REVIEW

Supported Transition Metal Catalysts for Organic Fine Chemical Synthesis: A Review

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Transition metal catalysts play an important role for synthesis of industrially and laboratory important organic fine chemicals to control the selectivity, activity and stability. In this review, we focus on mainly transition metal based supported catalyst, mainly oxide supported catalyst for heterogeneous catalytic hydrogenation and oxidation of some synthetically important organic molecules. First we discuss the industrially important catalytic organic synthetic reactions. This is followed by the role of supported metal catalysts in the heterogeneous synthetic catalytic reactions with specific attention to hydrogenation and oxidation of organic molecules. The role of base metals and noble metals in monometallic and bimetallic catalysts are then discussed. Some synthetic routes for preparation of oxide supported metal catalysts are also discussed. Finally, a general discussion of the metal-support interaction (MSI) in oxide supported metal catalysts is made.

Keywords: Heterogeneous catalyst, Transition metal, Oxidation, Hydrogenation, Important organic molecules.

INTRODUCTION

A chemical industry is in need of technology having maximum activity as well as selectivity towards organic synthetic reactions. Similarly, the requirement is also to adopt "clean" chemical processes having minimum impact on the environment. Hydrogenation and oxidation of organic functional group with high activity and selectivity is one of such requirement. Heterogeneous catalysis plays an important role in wide variety of industrial processes. The most important synthetic use of heterogeneous catalysts are for common synthetic organic transformation. The heterogeneous catalysts can be either oxides [1-6] or metals [7-11]. Most synthetically useful catalytic processes are run over metal catalysts [10-12]. The metal catalyst can be composed of a single metallic component or a mixture of metals [12]. Either of these types can be supported or unsupported. Metal catalysts are used primarily for hydrogenation, hydrogenolysis, isomerization and oxidation reactions, *etc.* [13-16].

The catalytic activity of dispersed metals on an oxide support is influenced by a number of factors. These include size, shape, extent of dispersion, relative amount of metals present, chemical nature of support and strength of interaction between the support and metal [17]. A support can alter the behaviour of metal in a number of ways. Several explanations have been given to understand enhanced activity of metal doped oxide supported catalysts [18]. They are easily prepared and can be characterized without too many difficulties. Due to this, metal catalysts are generally preferred for basic research. The active catalytic species is believed to be finely dispersed metal particles of sizes in the nano region. Lots of research works have been done on metal-support interaction in supported metal catalysts. Yet the exact nature of active site and the exact role of the support in terms of metal-support interaction are less understood.

Synthetically important organic reaction: Organic synthesis is a key step for the preparation of fine chemicals, pharmaceuticals, agrochemicals, food additives, dyes and pigments. An important factor in developing synthetic reactions is choosing the reaction route to the final product. Catalytic routes have been proven to be one of the most effective ways in simplifying the reaction routes to these compounds by increasing selectivity and reducing waste and hazardous materials handling [19-21]. Additionally, reactions should proceed under mild conditions to reduce the costs of energy. The ultimate aim is of course to adopt a green synthetic route for organic transformations. In

this context, good catalyst performance can be characterized by: (i) high activity and selectivity; (ii) little or no alteration of activity and selectivity with time; (iii) low sensitivity of activity and selectivity to contaminant in the feedstock; and (iv) favourable separation properties.

Organic synthetic chemists are in search of more active, selective and environmentally benign catalyst for their synthesis applications. Alkylation or arylation of aromatic or aliphatic, dehydrogenation, dehydration, hydrogenation, selective oxidation and isomerization are important organic synthesis reactions. A number of new precious catalysts are used for this type of synthetic reactions [22-24].

The alkylation of aromatic compounds is extensively used in the synthesis of various intermediates, fine chemicals and petrochemicals [25]. The necessary feature of this reaction is the replacement of the hydrogen atom of aromatic compound containing alkyl group derived using an alkylating agent. If acid catalyst is used, a replacement occurs in the aromatic ring and base catalyst replaced at side chain of the ring [26]. The commercial alkylations are acid catalyzed [25,27,28]. These include acidic halides such as $AlCl_3$, BF_3, acidic oxides, HF, H_2SO_4 [27], H_3PO_4 and zeolites [28]. The intramolecular isomeri-zation and the transfer alkyl groups between aromatic molecules are also catalyzed by acid catalysts [29-31].

Dehydrogenation of aromatic hydrocarbons (ethylbenzene, diethylbenzene) and alcohols are also industrially important. The ethylbenzene dehydrogenation (EBDH) products are styrene and H_2 [32,33]. Iron oxide is mainly used as a catalyst for the production of styrene [32]. The incorporation of V, Ce and Mo improved the catalytic properties of iron oxide [34]. Catalytic

dehydrogenation of primary and secondary alcohols gives corresponding aldehydes and ketones [34,35]. A large number of solid metal oxide catalysts have been effectively used for alcohol dehydrogenation [36,37]. Most of the oxide catalysts posses also dehydration activity and in some of them, such as alumina, the dehydration predominates [35]. The ratio of the dehydration and dehydrogenation depends on catalyst preparation and its purity. However, some exhibit only dehydrogenation activity, such as oxides of copper, zinc, chromium, iron, *etc.* [36-40]. Metals are also used as dehydrogenation catalysts. Copper is used most frequently, while silver is applied in the combined dehydrogenation-oxidative dehydrogenation processes for production of formaldehyde from methanol or acetaldehyde from ethanol. Noble metals Pt, Pd, Ru, Ir can also be used as oxidative-dehydrogenation catalysts [41-43].

Hydrogenation is the addition of H_2 molecule to a multiple bond (C=C, C≡C, C=O, C=N, C≡N, N=O, N=N, N≡N, *etc.*) to reduce it to a lower bond order (Fig. 1). Catalysts are required for the reaction to be usable as the non-catalytic hydrogenation takes place only at very high temperatures.

Platinum, rhodium, palladium and ruthenium form various highly active catalysts and operate at low hydrogen pressures and low temperatures [44-46]. Moreover, inexpensive metal catalysts, based on nickel (such as Raney nickel [47,48] and Urushibara nickel [49]) are established as economical alternatives for expensive catalysts. However, they often provide slow catalysis or operate at high temperatures. Two broad families of catalysts, homogeneous and heterogeneous, are simultaneously important for catalytic hydrogenation. The rhodium based Wilkinson's catalyst and the iridium based Crabtree's homo-
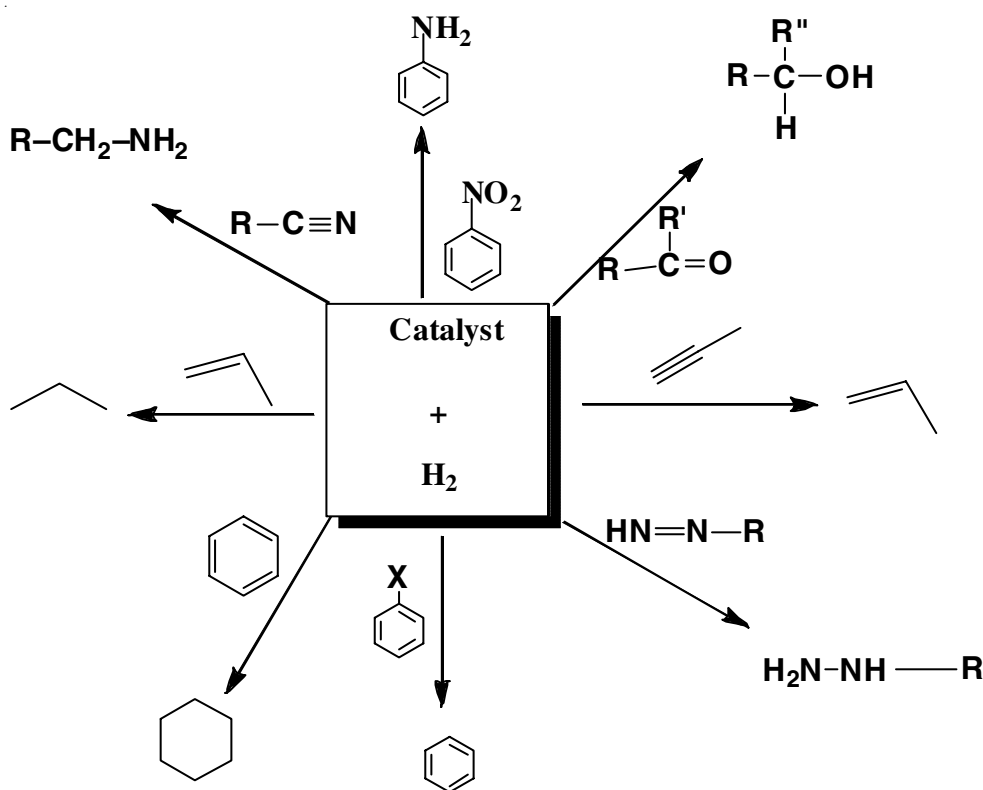

Fig. 1. Common hydrogenation reactions

geneous catalyst are exclusively used as hydrogenation catalyst [50-53].

Heterogeneous catalysts for hydrogenation are more common in industrial synthetic reactions. As in homogeneous catalysts, the activity of the catalyst is adjusted through changes in the environment around the metal, *i.e.* coordination sphere. Different faces of a crystalline heterogeneous catalyst show distinct activities. Similarly, the activity of the heterogeneous catalysts are affected by their supports, *i.e.* the material on which the heterogeneous catalyst is bound [53,54]. A number of new precious catalysts such as Pd/C [55], Pt/C [56] and immobilized Rh [57] catalyst have been successfully commercialized in recent years.

Selective oxidation of functional group is another industrially important catalytic reaction (Fig. 2). Catalytic oxidation in the liquid phase is widely used in bulk chemicals manufacture [58] and become increasingly important in the synthesis of fine chemicals.

A traditional process involving stoichiometric inorganic oxidants is receiving increasing environmental pressure [59]. Generally, in the liquid phase, catalytic oxidation employs soluble complexes or metal salts combined with inexpensive and clean oxidants such O_2, H_2O_2, or RO_2H [20,21].

However, compared with their homogeneous counterparts, heterogeneous catalysts present the advantage of facile recycling and recovering. Large-scale selective oxidation is based on heterogeneous metallic catalysts. Silver is exclusively used as an epoxidation catalyst for the production of ethylene epoxide from ethylene. Palladium is used as oxidative coupling catalyst for the production of vinyl acetate from ethylene and acetic acid. Cu, V, Mn, Ru, *etc.* are also used as oxidation catalysts for the cycloalkanes, cycloalkenes, benzene and benzyl alcohol [26,60-62].

Common organic hydrogenation reactions: The most common use of catalysts in organic synthesis is the hydrogenation of functional groups. The number of books and reviews published in this area underscores the synthetic importance of these reactions [63-66]. Hydrogenation is commonly a chemical reaction between molecular hydrogen (H_2) and another compound or element, usually in the presence of a catalyst. Hydrogenation of organic functional groups can be categorized into (a) addition of hydrogen across single bonds leading to cleavage of functional groups (hydrogenolysis), (b) addition of hydrogen to unsaturated groups as, for example, in the hydrogenation of ketone to alcohol and (c) removal of oxygen by hydrogen, for example, aromatic nitro to aniline (Fig. 3). Alkenes, alkynes, aromatics, heteroaromatics, ethers, ketones, esters, acids and amides can all be hydrogenated to industrially or synthetically important chemicals.

Catalytic hydrogenation can either be heterogeneous or homogeneous. Metal salts and complexes have provided some homogeneous hydrogenating agents [67-70]. The major disadvantage of the large-scale utilization of metal salts and complexes is their high cost. Due to the inefficient and stoichiometric nature of reactions, for hydrogenation, large quantities of metals or metal salts are required. Furthermore, separating products
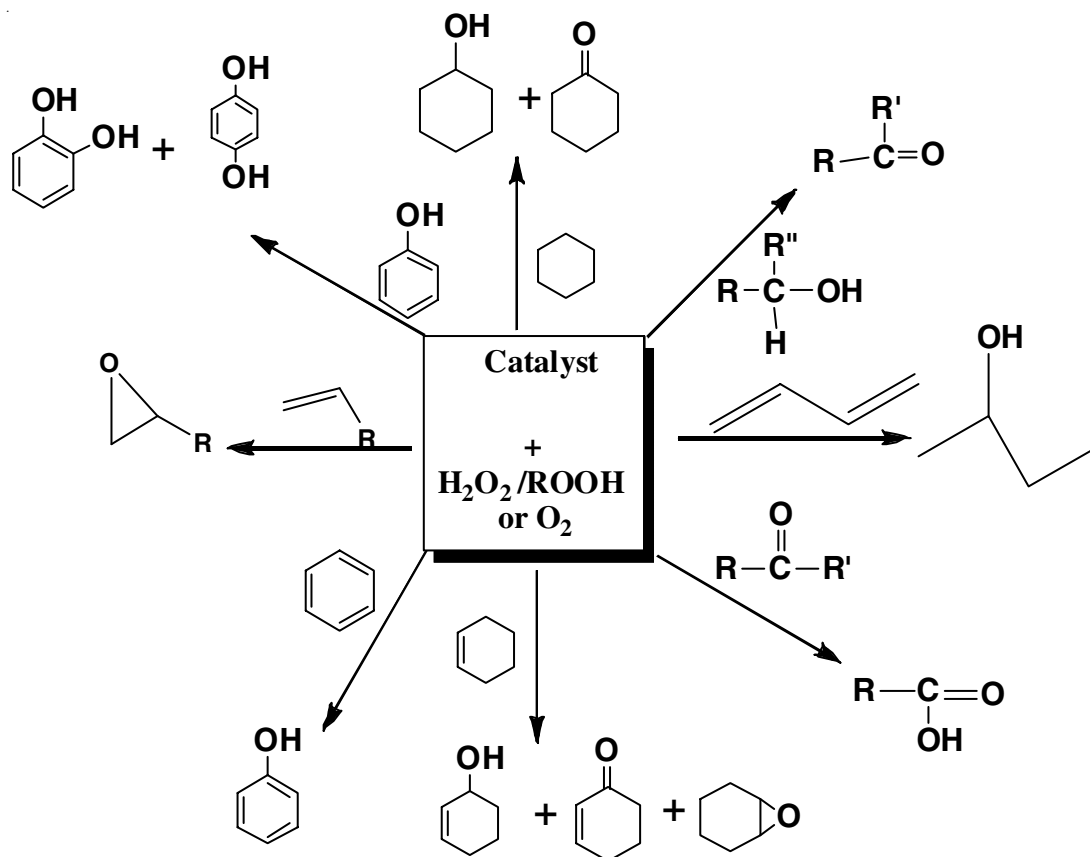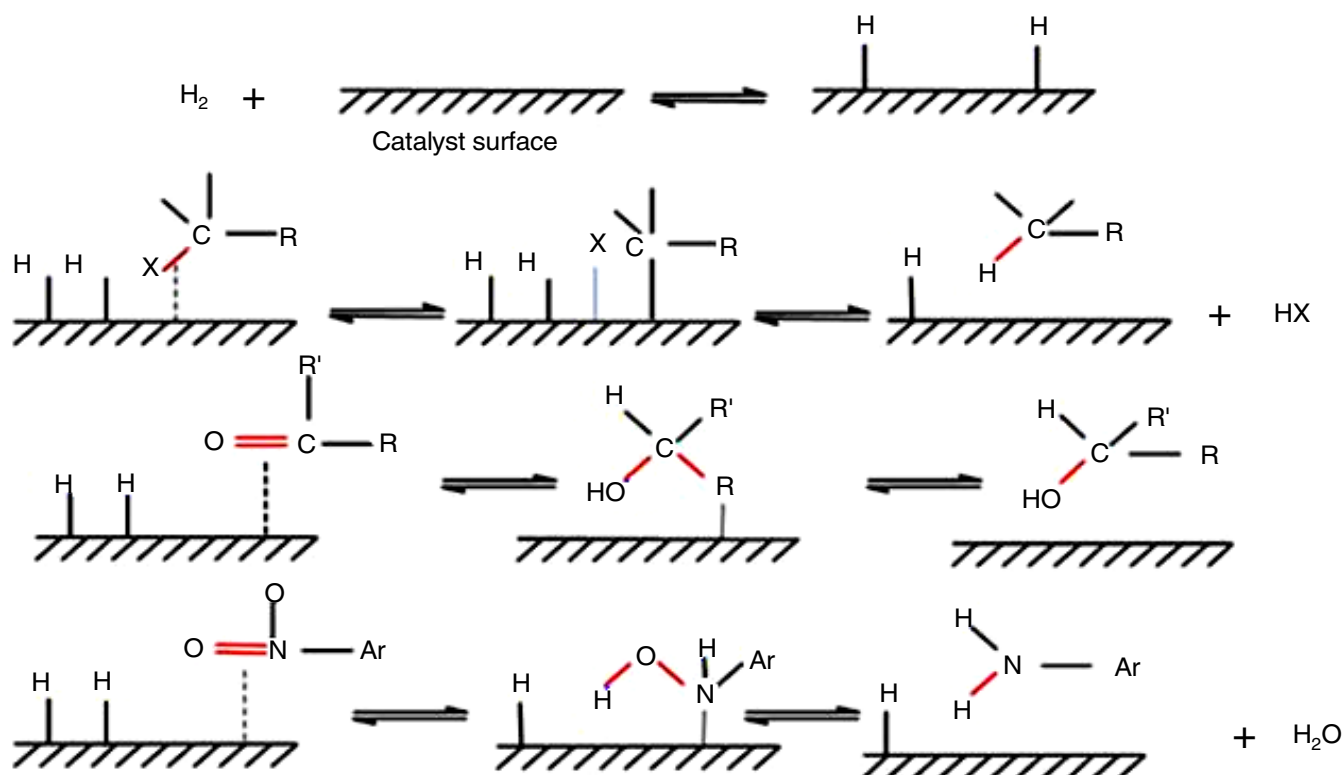

Fig. 2. Common oxidation reactions

Fig. 3. Catalytic hydrogenation of organic functional groups *via* (a) hydrogenolysis, (b) hydrogen addition and (c) oxygen removal by hydrogen [R, R′ = alkyl group; Ar = Aryl group and X = halogen]

from large volumes of metal complex or salt solutions can be inefficient and laborious. These disadvantages can be eliminated by using supported or unsupported heterogeneous metal catalysts, which leads to the easily separation of products and catalysts from reaction mixtures.

Metal-based catalysts are the most active for heterogeneous transfer hydrogenation. Palladium is highly active for the hydrogenation of alkynes or alkenes into alkanes and most commonly used catalyst for hydrogenolyses (benzylic and allylic C=O and C=N bonds, carbon-halogen and het=het, where het = N,O). For the hydrogenation of double bonds (C=N, C=C, and C=O), platinum is highly active [71,72]. When Pt is used, hydrogenolysis does not occur [17]. Under mild conditions, rhodium based catalysts are employed for the hydrogenation of aromatic compounds [73]. By contrast, at high pressures and temperatures, ruthenium usually is employed for the hydrogenation of carbonyl functional groups and aromatic compounds. Nickel, especially Raney nickel, is suitable for the hydrogenation of nitriles to amines and carbonyl groups (ketones and aldehydes) [74]. Under rather harsh conditions, copper-based catalysts are utilized in the hydrogenation of esters into the corresponding alcohols [75].

The catalytic activity of metals depends mainly on three factors (i) catalyst selection, (ii) reaction medium, (ii) reaction condition [76]. The order of the influence of these factors on selectivity is, in general, catalyst > reaction medium > reaction conditions. Catalyst selection depends on metal selection, chemical compassion of support, catalyst particle size, particle morphology and oxidation state of metal. The metal influences both the characteristic adsorption/desorption and the surface

reaction. So a right choice of metal is very important for an efficient catalytic reaction. Supports interact with the metal, which influences its structural (morphology and size) and electronic properties, thereby results a lot the catalytic reactions. The rate of the hydrogenation reaction depends on metal particle size and shape or morphology. The smaller the particles, the larger the surface area and thus the activity increase. The catalytic hydrogenation reactions are mainly run in liquid solvent medium. The solvent polarity and hydrogen adsorption capacity and acidity of the medium influence the catalytic reactions. The activity can also depend on the reaction temperature and pressure.
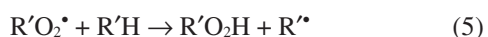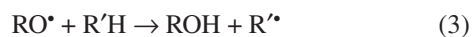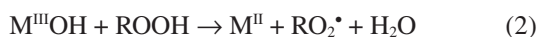
Metal catalysts can be finely divided, pure bulk metal, a skeletal or porous type (Raney Ni), nanoparticles and metals dispersed on different supports or carriers such as inorganic oxides ($BaSO_4$, $CaCO_3$, SiO_2 and Al_2O_3), carbon (charcoal), polymer, asbestos and zeolites. Some variations found in the metal catalytic activity in supported and free finely divided (blacks) forms results from various ageing treatments and preparation methods. Finely divided metals forms are prone to agglomeration, and in the long run, lose the catalytic activity. This agglomeration can even be accelerated through substrate action or substrate polymerization onto catalysts [77]. Metal precipitation on the support surface is advantageous because it results in a more uniform cluster or particle size of atoms than unsupported metals do and because it provides a large active surface area for the given metal mass (high specific surface density). Metal nanoparticles supported on mesoporous silicas [78,79], hydroxylapatites [80], porous carbons [81,82], zeolite [83], alumina [84] and titanium oxides [85] have been reported

to be highly active for various hydrogenation reactions. The direct synthesis of nanoparticles is limited and preparatory procedures are difficult. So supported metal catalysts are useful for hydrogenation reactions.

Hydrogenation of molecules containing single functional group is a common synthetic transformation. The selective hydrogenation of one functional group in presence of other groups is very important for the synthesis of industrially important chemicals. But if the functional groups have relatively similar or close activities, selectivity can sometimes be achieved by manipulating reaction condition or using proper catalysts. Therefore, recent research effort has been focused strongly on maximizing the catalytic efficiency of the precious metal catalyst by optimizing their physico-chemical properties [86,87], forming alloy structures [72], developing new catalyst supports [88], adding promoters [89,90] and modifying the metal-support interactions [91]. Both heterogeneous [92] and homogeneous metal catalysts [93] have been used in hydrogenation reactions for several decades.

Common organic oxidation reaction: Like hydrogenation, the oxidation of organic functional groups is an important synthetic reaction [58,59]. Most oxidation reactions are run using inorganic oxidants such as permanganate and chromium oxide. The disposal of their reduction products is environmentally unacceptable [20,21]. In the manufacture of bulk chemicals, catalytic oxidation has become very important due to its low impact on the environment. The conversions of alkenes, alkanes, alcohols, ketones, epoxides and aromatic compounds into the more valuable oxygen containing materials are important synthetic reactions in industries [58-62].

Many reactions are run either in vapour phase or in liquid phase and the reaction conditions are usually specific for the production of specific products. Various new catalytic systems have been developed for the oxidation in gas phase and in liquid phase using organic peroxides, H_2O_2 or O_2 as an oxidant [81-83]. The catalytic oxidation reactions are run either by free radical auto-oxidation process or by oxygen transfer process. One-electron oxidants, *e.g.*, Cu(II), Mn(III), Co(III), Ce(IV), Fe(III), *etc.* catalyze free radical auto-oxidation processes by promoting the decomposition of alkyl hydroperoxides into chain initiating alkoxy and alkyl peroxy radicals in one-electron transfer processes (**Scheme-I**, reactions 1 and 2). Strictly speaking the metal ion acts as an initiator of free radical auto-oxidation, which proceeds further *via* reactions 3-5, which does not involve the catalytic species.

$$ROOH + M^{II} \rightarrow M^{III}(OH) + RO^{\bullet} \qquad (1)$$

$$M^{III}OH + ROOH \rightarrow M^{II} + RO_2^{\bullet} + H_2O \qquad (2)$$

$$RO^{\bullet} + R'H \rightarrow ROH + R''^{\bullet} \qquad (3)$$

$$R''^{\bullet} + O_2 \rightarrow R'O_2^{\bullet} \qquad (4)$$

$$R'O_2^{\bullet} + R'H \rightarrow R'O_2H + R''^{\bullet} \qquad (5)$$

Scheme-I: Mechanism of metal catalyzed auto-oxidation

Metal ions which catalyze oxygen transfer reactions with H_2O_2 or RO_2H can be divided into two types based on the active intermediate: a peroxometal or an oxometal complex [92] (**Scheme-II**). Peroxometal pathway is usually favoured over early transition elements with d^0 configuration, *e.g.* Mo(VI), W(VI), V(V) and Ti(IV). On the other hand, over the late or first row transition elements, *e.g.* Cr(VI), V(V), Mn(V), Ru(VI), Ru(VIII) and Os(VIII), the oxometal pathway is usually followed. Some elements, *e.g.* vanadium involve both oxometal and peroxometal pathways depending on the substrate.
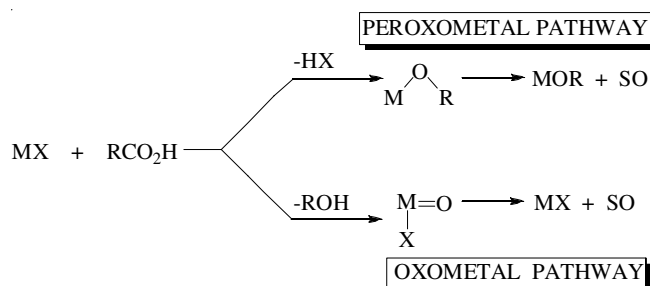
Scheme-II: Peroxometal *vs.* oxometal pathways [92]

Heteroatom oxidations and olefin epoxidation are the reactions involving peroxometal routes. By contrast, oxometal species exhibit the broader range of activities, such as allylic and benzylic oxidations. Peroxometal routes do not involve a change in the metal oxidation state, *i.e.*, activity is not restricted to only variable valence elements and the metal behaves as a Lewis acid. By contrast, the oxometal pathway involves a two-electron redox reaction of metal ions. Furthermore, most metals that catalyse oxygen transfer through oxometal or peroxometal pathways can catalyze one-electron transfer by using peroxides. Consequently, free radical processes frequently compete to a lesser or greater extent with oxygen transfer. When alkyl hydroperoxides are employed as oxidants, heterolytic *versus* homolytic processes are distinguished by using a suitable investigated molecule [93]. The unsupported metals usually form soluble peroxo complexes with H_2O_2 or peroxide so these reactions, in reality, homogeneously catalyzed [94]. Separations of the final products thus become very difficult. Supporting the metals in inorganic oxides (such as SiO_2, Al_2O_3) [95,96] or zeolite [96-98] only served to facilitate the dissolution of the metal species by dispersing the metal over the surface of the support and making it more accessible to the peroxides.

Different types of oxide supported metal catalysts such as Fe/MgO [99], Fe/Al₂O₃ [100], Co/Fe₂O₃ [101], Cu/Al₂O₃ [102], Cu/SiO₂ [103], V/SiO₂ [104] and Mn/Al₂O₃ [105] have been reported to be efficient systems for the production of industrially and chemically important products. These catalysts are usually prone to deactivation before the oxidation is completed. The deactivations are thought to be caused by either oxidation of the metals or blocking the active metal surface by the strong adsorption of the reaction byproducts or decrease of active metal component through metal leaching during oxidation.

A number of procedures have been employed to minimize this deactivation. Most of the early work in this area used large

amount of large sized metal particles [106]. These larger metal particles are more resistant to oxidation than the smaller particles present on the supports [107]. In addition, the large quantity of catalyst ensures that some active species will still be available towards the end of the reactions. The adsorption of byproducts can be eliminated by using more selective catalyst or changing solvent or reaction conditions [108]. Adding another metal particle/s significantly reduce the deactivation [109-112]. The metal leaching can be controlled by using proper support where metal support interaction is strong [113]. The metal leaching is also resisted by adopting specific preparation procedure and incorporating with other metals [114]. Association of two or more active metals can perform well in a reaction system with the enhanced degree of interaction of the components over a support with new redox and acid properties [115].

Selective oxidations *via* heterogeneous catalysis occupy a predominant place in both science of catalysis and synthetic based modern industry. These processes, such as benzene to phenol, benzyl alcohol to benzaldehyde, cyclohexane or cyclo-hexene to corresponding alcohols and carbonyl compounds have been extensively studied [116-119]. Ru, Pd, Mn, Fe, Co, Ni, V and Cu supported catalysts have been extensively used as catalyst for this type of reaction with H_2O_2 or *tert*-butyl hydrogen peroxide (TBHP) as the oxidant [120-122]. Still there are a large number of opportunities to develop suitable sup-ported metal catalysts for this type of reaction.

Supported metal catalysts in organic synthetic reaction: Catalytic reaction can be run over supported or unsupported metal catalysts. The active sites on a heterogeneous catalyst are found on its surface. Usually, the efficient catalysts have a large catalytically active surface exposed to the reaction medium. One way to maximizing the active surface of a catalyst is it can be used as a very fine powder as unsupported catalyst. The unsupported metals are found in variety of forms; single crystals, colloids, powders, blacks, skeletal and nanoparticles. Single crystals were used somewhat routinely in the early catalytic research for developing the mechanism in vapour phase reactions [123]. Since most of the synthetic reactions are run in liquid phase these single crystal metal catalysts find little use in the study of synthetic reactions. Black or powder is a metallic powder obtained by the reduction of metal salt or condensation of metal vapour [47]. But they are usually composed of relatively large particles having a low surface area and poor activity [17,48]. Skeletal metals are produced by leaching out one component of an alloy and leaving the active species behind in the form of porous materials having a high surface area [47-49]. How-ever, heating of unsupported catalysts usually results in sintering or agglomeration of the small particles into larger, less efficient entities [124]. The most common way to minimizing metal catalyst sintering is to distribute the active component over a porous, thermostable, inert support. The support may be inor-ganic oxides, active carbon, polymers and zeolites.

Catalysts with a supported metal comprise 0.1-20 wt.% metal from group 8 or 9, which is dispersed on the support surface, usually a high-surface area oxide [125]. These catalysts are widely used in industries and research laboratories. Because an active metallic phase exists as extremely small particles

with a dispersion degree (*i.e.*, the fraction of atoms exposed to the surface) of 10-100%, these catalysts are effective. These catalysts are widely separated from each other and firmly anch-ored to supports. Thus, they do not readily sinter or coalesce.

The activity of the dispersed catalyst particles in these supported catalysts is influenced by a number of factors, prim-arily the relative amount of catalytically active materials present, the surface area of the support, nature of the support and the strength of support-catalyst particles interaction. Metal catalysts with a low metal loading are generally composed of very small crystallites widely scattered over the surface of the support. Such crystallites generally have a high dispersion and the metal is efficiently used as catalyst. As the metal load increases, the crystallites become close to each other and frequently get larger in size. Thus the crystallites are become more resistant to thermal sintering. Obviously, if the catalyst crystallites are came in contact to each other then thermal coalescence can be expected to take place with a resulting loss of active surface area. The low metals loaded highly dispersed catalysts provide a maximum surface area per unit mass of metal. While the catalysts having larger number of catalyst particles spread over the support surface also provide a maximum metal surface area per volume of catalyst.

Generally noble metal catalysts have low metal loads and high metal dispersion, while catalysts containing the less expen-sive base metals have higher metal loadings. The surface area of a support is directly related to pore size, distribution and volume. The maximum surface area for the support or catalyst is the best possible arrangement. The surface area is not only associated with external surface of the particles but also with the surface of all the pores within the particles. A particle with small diameter pores will have a higher surface area than one with larger diameter pores having both the same total pore volume.

In case of vapour phase reaction involving molecules, catalyst particles having a large number of smaller pores and higher surface areas are preferred. Reactions of larger mole-cules are usually run in a liquid medium. For such reactions catalysts having smaller pores are inefficient since the diffusion restraints would severely hinder the reaction. Catalysts have larger pores with the catalytically active sites located near the surface of the support particles. So diffusion of the reactants to the active sites will not be a significant factor in the reaction.

Synthetic routes to oxide supported metal catalysts: The metal components are dispersed over the oxide support by various methods that include impregnation, precipitation and coprecipitation, deposition precipitation, ion-exchange, sol-gel, incipient wetness impregnation, spray drying, freeze drying, *etc.* [126,127]. However, all these processes are involved and sometimes require special equipment and are time consuming. Patil *et al.* [128,129] introduced a novel technique, the single-step solution combustion method, which involved the combustion of the metal salts with organic fuels, for the preparation of different fluorite, perovskite, spinel and mixed oxides [130,131].

Some advantages and disadvantages associated with the conventional methods which are coprecipitation and deposition-

precipitation are beneficial for synthesizing catalysts having high metal loadings (*e.g.* >10 wt.%) and those having low metal loadings of 0.01-5 wt.%, respectively. A limited coprecipitation cannot be applied to SiO_2 but supports Al_2O_3 because these hydroxide precursors or metal oxides cannot be coprecipitated using noble metal hydroxides. The sol-gel method can be used instead of coprecipitation for the SiO_2 support. Deposition-precipitation can be applied to basic metal oxides having the point of zero charge (PZC) of >5 pH. On the surfaces of supports of acidic metal oxide having PZC of < pH 5, noble metal hydroxides cannot be precipitated.

Metal-support interaction in supported metal catalysts: The concept of a metal-support interaction (MSI) is one of the oldest in heterogeneous catalysis. Initially, it was thought that the support material is inert and serves simply as a vehicle for keeping the catalytically active species separated and thus, minimizes sintering. This is accomplished because catalyst crystallities are formed some type of chemical bond to the support material by so they are not free to migrate across the surface and agglomerate or coalesce with other crystallities to form larger particles. Since, the catalyst particles are anchored to the support through some form of bonding the support can, potentially, also influence the activity of the catalyst [132].

This support effect can be assumed as taking place in two distinct ways. First, the support could modify the electronic character of the catalyst particles. This could affect the adsorption and reaction characteristic of the catalytically active sites. Another possibility is that the shape of geometry of the catalyst particles. The electronic effect could change the activity of the sites on the surface while geometric effect would modify the number of active sites present. The first specific suggestion of how the catalytic properties of a metal might be influenced by the support came about 85 years ago by Adadurov (1935). He proposed that metals would be polarized by the surface of oxides containing highly charged cations [133]. The catalytic property of the supported metal catalyst is strongly influenced by the metal support interaction [134-136]. According to Bond's proposition, the metal-support interactions are of three types, namely strong (SMSI), medium (MMSI) and weak (WMSI) [137]. As has been discussed, the SMSI is ascribed to transition metals supported on reducible oxides like CeO_2, TiO_2, $BaTiO_3$, *etc.* [138-143]. The metal-support interaction is increased with more reducible support. The weak metal-support interaction (WMSI) is generally associated with non-reducible oxides such as SiO_2, Al_2O_3, ZrO_2, *etc.* [144-147]. But the classification is not so straightforward. There are instances of SMSI effect in non-reducible oxide supports [148,149]. The difference between the two categories lies in the facts that MSI is induced under more serve conditions and the property of the catalyst is less pronounced in case of nonreducible oxides.

The catalytic activity of noble metals is decreased significantly as the metal-support interaction increase with reducible support. Several explanations are given for the deactivation behaviour associated with SMSI [150,151]. Four models are proposed for the origin of SMSI, namely, electron transfer, morphological effects, alloying and decoration [152]. Even after extensive studies, a fundamental understanding of the origin of the SMSI effect remains unclear and it is still a subject of current research [153].

Conclusion

From the foregoing discussion, it is suggested that there is lot of scope towards design of effective catalytic formulations. The preparation of industrially or synthetically important active catalyst for hydrogenation and oxidation reactions has been the constant motivation of researchers in this area of catalysis as outlined above. Inorganic oxide supported noble or base metal catalysts are extensively used as active catalyst for the synthetic organic reactions. It must be kept in mind that the sources of noble metal are limited and also the extraction procedure is costly, which in turn increases the cost of noble metals or its salts. Thus, urge is to reduce the amount of noble metal in the catalyst. But this should not affect the catalyst activity adversely. Conventional dispersion of metal component as zero-valent metal gives rise to finely dispersed nanocrystallities of size ~3-5 nm on oxide surface. Further reduction of metal crystallities size to ~1 nm will further increase the dispersion with lower amount of metal doping and hence the rate of reaction will be enhanced. Whatever may be the size of the crystallite, only the metal atoms at the surface of it takes part in chemisorption and catalytic action. The highest possible dispersion with highest activity can be achieved by dispersing each metal atom at the surface, which is not possible by the conventional methods of dispersing metals since due to metal-metal interaction, agglomerated metal crystallites are formed in the end. Thus the catalyst is multiphasic in nature. To make use of each metal atom as the adsorption site, the metal atoms should be placed at particular lattice positions. If the metals are substituted in support lattice in the form of metal-ion by using proper support or proper catalytic preparation methods, then the predominant electronic interaction will be a strong ionic interaction between metal ion and the oxide support. This means that substitution of metal ion in the support lattice is to be achieved forming single phase metal-ion substituted oxide. The metal ions in its positive oxidation state can easily be reduced by other oxidizable substances. Therefore, if the metal is dispersed as ionic form and if one is able to keep the oxidation state in positive state, in principle oxidation can be carried out over such ionically dispersed catalyst. The questions which automatically arise are: (i) How to substitute metal in its ionic form; and (ii) whether the catalytic capability would be the same in its oxidized state and in the zero-valent metallic state? So it is still challenging to prepare an efficient catalyst for synthetically important organic reactions in 21st century.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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