalyst Stability, Catalytic Performance, Catalyst Recyclability, Cost-effective Catalysts

INTRODUCTION:

An element that can produce cations with an inadequate d-subshell alternatively whose atom has a moderately filled d-subshell is known as a transition metal. The outermost d-orbitals of the transition metal ions are partially occupied by electrons, allowing them to readily give and accept electrons. Transition metals are essential components of biological systems because they act as catalysts for electron transport and enzymatic processes. Numerous enzymes contain them in their active regions, where they aid in a range of biological activities. For example, Carbonic Anhydrase enzyme, which is involved in the control of the body's pH and fluid balance, depends critically on the transition metal zinc. Comparably, hemoglobin (Hb), the protein that transports oxygen throughout the blood, depends on the transition metal iron.[i] Transition metal-catalyzed oxidation processes have become highly effective instruments in organic synthesis, facilitating the selective and effective synthesis of complex compounds. This chapter reviews key case studies, recent developments, and mechanistic insights in the field of transition metal catalysis for oxidation processes. The creation of materials, medicines, and fine chemicals depends on these reactions, which emphasizes how crucial it is to comprehend their mechanics, catalysts, and uses.

A. TRANSITION METAL BASED CATALYST DEVELOPMENT AND HISTORICAL CONTEXT:

Early Beginnings, metals have been used in various chemical reactions from ancient times; early civilizations used metals like iron and copper for a variety of purposes. On the other hand, catalysis was first formally studied in the 19th century. The word "catalysis," which describes compounds that accelerate chemical reactions without being consumed, was originally used in 1835 by Swedish chemist Jöns Jacob Berzelius. This was the start of a methodical investigation of catalytic reactions.

Development of Transition Metal Catalysis

Over the ensuing decades, there was a notable evolution in the comprehension and utilization of transition metal catalysis.

1) Late 19th and Early 20th Century:

Wilhelm Ostwald: Modern catalytic science was founded on the research on reaction rates and catalysis conducted by Wilhelm Ostwald in the late 1800s. Particularly significant were Ostwald's investigations on the use of platinum catalysts in the oxidation of ammonia to nitric acid.

Fritz Haber and Carl Bosch: The chemical industry was completely transformed at the starting of the 20th century by the Haber-Bosch process, which uses an iron catalyst to create ammonia from nitrogen and hydrogen gasses. This procedure highlighted the potential of transition metal catalysts in large-scale industrial applications while also demonstrating their practical significance.

2) Mid-20th Century:

Ziegler-Natta Catalysts: Giulio Natta and Karl Ziegler created organic compounds based catalysts which can help in polymerization of ethylene and propylene in the era of 1950s. The plastics industry was revolutionized by these catalysts, which were based on compounds of titanium and aluminum and allowed the creation of high-density polyethylene and isotactic polypropylene. In the year of 1963, Ziegler and Natta shared Nobel Prize in Chemistry for their research.

Organometallic Chemistry: Significant progress was also made in the exploration of molecules with metal-carbon bonds (M-C), or organometallic chemistry, in the middle of the 20th century. Chemists like the 1973 Nobel laureate Geoffrey Wilkinson and Ernst Otto Fischer made significant contributions to our knowledge of transition metal complexes and their catalytic characteristics.

3) Late 20th Century:

- **Homogeneous Catalysis**: When both catalyst and reactants exist in the same phase. Prominent instances of effective homogeneous catalysts are the rhodium-based catalysts for hydroformylation (the transformation of alkenes into aldehydes) and Wilkinson's catalyst for hydrogenation processes.
- **Asymmetric Catalysis**: Advances in asymmetric catalysis—where catalysts are engineered to provide chiral compounds with strong enantioselectivity—occurred in the 1980s and 1990s. Chemists like William S. Knowles, Ryōji Noyori, and K. Barry Sharpless—shared Nobel Prize of 2001.

4) Modern Developments Research on transition metal catalysis has concentrated on selectivity, efficiency, and sustainability in recent decades:

- **Green Chemistry:** The creation of new transition metal catalysts has been directed by the concepts of green chemistry, which prioritize the reduction of hazardous chemicals and the effective use of resources. In an effort to develop more sustainable catalytic processes, researchers have looked into using earth-abundant metals including nickel, cobalt, and iron as substitutes for precious metals.

- **Nanocatalysis:** The development of nanotechnology has made it possible to create nanocatalysts with improved surface areas and distinctive characteristics. Better activity, selectivity, and stability are frequently displayed by these catalysts, which makes them appropriate for a range of uses, such as environmental remediation and energy conversion.
- **Computational Catalysis:** Developments in high-throughput screening and computational chemistry have made it easier to rationally develop transition metal catalysts.
- **Biomimetic Catalysis:** Biomimetic catalysts, which draw inspiration from natural enzymes, are designed to mimic the selectivity and efficiency of biological systems.

B. MECHANISMS OF OXIDATION CATALYZED BY TRANSITION METALS:

Due to their fluctuating oxidation states and ability to form complexes, transition metals are crucial for promoting oxidation processes. The whole process entails the creation of a metal-oxygen species, which then provides the substrate with oxygen to produce the intended oxidized product.

$Mn^{(n+)}$ + Oxidant → $Mn^{(n+1)+}$ + Reduced Oxidant

$Mn^{(n+1)+}$ + Substrate → $Mn^{(n+)}$ + Oxidized Product

This cycle demonstrates how the transition metal catalyst is redox active.

1) Redox Cycles and Oxidation States:

Transition metals are able to mediate transfers of oxygen atoms or electrons because they can flip between different oxidation states. The transition metal alternates between its oxidized and reduced forms in a typical catalytic cycle. For instance, in a metal-catalyzed oxidation, a terminal oxidant (such as O_2 or H_2O_2) oxidizes the metal center, which is then followed by substrate oxidation and the regeneration of the reduced metal species.

2) Oxygen Species in Action:

A common characteristic of these reactions is the construction of active oxygen species, such as metal-oxo (M=O), metal-peroxo (M-OOH), and metal-superoxo ($M-O_2$) intermediates. Due to their high reactivity, these species can aid in a variety of oxidation processes, such as:

- **C-H Bond Activation:** C-H bonds are oxidation-prone when they are activated by transition metals. In oxidation reactions, this activation frequently determines the reaction's pace.
- **Epoxidation:** Epoxides are created when metal-oxygen species combine with double bonds.
- **Hydroxylation:** Metal-oxygen species help to introduce hydroxyl groups into organic compounds.

C. OXIDATION REACTIONS: SIGNIFICANCE IN INDUSTRIAL AND SYNTHETIC CHEMISTRY:

Industrial Applications of Oxidation Reactions:

- **Petrochemical Industry**:

Production of Basic Chemicals: Basic compounds including ethylene oxide, propylene oxide, and acetaldehyde are produced by oxidation processes. For instance, ethylene can be oxidized to produce ethylene oxide, a precursor of detergents, solvents, and antifreeze.

- **Pharmaceutical Industry**:

Drug Synthesis: Oxidation processes are used in the synthesis of several medicines. For example, an important stage in the manufacture of many medications, such as antibiotics and anti-inflammatory medicines, is the hydroxylation of aromatic molecules.

Active Pharmaceutical Ingredients (APIs): The functional groups of APIs are altered through oxidation processes, which improves their stability and biological activity. Developing safe and effective pharmaceuticals requires these changes.

- **Fine Chemicals and Agrochemicals**:

Synthesis of Fine Chemicals: It is possible to create fine compounds, such as perfumes, and colors, by oxidation processes. The introduction of oxygen-containing functional groups is made possible by these reactions, which is essential for giving these compounds their intended characteristics.

- **Environmental Applications**:

Pollution Control: The degradation of contaminants in exhaust gases and industrial effluents is accomplished through catalytic oxidation processes. For instance, air pollution is decreased by the use of various catalyst for oxidation of volatile organic compounds (VOCs) in industrial emissions. **Wastewater Treatment**: In wastewater treatment, advanced oxidation processes (AOPs) are used to convert organic contaminants into less toxic substances. In order to treat industrial wastewater and guarantee environmental safety, certain procedures are essential.

SYNTHETIC CHEMISTRY AND THE ROLE OF OXIDATION REACTIONS:

- **Functional Group Transformations**:

Alcohols (-OH) to Carbonyl Compounds (>C=O): there are many important reactions in organic chemistry, out of which one of the key processes in organic synthesis is the oxidation of primary as well as secondary alcohols to aldehydes and ketones, respectively.

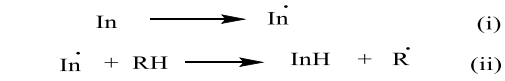
Oxidation of Alkenes: Alkenes undergo oxidation processes to produce diols, epoxides, and other useful intermediates. The creation of complex organic compounds and medicines requires these reactions.

D. ROLE OF TRANSITION METALS IN CATALYSIS

Homogeneous Transition-Metal Catalysis:

Oxidation by homolysis: Three general processes can be used to characterize the reaction amongst organic molecules and oxygen that occurs through a free radical chain mechanism via three steps : initiation, propagation, and termination. Equations depict the fundamental autoxidation mechanism that incorporates these three steps.[ii]

Initiation



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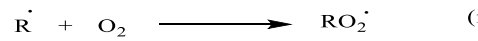
Propogation



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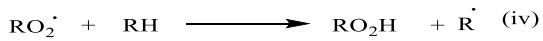

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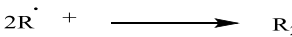
Termination



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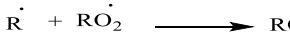

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Alkane autoxidation: cyclohexane

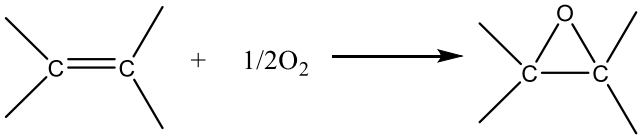
Cyclohexane can be oxidized in liquid phase by air in the presence of a homogeneous cobalt catalyst, yielding cyclohexanone and cyclohexanol as the main products. Cobalt naphthenate, for example, cobalt salt; which is soluble in cyclohexane that is typically cast-off as a catalyst to prevent excessive by-product forms.

The process to make adipic acid requires substantial use of cyclohexanol-cyclohexanone mixture that results from the auto-oxidation of cyclohexane.[iii]

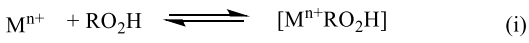
Heterolytic oxidation

- **Propene epoxidation catalyzed by transition metals**

The crucial interaction in the metal-catalyzed homolytic oxidations previously addressed is that which occurs amongst the metal and the hydroperoxide substrate.[iv] Adding oxygen atom to the double bond of the alkene is the overall outcome of alkene epoxidation:



Using heterogeneous silver-based catalysts, with the further help of air, or oxygen; ethene can be oxidized directly to yield efficiently ethylene oxide manufactured in the western world. ethylene oxide (equivalent moles of ethylene oxide formed for every mole of ethene reacted) in the range of 70% could be easily accomplished with temperature in the range of 250°C and pressures in the range of 10 to 30 atm. Initial transition metals in their higher oxidation states, such as W(VI), Mo(VI), and Ti(IV), are suitable catalysts. The basics of epoxidation process can be explained by the series of reactions that follow:



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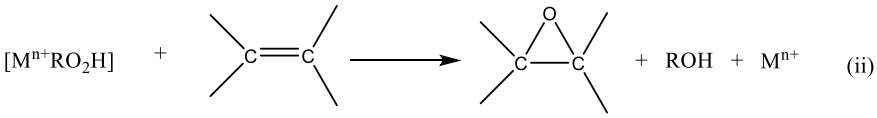
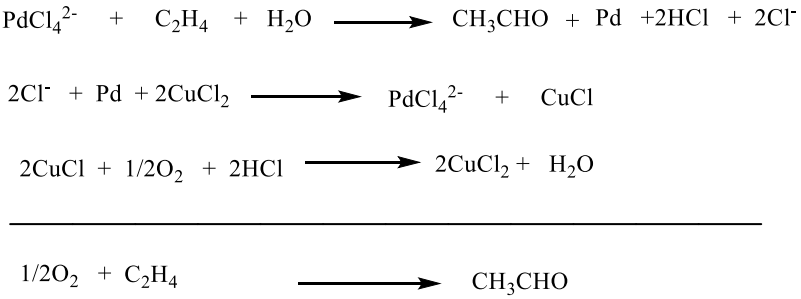


(ii)

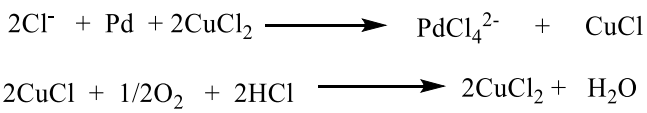
- **Alkene oxidation catalyzed by palladium complexes**

A amalgamation of $CuCl_2$ and $PdCl_2$ results in a catalytic system whose final reaction leads to the aerial- or oxygen-oxidation of ethene to ethanal. When cupric chloride is utilized, the reduced product, CuCl, could be easily reoxidized to cupric chloride in presence of air or oxygen.[v]



The Wacker process, which currently produces about 1.5 million tons of ethanal annually, is based on this series of processes.[vi]

As the resultant cuprous chloride (CuCl) may be easily reoxidized by aerial oxidation or oxygen, cupric chloride is virtually often employed as the oxidant of the palladium in commercial Wacker processes.



What Separates Heterogeneous from Homogeneous Catalysis?

The specific reaction needs, such as catalyst recovery, reaction conditions, and ease of separation, determine whether to use homogeneous or heterogeneous catalysis.[vii]

Homogeneous Transition-Metal based Catalysts	**Heterogeneous Transition-Metal based Catalysts**
a) Frequently involve soluble metal complexes, as those of iron, cobalt, or ruthenium. b) Redox cycles are carried out by the metal core, which directly interacts with the reactants to promote oxidation. c) Utilized in the production of pharmaceuticals, organic compounds, and fine chemicals. d) An illustration of manganese porphyrins in alkene oxidation reactions.	a) Often involve metals or metal oxides supported atop inert materials, such as platinum, palladium, or vanadium oxide. b) Adsorption of reactants, surface reactions, and desorption of products are signs of surface reactions. c) Extensively employed in industrial operations, including the synthesis of chemicals and automobile catalytic converters. d) An illustration of vanadium pentoxide (V_2O_5) which is utilized to oxidize sulfur dioxide and produce sulfuric acid.

E. SUPPORTED CATALYSIS AND NANOCATALYSTS:

The fact that transition-metal catalysts can promote a variety of reactions, including oxidation processes, makes them very useful. In this field, assisted catalysis and nano catalysts have become important methods for improving catalytic efficiency.

1. Nanocatalysts in Oxidation Reactions

Catalysts that function at the nanoscale, typically with sizes between 1 and 100 nanometers, are recognized as nanocatalysts. Since these nanocatalysts acquire special qualities, which include high surface area-to-volume ratios along with quantum size effects, nanocatalysts are very useful in catalytic processes.[viii]

a) Fundamentals and Qualities

Due to their huge surface area compared to volume, nanocatalysts offer more active sites for reactants to interact with the catalyst. Materials' electrical characteristics can alter at the nanoscale, improving catalytic activity and selectivity. By increasing their surface energy, nanocatalysts can become more reactive and perform better in oxidation reactions.

b) Manufacturing of Nanocatalysts

- **Bottom-Up Approaches:** These include techniques where atoms or molecules combine into nanostructures, like hydrothermal synthesis, sol-gel processes, and chemical vapor deposition.
- **Top-Down Approaches:** Lithography and ball milling are two methods that reduce bigger particles to nanoscale levels.
- **Stabilization and Functionalization:** Stabilization is frequently necessary for nanocatalysts to avoid agglomeration. In reaction media, functionalization with ligands or polymers can increase their stability and dispersibility.

Oxidation Reactions Involving Nanocatalysts

- **Selective Oxidation of Alcohols:** Selectively oxidizing primary or secondary alcohols to aldehydes or ketones, molecular oxygen (O_2) is activated by nanocatalysts, such as gold or platinum nanoparticles supported on metal oxides. Example- Gold nanoparticles supported on titanium dioxide (Au/TiO_2) catalyze the oxidation of benzyl alcohol to benzaldehyde.
- **Epoxidation of Alkenes:** Oxygen is activated by nanocatalysts such as silver or palladium nanoparticles, which then introduce an oxygen atom into an alkene's double bond to generate an epoxide. Example- Propylene epoxidates to propylene oxide under the catalytic action of silver nanoparticles supported on carbon (Ag/C).
- **Environmental Applications - CO Oxidation:** In catalytic converters, carbon monoxide (CO) is converted to carbon dioxide (CO_2) by means of nanocatalysts, such as

platinum or palladium nanoparticles supported on metal oxides.[ix] Example- Within automotive exhaust systems, the oxidation of CO to CO_2 is catalyzed by platinum nanoparticles supported on cerium oxide (Pt/CeO_2).

- **Hydrogen Peroxide Production:** Nanocatalysts catalyze the selective oxidation of hydrogen to hydrogen peroxide (H_2O_2).They are usually based on palladium or gold nanoparticles supported on metal oxides .Example- Direct generation of hydrogen peroxide from hydrogen and oxygen is catalyzed by palladium nanoparticles supported on iron oxide (Pd/Fe_2O_3) [x]

2. Supported Catalysis in Oxidation Reactions

Dispersing active metal species onto a solid support material is the process of supported catalysts. This tactic keeps the catalyst's catalytic activity high while improving its stability and reusability.

a) Fundamentals and Qualities

Oxides (silicone, alumina, titania), carbon-based materials (graphene, activated carbon), and zeolites are examples of common supports. In order to maximize the exposure of catalytic sites to reactants, supports aid in the dispersion of the active metal species. By stabilizing the active metal species, supports can stop deactivation and sintering.

b) Techniques for Preparing the Catalyst

- **Impregnation:** To create the supported catalyst, the support is immersed in a metal precursor solution, then dried and calcined.
- **Co-precipitation:** Co-precipitation of metal precursors and support materials from solution is followed by calcination.
- **Chemical Vapor Deposition:** Metal precursors are carefully evaporated and then put onto the support.

Mechanisms of Oxidation Reactions

- **Dispersion of Active Sites -** The active metal species are dispersed by the support material, increasing the quantity of exposed active sites. By dispersing the metal, the maximal surface area available for catalytic reactions is ensured. Example - (Al_2O_3) dispersed platinum nanoparticles give reactants a large platinum surface area on which to interact.
- **Adsorption and Activation of Reactants -** Reactants are absorbed by the support material and are thus brought in close contact with the active metal sites. Reactants can more easily be activated by this close proximity by interacting with the metal.
- **Electronic and Geometric Effects -** The active metal species' electrical characteristics can be changed by the support, increasing their reactivity.
- **Stabilization of Active Species -** By stabilizing the active metal species, the support material avoids deactivation and sintering (agglomeration). The catalyst's lifetime is increased and its activity is sustained by this stabilization. Example- Metal nanoparticles can be stabilized by carbon supports, which keeps them from clumping together and going inactive during high-temperature processes.

REACTIONS INVOLVED:

In light of their increased selectivity, activity, and stability, supported catalysts are frequently employed in a variety of oxidation processes.

- **Selective Oxidation of Alcohols**

Reaction: Alcohols are oxidized by supported metal catalysts to produce ketones or aldehydes.[x]

Catalyst Example: In mild circumstances, the oxidation of alcohols to their respective aldehydes is catalyzed by Au/TiO_2 (gold on titania).

- **Oxidation of Hydrocarbons**

Reaction: Acids, alcohols, and epoxides are the products of hydrocarbon oxidation.

Ex**:** Ethylene is converted to ethylene oxide via the catalytic action of vanadium pentoxide on titania,

- **Oxidation of Carbon Monoxide**

Reaction: A critical process in the reduction of pollution is the oxidation of carbon monoxide (CO) to carbon dioxide (CO_2).

Ex.: In catalytic converters, Pt/Al_2O_3 (platinum on alumina) is utilized to oxidize CO in automobile emissions.

- **Environmental Applications: Decomposition of Volatile Organic Compounds (VOCs)**

Reaction: By oxidizing to CO_2 and H_2O, VOCs lessen dangerous emissions.

Catalyst Example: Vapor-forming compounds (VOCs) including xylene and toluene are oxidized by palladium on silica, or Pd/SiO_2.

- **Water Oxidation for Hydrogen Production**

Reaction: One of the essential half-reactions in the water-splitting processes that produce hydrogen is the oxidation of water to produce oxygen.[xi]

Catalyst Example: In an electrolyzer, the oxygen evolution process (OER) is catalyzed by iridium oxide on titania, or IrO_2/TiO_2.

F. ENZYME-INSPIRED CATALYSTS:

Enzymes are nature's catalysts, exhibiting remarkable efficiency, specificity, and selectivity in biochemical reactions. Inspired by these biological catalysts, scientists have developed enzyme-inspired catalysts that mimic the structural and functional properties of enzymes using transition metals.[xii]

Fundamentals of Catalysts Inspired by Enzymes

- **Mimicry of Active Sites**

1) **Mimicry in Structure:** Metal ions mediated by organic ligands are frequently found in the active site of enzymes. Catalysts inspired by enzymes reproduce the catalytic capabilities by imitating this coordinating environment. Example: Using iron-porphyrin complexes to mimic the heme core of cytochrome P450 enzymes.

2) Functional Groups: Amino acids, carboxylates, and imidazoles are examples of functional groups that can be added to the ligand framework to replicate the secondary coordination sphere of enzymes.

- **Identification and Binding of Substances**

1) **Selective Binding:** Creating catalysts that have precise substrate binding locations, much to the lock-and-key paradigm of interactions between enzymes and substrates. An illustration would be transition metal complexes that bind particular organic molecules only when they have pocket-like structures.

2) **Induced Fit Mechanism:** Catalysts that, when they bind to a substrate, change their conformation, increasing their catalytic activity. One example would be ruthenium complexes whose shape is altered as they attach to organic substrates.

- **Catalytic Mechanisms**

1) **Redox Cycling:** Redox cycles, in which the transition metal switches between several oxidation states to promote oxidation processes, are the mechanism behind the operation of many catalysts inspired by enzymes. Manganese porphyrins that go through the Mn(II)/Mn(III)/Mn(IV) redox cycles are one example.

2) **Proton-Coupled Electron Transfer (PCET):** Mechanisms that resemble biological systems and include the transfer of protons and electrons. For instance, iron compounds that help PCET oxidize organic molecules.

Developing and Manufacturing Enzyme-Inspired Catalysts

In order to replicate the dynamic sites and processes of enzymes, transition metals, ligands, and coordination environments must be carefully chosen during the design and manufacture of enzyme-inspired catalysts.

- **Selection of Transition Metal**
- **Ligand Design**

1) **Porphyrins and Macrocycles:** Ligands that offer a strict, well-defined environment for coordination. Porphyrin-iron complexes for targeted oxidation, for example.

2) **Polypyridyl Ligands:** Ligands with adaptability and electrical property modulation capabilities. Ruthenium polypyridyl complexes, for example.

3) **Biomimetic Ligands:** Ligands that contain peptides, amino acids, and other compounds.

For instance, copper combines with mimics of histidine and cysteine.

- **Iron (Fe)**

Function in the Catalysis: Iron is a common material for catalysis because it is readily available, reasonably priced, and adaptable. There are several oxidation states of iron (Fe(II), Fe(III), Fe(IV), and Fe(V)), which allow for a range of redox processes.

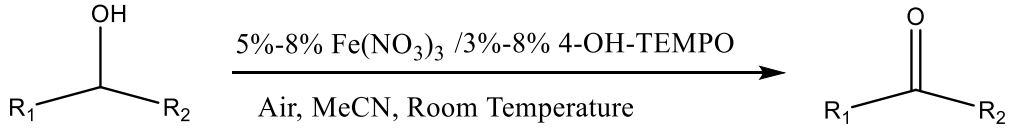
Reactions:

1) Oxidation of Alkanes: $RH + O_2 \rightarrow ROH$ (with iron-porphyrin catalyst)

2) Oxidation of Phenols: Phenol + $H_2O_2 \rightarrow$ Quinone + H_2O (with Fe(II) catalyst)

First Fe-catalysed system was reported by Martin and Suarez that used mixture of FeBr3 and $Fe(NO_3)_3$ and operated well in atmospheric air at room temperature. Secondary and benzylic alcohol were oxidised by this catalyst the yield was good and no other oxidation product were sensed in the reaction mixture.[xiii] Liang and co-workers stated that aerobic oxidation of alcohol catalysed by Fe as catalyst and $NaNO_2$/TEMPO as co-catalysts. The reaction used 5mol% FeCl3, 5mol% $NaNO_2$ and 2mol% TEMPO in trifluorotoluene (TFT) under air pressure and temperature. This system worked well for aromatic alcohols such as primary, secondary benzylic alcohol and cinnamyl alcohol shown very good reactivity but primary aliphatic alcohols displayed modest modest selectivity to form aldehyde morover both acid and ester are produced as byproducts. When 4-substituted TEMPOs are used instead of TEMPO variety of primary alcohol are efficiently oxidised to the corresponding aldehyde.[xiv]

For the aerobic oxidation of diversed primary and secondary alcohols researchers developed a catalytic system which is environment friendly, economical, easily accessible and safe to use. $Fe(NO_3)_3.9H_2O$ was employed as catalyst and 4-OH-TEMPO as co-catalyst in acetonitrile (CH_3CN) under ambient atmospheric pressure and temperature [xv] (scheme 5).



Scheme 5 $Fe(NO_3)_3$ /4-OH-TEMPO system is used as catalyst for alcohol oxidation

Epoxidation of various types of alkenes were done using Iron(3) oxamato complex along with 2-methylpropanal and molecular oxygen. This method is comfortably utilized for the conversion of olefinic alcohols into their equivalent epoxy alcohols.[xvi] Photocatalytic oxidation of cycloalkenes in presence of O2 and iron(3) porphyrin complexes was reported by Henning and co-workers.[xvii] It was observed that alkenes that have strained carbon-carbon double bonds prefer to make epoxides, on the other hand alkenes that have unstrained carbon-carbon double bond prefer to give allylic oxidation. Oxidative Dehydrogenation (ODH) of ethane by Iron phosphate phases at higher temperature in the range of 400 to 675˚C have also been studied. It was found that Iron catalyst having phosphorous and iron in the ratio of 1.2:1 can catalyse the

ODH of ethane more efficiently with more than 40% conversion along with 82% selectivity in 1atm pressure.[xviii] Evans and team studied thoroughly the oxidation of ethyl benzene with iron-haloporphyrins (solvent less system was required), in presence of O_2 at 30-110˚C.[xix] Murahashi and his team observed that oxidation of ethylbenzene can be done using powder of Fe, $FeCl_3$ and $Fe(OAc)_3$ along with n-heptanal and acetic acid.[xx] Intermediate for this system is proposed to be a high-valent iron-oxo species.

- **Copper (Cu)**

Function in the Catalysis: As copper can cycle between Cu (+1) and Cu (+2) oxidation states, it is frequently utilized in oxidation reactions. In the processes of electron transfer and oxygen activation, copper catalysts are especially useful.

Reactions:

1) Oxidation of Alcohols: $RCH_2OH + O_2 \rightarrow RCHO + H_2O$ (with CuCl catalyst)

2) Oxidation of Aromatic Amines: Aniline + O_2 → Azobenzene (with Cu(II) acetate catalyst)

- **Palladium (Pd):**Palladium is a very powerful catalyst for C-H oxidation and activation processes. It can facilitate a variety of changes by cycling between the Pd(0) and Pd(II) states. Mechanisms: **Pd(0)/Pd(II) Catalysis:** The oxidative addition and reductive elimination processes are frequently used in palladium catalysts.

$Pd(0) + R\text{-}X \rightarrow Pd(+2)\text{-}R + X^-$

Reactions:

1) **Wacker Process (Oxidation of Ethylene to Acetaldehyde):**

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl$$

Oxidation of Alkenes: Alkene + O_2 → Epoxide (with Pd(II) catalyst)

- **Manganese (Mn):**The ability of manganese catalysts to imitate the oxygen-evolving complex in photosynthesis makes them noteworthy. There are several oxidation states that manganese can cycle through: Mn(+2), Mn(+3), Mn(+4), and Mn(+5).

$Mn(III)\text{-}O^{\cdot} + R\text{-}H \rightarrow Mn(II) + R^{\cdot} + OH^-$

Reactions:

1) Oxidation of Alkenes: Alkene + $KMnO_4$ → Diol (with $KMnO_4$ as Mn catalyst)

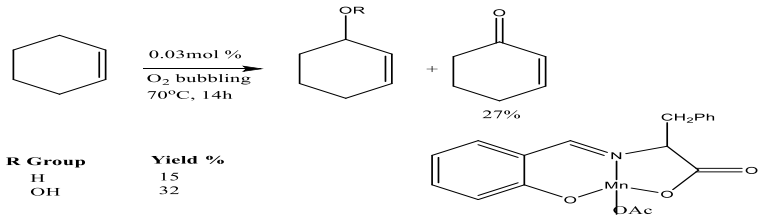
2) **Oxidation of Water (Oxygen Evolution Reaction):**

$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ (with Mn oxide catalyst)

Typically, it is found that catalytic activity depends on the smaller size of NPs, smaller the size of NPs, higher the catalytic activity in oxidation reaction, but these NPs are not stable and aggregate this reduce their stability and catalysing power.[xxii] This problem can be solved by immobilizing the dynamic species of NPs on solid supports. Xiang and co-workers observed that embellishment of MnO_2 NPs on Graphene oxide (GO) showed high catalysing power in oxidation of benzyl alcohol to benzaldehyde with air as oxidant.

Manganese (3) porphyrin complexes bound on silica support selectively help in catalyzing the oxidation phenomenon of alkyl substituted benzene to ketone. Manganese porphyrin complexes are synthesized by Ghiaci and co-workers by immobilization of catalyst on silica support.[xxiii] This catalyst is selective and efficient for oxidation of hydrocarbon as it possesses shape selectivity for substrate and matrix support which provide required atmosphere for C-H bond oxidation.[xxiv] Suib and co-workers observed solvent-free oxidation of toluene by preparation of gamma-MnO2 octahedral molecular sieves as catalyst for the reaction with molecular oxygen and resulted in 47% conversion, 57% selectivity for benzoic acid and 15% for benzaldehyde.[xxv] Chiral manganese Schiff base complex help in catalyzing the oxidation of cyclohexene to form cyclohexanol in combination of cyclohexanone, and cyclohexenyl hydroperoxide under atmospheric oxygen (scheme 6). [xxvi]

Various complexes of manganese could be used for the oxidation of unfunctionalized alkenes to produce corresponding alcohols in presence of molecular oxygen, $NaBH_4$ and $[NBu_4]BH_4$, formed product in this reaction is ketone then undergo reduction to alcohol in situ by an excess of borohydride.[xxvii] Hydration of α, β-unsaturated esters to α -hydroxy esters employing $Mn(dmp)_2$ was reported by Mukaiyama and co-workers with oxygen being their phenylsilane in 2-propanal.[xxviii]



SCHEME 6 Oxidation of Cyclohexene to corresponding oxidized forms

- **Ruthenium (Ru):**In oxidation reactions, ruthenium is incredibly useful and efficient, especially when it comes to promoting oxygen activation and hydrogen transfer. There are various oxidation states of ruthenium, ranging from Ru(0) to Ru(VIII).

Reactions:

- **Oxidation of Alcohols:** $RCH_2OH + RuCl_3 + NaIO_4 \rightarrow RCHO + RuCl_2 + NaIO_3 + H_2O$
- **Oxidation of Alkenes:** Alkene + $RuO_4 \rightarrow$ Diol (with RuO_4 as catalyst)

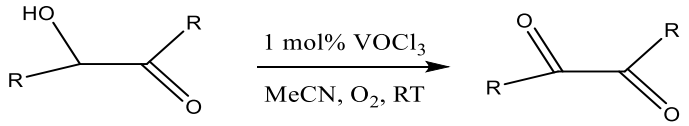
- **Vanadium (V):** As vanadium catalysts can create high-valent oxo species (e.g., VO_2^+, VO_4^{3-}), they are useful in oxidation processes. Both homogeneous and heterogeneous catalysis employ vanadium compounds.

Reactions:

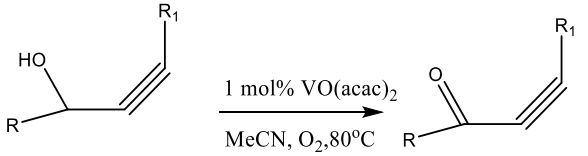
1) **Oxidation of Sulfides to Sulfoxides:** $R_2S + VO(acac)_2 + H_2O_2 \rightarrow R_2SO + H_2O + VO(acac)_2$
2) **Oxidation of Aromatics:** Benzene + $V_2O_5 + O_2 \rightarrow$ Phenol (with V_2O_5 catalyst)

Vanadium is used as catalyst in many Oxidation reactions like oxidation of several alpha-hydroxycarbonyl compounds, oxidation of aryl, vinyl and aliphatic Propargyl alcohols, oxidative kinetics resolution (OKR) of alpha-hydroxy esters, phosphonates and amides. Vanadium have got usage in epoxidation of alkene, allylic oxidation of isophorone using polyoxometalates.

In starting studies vanadium catalyzed Oxidation reaction were limited to α-hydroxyl carbonyl compound and propargylic alcohols [xxix] (Scheme 1 and 2), for oxidation of α-hydroxycarbonyl compounds 1 mol% $VOCl_3$ in acetonitrile at ambient temperature is used [xxx] whereas for oxidizing propargylic alcohols, 1 mol% $VO(acac)_2$ in acetonitrile at slightly higher temperature (80°C) is used [xxxi]

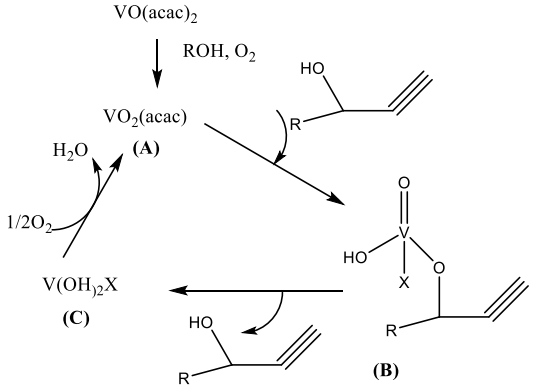


Scheme 7: Vanadium complexes Catalysed aerobic oxidation of α-hydoxycarbonyls



Scheme 8: $VO(acac)_2$ catalyzed oxidation of propargylic alcohols to corresponding ketones

Detailed study of the mechanism of reaction represented evidences that V(+5) is catalytically dynamic species in oxidation.[xxxii] Proposed mechanism involve preliminary oxidation of V(+4) to V(+5) by molecular oxygen then alcohol attack to form an intermediate V-alkoxide species (Scheme 9), followed by exclusion of alkoxide to give desirable product and V(+3) species, this V(+3) will again be oxidised to form active V(+5) catalyst.[xxxiii]



SCHEME 9 Mechanism for Vanadium complex-catalyzed oxidation of propargylic alcohols.

Jiang and Ragauskas proposed an environmentally benign procedure for vanadium catalyzed Oxidation procedure, they found that the mixture of $VO(acac)_2$ complex and 1,4-diazabicyclo(2,2.2)octane (DABCO) in ionic liquid (IL) at 80-100˚C catalyse the oxidation process between benzylic and allylic alcohols.[xxxiv] Velusamy and Punniyamurphy explored the scope to broaden the horizon of oxidation to allylic, benzylic, and aliphatic alcohols used V_2O_5(5mol%) as the catalyst,[xxxv] requirement of the reaction is half equivalent of K_2CO_3 in toluene (best alternative of benzene) as solvent at 375 K.

- **Platinum (Pt):** In oxidation reactions, platinum is frequently utilized, especially in industrial processes and catalytic converters. Platinum has the ability to promote both oxygen reduction and C-H activation.

Reactions:

- **Oxidation of Carbon Monoxide to Carbon dioxide:** $CO + O_2 \rightarrow CO_2$ (with Pt catalyst)
- **Hydrocarbon Oxidation:** Hydrocarbon + $O_2 \rightarrow CO_2 + H_2O$ (with Pt catalyst in catalytic converters)
- **Nickel (Ni)**

Reactions:

- **Oxidation of Alkenes:** Alkene + $NiO_2 \rightarrow$ Epoxide (with NiO_2 as catalyst)
- **Oxidation of Alcohols:** $RCH_2OH + Ni(OH)_2 \rightarrow RCHO + Ni(OH)_2$

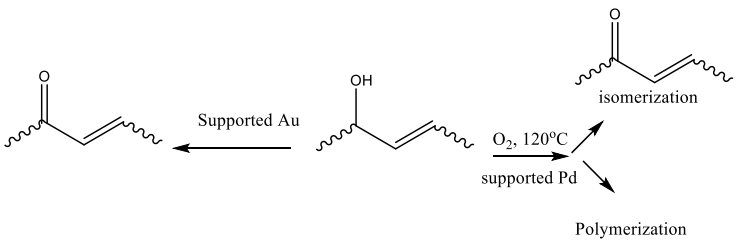
Titanium (Ti): Titanium Oxide (TiO2) is used in Epoxidation of Alkene and its Nanoparticles are used as Photocatalyst. TiO2 is generally exploited for its photochemical applications where TiO2 can be optimally used for the degradation of various inorganic and organic pollutants, light induced organic transformations and production of hydrogen gas by water splitting.[xxxvi] The catalyst is said to be most effective when it have Silica zeolite modified with Titanium, having Si\Al ratio of 1900.[xxxvii]

Gold (Au): For a very long duration, Gold has been a noble metal; then it was proved that it has high catalytic activity, its profound catalytic presentation is greatly managed by controlling size of particle and selecting supporting metal oxide. Rossi, Prati and co-worker were the first team to clearly validate that gold nanoparticles supported on scaffolders can be very efficient catalytic system for oxidation of alcohols.[xxxviii] Au-SiO_2 catalytic system is effective when

gaseous reactants are taken and as such there is no need to add base in it.[xxxix] Hutchings his team demonstrated that when Au is braced on graphite, this system has a capability to oxidise glycerol to glycerate selectively, dioxygen was used as the oxidant in water and yield was found to be approximately 60%. It was noted that the selectivity to form glyceric acid form the conversion of glycerol were dependent on the concentration of glycerol and NaOH.[xl]

Deposition of gold on bare TiO_2, TS-1, Ti-Beta TiO_2/SiO_2, and Ti-MCM-48 in highly dispersed form the dispersed particles will be hemispherical and nanosized having diameter 2.0-4.0 nm, when used as catalyst it results in corresponding oxide having selectivitiy >90% and conversion upto 9.8% in the temperature range from 30˚C to 160˚C [xli-xlii] when $Au/TiO_2/SiO_2$ catalyst is modified via Platinum, it showed marvelous results for the epoxidation of Propene in term of activity as well as selectivity. When Platinum is incorporated with $Au/TiO_2/SiO_2$ catalyst the ratio of water-propene oxide decreases whereas activity of epoxidation remains unchanged. Hydrogenation of Propene does not lead to formation of unwanted Propane below temperature of 100˚C [xliii]. Cyclohexane is oxidized to give a mixture of corresponding oxides i.e. cyclohexanol and cyclohexanone when treated with calcinated Au/ZSM-5 molecular sieve along with atmospheric oxygen [xliv] having 92% selectivity and conversion up to 16%.

Corma and his team observed that Au/CeO_2 catalytic system oxidize alcohols to corresponding aldehydes and ketones, this is a significant advancement in the area of oxidation of alcohols.[xlv] In these reactions the catalyst is active in solvent-free conditions, it uses molecular oxygen as oxidant and do not require addition of base to get high activity. When compared with Pd gold present unique selectivity for oxidation of allylic alcohols.[xlvi]



Scheme 10: oxidation of allylic alcohols using Au catalytic system

Rossi and the team found that "naked" gold colloidal particles dispered by water act as an efficient catalyst to oxidise Glucose to Gluconic acid.[xlvii]

COPPER (Cu): The first copper catalysed aerobic oxidation of alcohols was reported by Semmelhack in 1984 using combination of copper with the firm nitroxyl radicle from TEMPO (2,2,6,6-tetramethyl-1-piperidine-N-oxyl) having Dimethy Formamide as solvent (DMF), but this system has a limitation that it worked well with primary alcohol in activated form only.[xlviii] Neckers and Kurusu reported that the oxidation of cyclohexane can be achieved through the copper complex immobilised on silica gel in company of acetic acid and zinc powder with molecular oxygen to give mixture of both cyclohexanol and cyclohexanone, this reaction have conversion of 4.3% [xlix]. Marko and team did significant development of catalytic system, in their study CuCl (5mol%) in combination with di-tert-butylazodicarboxylate, (5mol%) DBAD and (5mol%) phenantroline resulted in oxidation of alcohols without affecting other functional group present along. typically 2 equivalents of base (K_2CO_3) is required along with this system and is not found to be much suitable for oxidation reaction of primary aliphatic alcohols.[l] This elementary condition is useful for oxidation of alcohols having alpha-stereo genic centres into product with no racemisation. Shul 'pin and co-workers observed that combination of cyclohexanol and cyclohexanone is obtained into 50:1 by oxidation of cyclohexane using quinone and $Cu(OAc)_2$ complex (ratio5:1) in CH_3CN with air and triphenylphosphine under light.[li]

Copper(I) Chloride is employed for oxidation product phenol from benzene in presence of oxygen, hydroxy radicle is proposed to generate active species, the reaction is said to proceed via reduction of the catalyst from Cu(II) to Cu(I) in presence of H_2 and palladium as cocatalyst.[lii] Enantioselective Baeyer-Villiger oxidation of various cyclic ketones is reported by Bolm and coworkers employing copper complex with pivalaldehyde and O_2. In presence of 1mol% of copper complex oxidation of racemic 2-phenylcyclohexanone takes place into optically active Lactone with 41% yield, S configuration is shown by the left unreacted ketone. For the above reaction the finest result is obtained in the solution of benzene at optimum range of temperature.[liii] Underived cyclohexanones exhibit limited scope for this reactionb, optically active lactone can only be given by 2-aryl-substituted compounds.

COBALT (Co): First Co-catalyzed oxidation of alcohols was observed by Tovrog and his team using Co-nitro complexes in 1981.[liv] Since then several studies have been conducted but unfortunately many of them have some drawbacks like attaining optimum temperature, sacrificial reagents or some additives like bases. Epoxidation of alkene is catalyzed by Cobalt(2) complexes having beta-diketone ligands along with electron donating units in the company of 2-methylpropanal and diethyl acetal.[lv] Aerobic epoxidation of alkene is done by incorporating solid supported cobalt catalyst and polymer in presence of aldehydes. Blay and-coworkers explored a system which contain o-phenylelebis(N-methyloxamidate) cobalt(3) complex and pivaldehyde, this system help in competent translation of ˚propargylic alcohols to suitable α,β-acetylenic carbonyl compounds (yn-ones).[lvi]

G. TRANSITION METAL OXIDES (TMOs) AS CATALYST

One of the most significant constituents in technology is transition metal oxides (TMOs), which have a variety of uses in the chemical processes, energy storage devices, and electronics sectors. TMOs can be utilized as catalytic agents in various industries. Transformation of feedstock into useful chemicals, actuators, and sensors.[lvii] Surface functionalization and compositional changes allow for the fine tuning of TMO surface characteristics, such as acidity, basicity, and redox behavior. These adjustable surface characteristics are crucial for controlling stability, selectivity, and catalytic activity. TMOs as supports offer a number of benefits, particularly for catalytic uses.[lviii] They are the best options for high-temperature catalytic processes because of their resistance to sintering, chemical resilience, and thermal stability.[lix]

2. ***Creation and description of TMOs***

Based on pore size, materials made up of porous metal oxide are divided into three major classes:

1. Macro-porous (pore diameter greater than 50 nm)
2. Meso-porous (pore diameter between 2 and 5 nm)
3. Micro-porous (pore diameter less than 2 nm).[lx]

Mobil Corporation's groundbreaking work on meso-porous materials paved the way for a great deal of study on the preparation and application of porous TMOs. Because of their large surface areas and enhanced mass transfer in the interior of the pores, nano-size mixed valent meso-porous oxides have pinched a lot of attention in the fields of adsorption, electrochemistry, and catalysis.[lxi]

It is crucial to have adequate regualte on variables like temperature, pH, type of surfactant involved, solvents, precursors, scalability solubility in the reaction matrix, time to finish reaction, and so on when designing any specific porous materials based on the method involved in the synthesis (either top-down or bottom-up approach) and anticipated product.[lxii]

The pore diameters of TMOs have an impact on surface reactions. When meso-porous materials are constrained by a lower pore size, macro-porous arrangements can provide improved mass transference of reactants to the dynamic positions of porous TMOs.[lxiii]

The mixed valent states and tunnel architectures of octahedral molecular sieves (OMS), make them ideal for better redox chemistry. A quick and easy solvent-free mechanochemical nanocasting method was used to create mesoporous TMOs of Zr, Fe, Cu and Co [lxiv].

Current Catalyst Systems for Transition-Metal Catalyzed Oxidation Reactions: Limitations and Challenges

Transition-metal catalysts, which provide increased efficiency and selectivity, have completely changed oxidation reactions. These methods do, however, also have several downsides and difficulties that perimeter their wider use and effectiveness.

- **Catalyst Deactivation**

1) Mechanisms of Deactivation

Leaching: A reduction in catalytic activity caused by the release of active metal species from the support into the reaction media.

Ex: Wacker oxidation of ethylene to acetaldehyde involves palladium leaching.

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl$$

Poisoning: The catalyst becoming inactive as a result of contaminants or reaction byproducts adhering to its active areas.

Ex: Sulfur poisoning in platinum catalysts used to oxidize hydrocarbons.

Hydrocarbon + O_2 → CO_2 + H_2O (with Pt catalyst; deactivation by sulfur compounds)

2) Structural Changes

Sintering: High-temperature metal nanoparticle aggregation, which decreases the active sites and surface area.

Ex: When methane oxidizes, nickel particles sinter.

CH_4 + O_2 → CO_2 + H_2O (with Ni catalyst; deactivation by sintering)

Phase Change: Under reaction conditions, the conversion of the active catalyst phase into an inactive form.

Ex: CuO to Cu_2O transition during methanol oxidation

CH_3OH + O_2 → HCHO + H_2O (with CuO catalyst; phase change to Cu_2O)

3) Solutions to Deactivation

Stabilization Strategies: Adjusting supports or using promoters to stop leaching and poisoning.

Ex: To improve stability against leaching in oxidation reactions, dope Pd catalysts with gold.

Nano-structuring and Alloying: Creating catalysts using metal alloys or stable nanostructures to stop phase shifts and sintering.

Ex: Bimetallic Pt-Ni catalysts, are used to oxidize hydrocarbons steadily.

- **Selectivity Issues**

Over-Oxidation: The challenge lies in selectively oxidizing substrates without excessively oxidizing them to produce unwanted compounds.

Ex: The oxidation of alcohols to ketones or aldehydes without letting further oxidation to carboxylic acids.

RCH_2OH + O_2 → RCHO + H_2O (with Ru catalyst; risk of over-oxidation to RCOOH)

By-Product Formation: Creation of byproducts that hinder product purification and lower yield.

Ex: When alkenes oxidize to epoxides, side products are formed.

Alkene + O_2 → Epoxide (with TiO_2 catalyst; by-products include diols and aldehydes)

- **Solutions to Selectivity Issues**

Ligand Design: Ligands have been tailored to regulate the steric and electrical milieu surrounding the metal core.
Ex: large phosphine ligands in palladium catalysts to improve alcohol oxidation selectivity.
Reaction Condition Optimization: Adjusting reaction parameters like solvent, pressure, and temperature precisely to support the intended pathway.
Ex: To improve selectivity in alkene oxidation, lower the temperature and use particular solvents.

- **Scalability and Cost**

Precious Metal Catalysts: Expensive and scarce precious metals such as ruthenium, palladium, and platinum.
Ex: Pt catalysts in catalytic converters for the oxidation of hydrocarbons are quite expensive.
Hydrocarbon + O_2 → CO_2 + H_2O (with Pt catalyst; cost limitation)
Scalability of Synthesis: Difficulties in increasing the synthesis of complex catalysts while preserving their activity and homogeneity.
Example: the challenges associated with increasing the manufacturing of supported metal nanoparticles for use in industry.

- **Solutions to Scalability and Cost Issues**

Earth-Abundant Metals: Creating catalysts using cheap, readily available metals such as nickel, copper, and iron.
Ex: iron-porphyrin complexes that selectively oxidize hydrocarbons.
Hydrocarbon + O_2 → Alcohol/Ketone (with Fe-porphyrin catalyst; cost-effective)
Efficient Synthesis Methods: Developing synthetic methods to create catalysts that operate consistently at scale.
Ex: scalable nanofabrication techniques and sol-gel procedures can be used to produce catalysts.

- **Environmental and Safety Concerns**

Toxicity and Hazardous By-Products: Possible toxicity of catalysts made of transition metals and the production of dangerous byproducts.
Ex: the toxicity of catalysts based on chromium in industrial oxidation processes.
Diverse oxidation processes using Cr catalysts: issues with the environment and human health
Handling and Disposal: Difficulties in managing spent catalysts and reaction byproducts safely and properly.

Conclusion:

Transition-metal catalysts have emerged as essential tools in facilitating selective and efficient oxidation reactions. Their unique electronic properties and ability to participate in redox cycles enable a wide variety of oxidative transformations, ranging from alcohol oxidation to hydrocarbon functionalization. Both homogeneous and heterogeneous systems, along with nanoscale and bioinspired catalysts, have significantly contributed to advancements in sustainable chemical processes. Despite their widespread applicability, challenges such as high cost, limited recyclability, and environmental concerns associated with certain metals continue to prompt the search for greener alternatives.

Future Perspectives:

Looking ahead, the development of eco-friendly and economically viable catalysts remains a primary research focus. The use of earth-abundant metals, recyclable catalytic systems, and non-toxic oxidants like molecular oxygen and hydrogen peroxide is expected to drive innovation. Moreover, interdisciplinary approaches integrating nanotechnology, computational modeling, and green chemistry principles can lead to the discovery of next-generation catalysts with enhanced activity, selectivity, and durability. Expanding the scope of catalytic oxidation in industrial and environmental applications will also require addressing scalability and

regulatory aspects, ensuring these technologies are both practical and sustainable for long-term implementation**.**

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