금속 나노 촉매를 활용한 선택적 알코올 산화 반응

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Supported Metal Nanoparticles:
Their Catalytic Applications to Selective Alcohol Oxidation

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초   록

본 리뷰 논문은 지지화된 또는 고정화된 금속들 중 선택적 알코올 산화 반응에 적용된 나노 크기의 여러 금속 촉매들에 대해 집중적으로 서술한다. 금속 나노 촉매들은 넓은 표면적을 지닌 고체 지지체들의 표면 위에 금속 나노 입자들의 고른 분산을 통해 얻어진다. 이러한 나노 촉매들은 유기 합성, 연료 전지, 바이오 디젤 생산, 오일 크래킹, 에너지변환 및 저장, 의약, 수처리, 고체 로켓 추진체, 염료 제조 등 학문적·산업적 측면 모두 다양하게 사용될 수 있다. 더욱이, 응용성이 풍부한 중간체들을 생산하는 호기성 알코올 산화 반응에서 금속 나노 재료는 촉매로써 매우 중요하다. 금, 팔라듐, 류테늄, 바나디움 등과 같은 지지화된 금속 나노 촉매들의 알코올 산화 반응은 기존의 화학 당량적 반응과 달리 비용을 경감시키고 부반응물들을 줄임으로써 경제적이고 친환경적이다. 뿐만 아니라, 상온에서 진행된 나노 촉매 알코올 산화 반응에 대해서도 소개된다.

Abstract

This review article highlights different types of nano-sized catalysts for the selective alcohol oxidation to form aldehydes (or ketones) with supported or immobilized metal nanoparticles. Metal nanoparticle catalysts are obtained through dispersing metal nanoparticles over a solid support with a large surface area. The nanocatalysts have wide technological applications to industrial and academic fields such as organic synthesis, fuel cells, biodiesel production, oil cracking, energy conversion and storage, medicine, water treatment, solid rocket propellants, chemicals and dyes. One of main reactions for the nanocatalyst is an aerobic oxidation of alcohols to produce important intermediates for various applications. The oxidation of alcohols by supported nanocatalysts including gold, palladium, ruthenium, and vanadium is very economical, green and environmentally benign reaction leading to decrease byproducts and reduce the cost of reagents as opposed to stoichiometric reactions. In addition, the room temperature alcohol oxidation using nanocatalysts is introduced.

Keywords: alcohol oxidation, aldehyde, supported metal, metal nanoparticle, nanocatalyst

1. Introduction

Nanomaterials are small materials having at-least one dimension on a nanometer scale. In the nanomaterials, small number of atoms are arranged together and the material particles have a diameter of few nanometers[1]. They have marvelous electrical, chemical, mechanical, optical and catalytic properties more than their bulk counterparts because of their atomic arrangements which are a few tenths of nanometer[2]. Nanotechnology is the study of a phenomenon involving small scale materials and their various applications. Since the terms of nano-materials and nanotechnology have been coined, they have found wide applications in almost every field of science and engineering due to their distinguishing properties and activities. The new small structures such as miniature transistors, sensors, transducers, actuators, nanoboats, memory elements, super computers, and nanopumps are few examples of the appliances that have resulted from the progress of nano-technology[1]. Silver nanoparticles have been employed in the health-care department for medicinal and antibacterial purposes for a long time. Similarly, right from the fourth century gold nanoparticle colloids have been applied for different coloring of Lycurgus cups as well as

the soluble gold containing salts to cure different disease in the middle ages. In the modern age gold nanoparticles are very attracting materials for cancer therapy and other diseases. The nanorobots and nano-injectors are prospective nanotechnologies with great numerous clinical applications to enhance patient treatment. Except these marvelous medical breakthroughs; nanotechnology claimed faster computers, clean environment, faster chemical reactions and cheap production of goods. The nanomaterials are expected to be part of the various products such as tennis rackets and baseball sticks, self-cleaning windows and cars, food, safety vehicles, helmets and jackets, paints, automotive and airplane structures, wind and turbine blades, cosmetics, etc.[1].The products manufactured from nanomaterials are made from the atoms. These products have distinguished features and properties that depend on the arrangement of atoms. For example, the different arrangements in the atomic structure of carbon can results in coal, diamond, Bucky ball, graphite, and carbon nanotubes. Recently, the graphene sheets have been separated from the graphite and applied widely in electronics, electrochemistry and structural applications[1].

Catalysis is an important field of application for nanomaterials[3]. The solid supported heterogeneous catalysts have grabbed a lot of attention in the contemporary era. During the modification of these catalysts, metal nanoparticles are dispersed over the surface of the solid supports[4]. The adverse effects of chemical reactions envisaged at the end of twentieth century have raised more attention so that more efforts are being expanded to eliminate wastes and enhance chemical reaction efficiency. For a long time, stoichiometric reactions have been applied in the fine chemicals and pharmaceutical laboratories and industries. These reactions produced lots of wastes and polluted the environment. In 1990, Barry Trost first introduced the concept of "Atom Economy (AE)" which was widely accepted[5,6]. Later in 1992, the concept of "Environmental Impact Factor (E-Factor)" was brought by Roger Sheldon[7,8]. These two concepts have helped to reduce the environmental wastes produced during the chemical reactions. The so called twelve principles of green chemistry were based over these concepts. The rules of green chemistry are strictly followed by the researchers and the scientists in the recent research to develop the environmentally benign reactions.

The nanocatalysis concept is heralded to be one of the strong candidates of green chemistry principles to eliminate the intrinsic hazards and wastes from the chemical processes[9]. Therefore, almost 60% of chemical reactions are based on the catalysis and about 90% chemical reactions involved catalysis in commerce today[10,11]. Advanced level characterization tools make it possible to understand the relationship between structure and catalytic activity of the catalysts at nanoscale level and designing a catalyst with enhanced activity. The supported metal nanocatalysts are eminent in the laboratory and industry as they exhibit higher catalytic activity and stability during the reactions. Moreover, the efficient recovery and reusability of the supported metal nanocatalysts from the reaction mixtures makes them prominent from homogeneous catalysts. Due to their greater activity and selectivity, nanocatalysts make the reaction clean and green by reducing the by-products[11,12]. The elimination of the stoichiometric components

from the reactions allows reducing the wastes and cost, thereby makes the reactions economical and environmentally acceptable. Therefore, supported metal nanocatalysts find a wide range of applications in the fields of pharmaceutical industry, fuel cells, energy conversion and energy storage, water purification, biodiesel production, electrochemistry, dye, petrochemical, solid rocket propellants, etc.

The increased relative surface area and quantum effects at the nanoscale level are the two major factors which control the properties of nanocatalysts. These factors can easily enhance or reduce the catalytic activity and selectivity of any catalyst[1]. The small particle size of the active site is pivotal in the catalysis reaction as it allows the large number of atoms on the surface of the solid support as compared to inside. The surface atoms can be found on the edges, corners and terrace of the nanoparticles, thereby affecting the activity of the nanocatalysts[3]. It is accepted that there is a correlation between surface edge and corner atoms and chemical reactivity of the nanocatalysts. The atoms located at edges and corners give greater reactivity as compared to terrace atoms[13]. Although surface atoms are more reactive and have high surface area, their surface energy is very high and they tend to agglomerate during the processing. Therefore, there is need to develop the novel techniques to anchor the metal nanoparticles on the surface of the solid support to maintain their high catalytic activity and selectivity[12]. In addition, the selection of the appropriate solid support is an important factor to be considered to get the even distribution of the metal nanoparticles. The metal nanocatalysts are produced by metal impregnation[14,15], hydrothermal synthesis[16], ion exchange [17,18], chemical deposition-precipitation[19-22], anion/cation adsorption[23], pyrolysis[24,25], sol-gel[26-29], colloidal synthesis[30,31], wet chemical[32] and sonochemical method[33-35]. These methods have been adopted to synthesize the nanocatalysts with fine and even distribution of metal nanoparticles on the solid supports.

In chemical laboratories and industries, selective oxidation of alcohols is a very significant reaction. The products of this reaction are mostly applied as intermediates in fine chemical, pharmaceutical, paint, polymers, detergents, fragrance, etc. This reaction is carried out with various catalysts (i.e. dichromate and permanganate) and produces lot of wastes to the environment. Therefore, development of new catalysts is a prime focus by the researchers and scientists to fulfill the green chemistry principles. In recent, the supported metal nanocatalysts have been reported for the alcohol oxidation reaction which shows the greater catalytic activity to get high TONs and TOFs. For instance, supported gold, ruthenium, palladium, platinum, copper, chromium, and silver nanocatalysts have been applied for the aerobic oxidation of the alcohol. The most significant feature of these catalysts is that they work under the environmental conditions with the green oxidants such as dioxygen, air or hydrogen peroxide. They do not need co-catalyst to carry out the reactions and can be recovered and recycled for several times. This review describes those kinds of various supported metal nanocatalysts which have been applied for the selective oxidation of alcohols involving mechanistic studies.

2. Supported Metal Nanocatalysts for Alcohol Oxidation

The supported gold and ruthenium nanocatalysts are the most explored catalysts for various reactions for their unique catalytic activities. Specially, the discovery of the supported gold catalyst by Haruta[36] opened up the doors for the oxidation of carbon monoxide[4,37-40] and alcohol oxidation[24,41-50]. The incredible work done by the Noritaka Mizuno group[51-55] and Kaneda group[56-61] for the supported ruthenium nanocatalysts is a big contribution to the aerobic oxidation reactions. Similarly, palladium catalyst for the alcohol oxidation is marvelous due to its well-known efficient catalytic activity[17,26,33,62-70]. Other supported metal catalysts such as platinum[22,30,71], iridium[72], silver[18], copper[20,73-76], vanadium [77], cobalt[78] and chromium[79] have been reported for the aerobic oxidation of alcohol. However, this reaction is still suffering from many drawbacks. The filthy work to separate the product from reaction mixture, less number of alcohol substrates scope by the catalysts, lower selectivity towards the desired products, the wastes produced by metal homogeneous catalyst, and the large wastes produced by the stoichiometric oxidants used for the oxidation reactions are some of the downsides which muddle the environment and lower the efficiency of the this reaction and make it difficult to come under the shade of green chemistry[80]. There is a need to find out the new catalysts or catalytic systems which can give rise to the activity and selectivity towards the desired products by making a lower impact on the environment and enlarging the scope of alcohol substrates to get the high TONs and TOFs. The supported metal nanocatalysts since their discovery have attained a considerable attention by the researchers and have been explored for the oxidation of alcohols as well as other organic reactions. The supported metal nanocatalysts show high selectivity towards the aldehydes and ketones by avoiding the over oxidation to the carboxylic acids. The catalysts recovery workup is easy and they apply air, dioxygen or hydrogen peroxide as terminal oxidants, thereby, making the aerobic oxidation reaction environmentally viable and economically acceptable. However, supported metal catalytic systems need improvements to be accepted for the industrial scale reactions. In this section, the aerobic selective alcohol oxidation of alcohols will be described with various supported metal nanocatalysts.

2.1. Supported Gold Nanocatalysts

Gold supported titanium oxide ($Au@TiO_2$) nanocatalyst has been reported for the oxidation of various alcohols. In this study, unique effect of water was detected for the oxidation of alcohol. The $Au@TiO_2$ showed the high catalytic activity for the oxidation of various alcohols under the atmospheric condition of oxygen. The reaction rate for the reaction having water with p-xylene as solvent has 7 times higher activity than reaction done in the absence of water. Author proved that water plays a dual role in the oxidation reactions. In multiphase reaction, water acted as promoting agent by facilitating the formation of unique droplets and the adsorption and activation of dioxygen to carry out the reaction smoothly[81]. In other reports, ceria, hydrotalcite
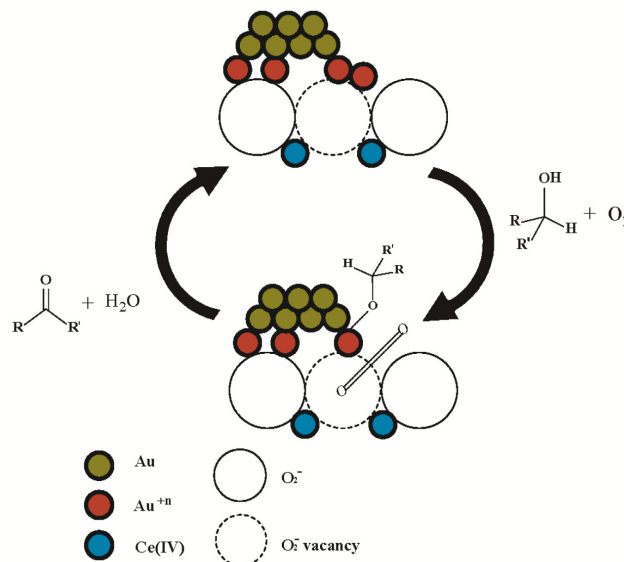
Figure 1. A plausible reaction mechanism for the alcohol oxidation with $Au@CeO_2$ nanocatalyst.

(HTC) and mesoporous silica supported gold nanoparticles catalysts have been reported for the aerobic oxidation of a long range of alcohols[82-84]. The catalysts showed the efficient catalytic activity and selectivity towards the aldehyde and ketones in the absence of any co-catalyst and presence of oxygen as terminal oxidant. Solvent free oxidation of alcohols with $Au-Pd@TiO_2$ has been reported by Enache et al.[62,85]. In this report, effect of gold nanoparticles on the catalytic activity $Au-Pd@TiO_2$ nanocatalyst has been studied for the solventless oxidation of alcohols. They showed very high TOFs of 270,000 per hour for the alcohol oxidation. The catalyst had core of Au rich particles while the shell was composed of Pd, which Au has influenced the catalytic activity of the Pd in $Au-Pd@TiO_2$ nanocatalyst. The gold nanoparticles for $Au-Pd@TiO_2$ acted as electron promoter for palladium, thereby enhancing the catalytic activity and selectivity for the alcohol oxidation reactions more than $Pd@TiO_2$. A solvent free alcohols oxidation for aliphatic substrates with $Au@CeO_2$ nanocatalyst was reported by A. Abad et al.[86]. 1-Phenylethanol yielded acetophenone while primary and secondary aliphatic alcohols converted to esters and ketones respectively. The $Au@CeO_2$ generated high TOFs ($32,558$ h^{-1}) for the oxidation of 1-phenylethanol. Although the catalyst can be reused for the oxidation of alcohol, it was observed that catalyst activity was affected by the carboxylic acids even with the minor amount generated during the reaction. Carboxylic acid might bind with the surface gold atoms preferentially and reduce its ability to make the gold-alcoholate intermediates. The proposed reaction mechanism for the alcohol oxidation with $Au@CeO_2$ nanocatalyst is shown in Figure 1. Oxygen physiosorption on the ceria defective sites generates cerium peroxyl $Ce^{iv}-O-O\cdot$ radicals, while gold positive ions on the ceria and gold interface produced the gold-alcoholate species. In the next step, ketone formed by the combination of surface bounded gold-alcoholate and cerium peroxyl radicals. In this way, metal hydroperoxide resulted in further conversion to cerium oxide by the action of gold. The effi-

cient catalytic activity of the Au@CeO₂ can be attributed to the oxygen vacant sites on ceria surface and other structural features. The nanosize ceria and the presence of the gold positive species are thought to be responsible for these structural features which ultimately resulted in the excellent activity and selectivity for the alcohol oxidation reactions under the green and clean oxygen atmosphere.

Gold nanoparticles were anchored on mixed oxide of Cu-Mg-Al solid support and effect of various mixtures of oxides was studied for the oxidation of alcohols with supported gold catalysts. With Cu, Mg and Al different binary and ternary mixed oxides were synthesized by varying the molar concentration of the elements. The catalytic activity of the various nanocatalysts having binary and ternary oxides supports was probed for the oxidation of alcohol. It was reported that the activity and selectivity of the nanocatalysts depended on the molar concentration of the Cu and Mg and the supported gold nanocatalyst over Cu:Mg:Al mixed oxide with molar ratio of 5 : 1 : 2 showed the best results. Further tests demonstrated that Au@ Cu₅Mg₁Al₂Ox nanocatalyst was highly efficient for the liquid phase oxidation of long range of alcohols and it produced the TOF of 1300 h⁻¹ for the aerobic oxidation of 1-phneylethanol[24]. Gold nanoparticles were supported over the conventional β-MnO₂ and β-MnO₂ nanorods to produce Au@β-MnO₂(C) and Au@β-MnO₂(R) by the homogeneous deposition-precipitation method. The activity of both catalysts was gauged for the aerobic oxidation of benzyl alcohol. Although selectivity for both catalysts was higher than 98%, Au@β-MnO₂(R) demonstrated three times higher yield for the benzyl aldehyde. Furthermore, the Au@β-MnO₂(R) was showed the excellent catalytic activity and selectivity for the long array of alcohols. The enhanced activity of the Au@β-MnO₂(R) was credited to the strong interaction of the gold with the β-MnO₂ nanorods due to nanosized support and generated large amount of surface gold oxide species and oxygen vacancies[21].

2.2. Supported Palladium Nanocatalysts

The supported palladium nanocatalysts are recognized in the industries because of their efficient catalytic activity and selectivity towards many organic reaction. So far many supported palladium nanocatalysts have been documented for the aerobic oxidation of alcohols. Pd(II) supported over hydrotalcite (Pd@HTC) was reported for the oxidation of alcohols under the atmospheric pressure of air. The catalyst showed chemoselective oxidation behavior for the allylic alcohols without hydrogenation and isomerization of the double bonds[67,87]. An enantioselective oxidation of alcohol was also studied by Jensen et al. for the Pd based nanocatalyst[88]. A high performance through Pd nanocatalyst immobilized on hydroxyapatite (HA) and nonstoichiometric Ca-deficient hydroxyapatite was produced for the aerobic oxidation of alcohols. By the control synthesis process, PdCl₂ was anchored on the HA to form PdHA-0 nanocatalyst and Pd^II phosphate species were detected for the PdHA-1 nanocatalyst synthesized from Ca-deficient HA. The PdHA-1 nanocatalyst showed the enhanced catalytic activity for the oxidation of alcohols and very high TONs of 236,000 were calculated for the 1-phenylethylalcohol oxidation reaction. Moreover, PdHA-1 showed outstanding performance for the Heck and Suzuki
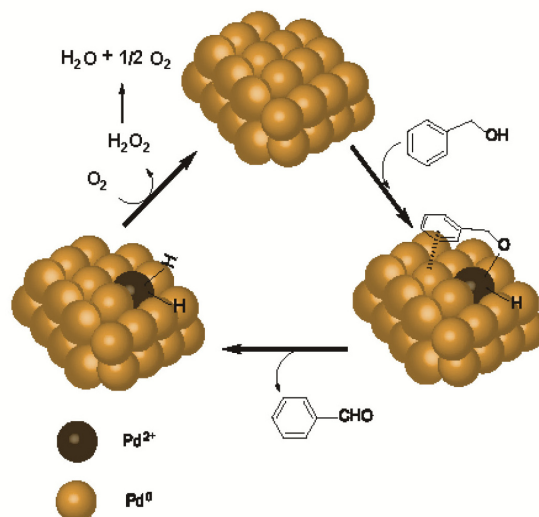

Figure 2. A proposed mechanism for the aerobic oxidation of alcohol over Pd nanoparticles surface.

reactions as well. The reaction between bromobenzene and styrene generated TONs of 47,000[89]. A possible reaction path for the oxidation of alcohol over the surface of Pd nanoparticles is shown in Figure 2. A Pd-alcoholate was produced by the surface reaction of O-H species from alcohol to the unsaturated edge atoms of Pd(0). The Pd-alcoholate underwent the β-hydride elimination which gave the aldehyde/ketone and Pd hydride species in the next step. In the final step, Pd hydride reacted with dioxygen to reproduce Pd(0) with the emission of H₂O[17]. Magnetically separable nanocatalysts are very attractive from the green chemistry view point because of the ease of recovery of the catalyst from the reaction mixtures. Polshettiwar and co-workers reported an efficient Pd supported on ferrite nanocatalyst for the alcohol oxidation. They demonstrated the high TONs of 720 for benzyl alcohol and the catalyst was easily recovered by placing a magnet with the wall of the reactor tube. They expanded the scope of the catalyst and carried out the oxidation of various olefins with Pd@F₂O₃ nanocatalyst as well. The reaction generated TONs ranging from 600-800 for all the reactions[66]. Similarly, a dual activity for catalytic oxidation of alcohols and hydrogenation of olefins was reported with Pd nanoparticles-aluminum hydroxide nanocatalyst[26]. A long range of aliphatic, benzylic allylic alcohols have been investigated with Pd@MgO nanocatalyst without any additive under the oxygen atmospheric conditions[68]. The selectivities for the products from benzylic and aliphatic alcohols were almost 100% in all cases while small amount of other compounds was produced in the allylic alcohols due to hydrogen transfer reaction. The possible reaction mechanism for this Pd@MgO nanocatalyst is shown in Figure 3. In the reaction mechanism study, metal alcoholate intermediate was discovered by the competitive reaction of primary and secondary alcohols. It was also observed that the reaction rate of the substrates with electron withdrawing groups were reduced than electron donating groups, which also confirmed the metal alcoholate intermediate formation. In addition, the MgO is a reducible support and can act as ligand for Pd that promoted
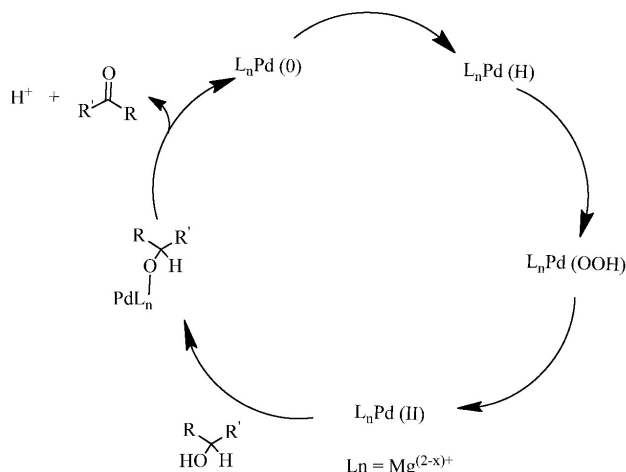
Figure 3. A possible reaction mechanism for the alcohol oxidation with Pd@MgO nanocatalyst.
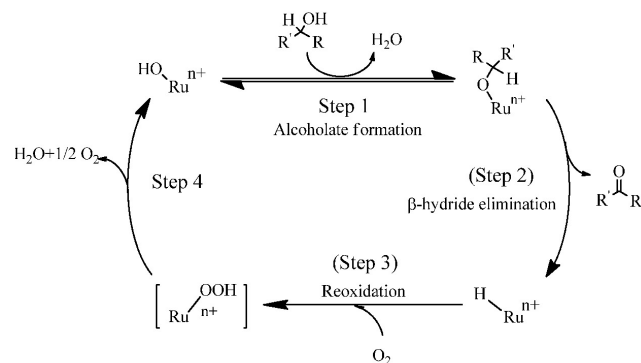

Figure 4. A proposed reaction mechanism for supported Ru nanocatalysts for aerobic oxidation of alcohols with molecular oxygen.

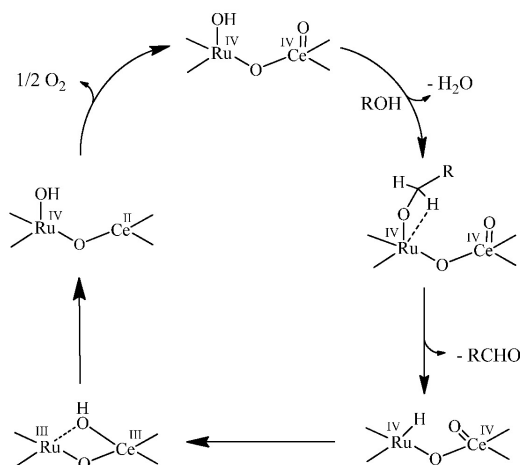Figure 5. Reaction mechanism for the alcohol oxidation over Co-Ce-Ru nanocatalyst.

the Pd-alcoholate formation in this reaction. In the next step, β-hydride elimination resulted in the carbonyl products and Pd-hydride species. The addition of O_2 further gives back the Pd(0) site to complete the reaction cycle. The reaction did not occur in the nitrogen atmosphere and was sensitive to the pressure of the oxygen. The concentration of Pd was also found to be a major factor controlling the rate of reaction which suggested that the oxidation of palladium with oxygen to give back Pd(0) species is the rate limiting step in the oxidation of alcohols with Pd@MgO.

Continuous flow reactors are the new class of method used for the organic synthesis. They are classified clean reactions because the reactions are carried out at very low temperature as compared to conventional batch reaction and no workup is required after completing any catalytic reaction to remove the catalyst. Hence, making the system is more economical and environmental friendly by producing the products with very high yields and selectivity[90,91]. They have been applied for many homogeneous catalytic reactions. However, they are limited to the solid supported heterogeneous catalysts as solid pack-bed reactors are somehow difficult to make. Pd supported on PEG-modified silica support and hybrid mesoporous silica particles nanocatalysts were reported for the alcohol oxidation in continuous flow reactor in the presence of super critical carbon dioxide under moderate reaction conditions[69,92]. Aliphatic alcohols were difficult to oxidize in this reaction while benzylic and allylic alcohols afforded high yields and selectivities for aldehydes and ketones.

2.3. Supported Ruthenium Nanocatalysts

Ruthenium nanocatalysts have been explored extensively for the aerobic oxidation of alcohols. Since ruthenium gives oxidation states ranges from +2 to +8, it finds wide applications in the catalytic reactions. For alcohol oxidation reactions, supported ruthenium nanocatalysts demonstrated the excellent catalytic activity and selectivity for aldehyde and ketones. Ru nanocatalysts immobilized by hydroxyapatite from Kaneda et al. were the pioneer work in the field of alcohol oxidation

by supported Ru nanocatalysts[56], following a big number of supported ruthenium nanocatalysts reported by the various researchers from all over the world. Later, the work done by the Mizuno group for the oxidation of alcohol with supported Ru nanocatalysts is marvelous. They have reported many reusable supported Ru nanocatalysts such as Ru@Al$_2$O$_3$[51,55], Ru@TiO$_2$[52] and Ru@Fe$_2$O$_3$[54] for oxidation of wide range of alcohols. In their studies, they have achieved high TONs and TOFs for various primary and secondary alcohol substrates including benzylic, aliphatic, heteroatomic, allylic, cyclic and complex structured. The reaction mechanism for the alcohol oxidation with these catalysts is shown in the Figure 4. Ruthenium alcoholate formation was followed by the β-hydride elimination to produce aldehydes/ketones with Ru-hydride. Ru-hydride underwent oxidation and produce ruthenium hydroxide active site to complete the catalytic reaction cycle[53].

A versatile supported ruthenium nanocatalyst of [RuCl$_2$(*p*cymene)]$_2$-activated charcoal was investigated for the aerobic oxidation of alcohols. The same catalyst was suggested for the silanes hydrolytic oxidation and dehydration of aldoximes to produce the desired products with high yield and selectivities[93]. A highly active trimetallic nanocatalyst of Co-Ce-Ru was reported for the oxidation of alcohols
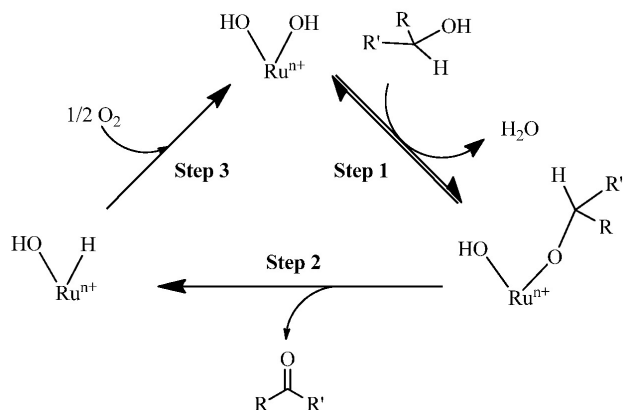
Figure 6. Mechanistic study showed that only one hydroxyl group was involved in the alcohol oxidation with RuCoHA nanocatalyst.

Figure 7. A mechanistic cycle for the alcohol oxidation with RuMN$_2$@HTC nanocatalyst.

[58,60]. Ru was supported on the surface of mixture of CeO$_2$/CoO(OH) support. Especially, the catalyst exhibited the outstanding activity for the aliphatic alcohols to produce carboxylic acids with excellent yields and selectivity. The reaction mechanism (Figure 5) and activity of the Co-Ce-Ru was described in terms of the surrounding structure of each metal. It was described that Ru(IV) species were involved for the oxidation of alcohols to form aldehydes. The reaction mechanism cycle was same as mentioned for the oxidation of alcohols with Ru@Al$_2$O$_3$ to form the aldehyde/ketones and Ru-hydride species. However, in this reaction β-hydride elimination was found to be the rate determining step. The activity of Co(III)-Ce(IV)-Ru(IV) was accounted by the CeO$_2$ which enhanced the rate of β-hydride elimination step, thereby improving the rate of reaction as well. As binding oxygen between the two metals in bimetallic complexes was reported as promoter for alcohol oxidation[94], it was assumed that Ru(IV)-O-Ce(IV) bond accelerated the Ru-alcoholate species formation and β-hydride elimination from Ru-alcoholate to form Ru(IV)-O-Ce(II) species[58]. Ru(IV)-O-Ce(IV) species was regenerated by the aerobic oxidation of Ce(II) species. The reaction of aliphatic alcohols with Co(III)-Ce(IV)-Ru(IV) nanocatalyst was supposed to follow free-radical path and CoO(OH) phase was responsible for this pathway[95] because Co(III) species was thought to initiate the formation of peracids by radical chain reaction between dioxygen and aldehydes[96].

Hydroxyapatite (HA) is natural mineral and part of the bones and teeth. HA have Ca^{2+} ions which can be exchanged with other ions to alter the surface chemistry of it. Therefore, it has been explored many researchers for supporting Ru over its surface. For instance, ruthenium has been incorporated in HA[97], Co-hydroxyapatite[98], organically modified HA[32], and HA-encapsulated superparamagnetic γ-Fe$_2$O$_3$ [57], were reported. In the RuCoHA nanocatalyst reaction mechanism investigations, dihydroxo-ruthenium species (i.e. Ru^{+n}(OH)$_2$) were found to be active sites for the alcohol oxidation. Moreover, the detailed reaction studies for benzyl alcohol showed that either β-hydrogen or the reoxidation of Ru-hydride species are the rate limiting factors. For aliphatic and cyclic alcohols it was concluded that the rate
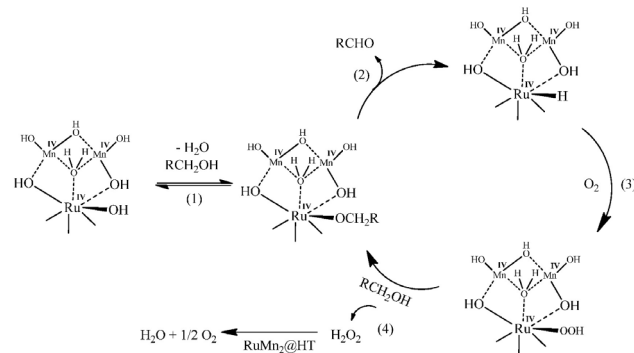
of reaction was not limited by the reoxidation of Ru-hydride sites[98]. The mechanistic study of the catalyst also showed that only one hydroxyl group was involved for the alcohol oxidation with RuCoHA nanocatalyst as shown in Figure 6.

Ruthenium dioxide (RuO$_2$) nanoparticles were incorporated in the supercages of faujasite zeolite (FAU). RuO$_2$-FAU nanocatalyst showed the extraordinarily high activity for activated and unactivated alcohols oxidation. RuO$_2$-FAU nanocatalyst showed higher catalytic activity for alcohol oxidation than bulk hydrous RuO$_2$[16]. An efficient alcohol oxidation was also reported for Ru supported on cerium oxide[99], nickel hydroxide[100] and zirconia[14] nanocatalysts. A heterometallic supported nanocatalyst of Ru^{IV}Mn^{IV}Mn^{IV}-HTC has synthesized and devised for the efficient aerobic oxidation of alcohols under green environmental conditions[59]. It was claimed that it is first study which described the metal cations and with hydroxide and oxide species, since it was proved that Mn-Mn and single cation of Ru^{IV} were linked by water and hydroxyl groups. The RuMn$_2$@HTC nanocatalyst showed five times higher TOF (140 h^{-1}) than for Ru supported on HTC nanocatalyst. The RuMn$_2$@HTC also oxidized a wide variety of alcohol substrate under atmospheric conditions. This high catalytic activity of the RuMn$_2$@HTC was attributed to the unique structure of the catalyst. The mechanism for the alcohol oxidation on this heterometallic nanocatalyst is shown in Figure 7. The Mn cations are believed to play a pivotal role to enhance the catalytic activity of the RuMn$_2$@HTC nanocatalyst. However, it was observed that alcohol oxidation reaction follows the well accepted cycle of metal alcoholate formation, β-hydrogen elimination and finally metal hydroxide species formation to get back the catalyst. There are very few reports about the alcohol oxidation in the water with supported metal nanocatalysts under oxygen atmosphere. A solid supported nanocatalyst of Ru over carbon nanotubes (CNTs) have been reported for the aqueous oxidation of alcohols in the atmospheric conditions of air or oxygen[19]. The water as a solvent enhanced and speeded up the catalytic reaction for the alcohol oxidation with Ru@CNTs nanocatalyst. The enhanced catalytic activity of Ru@CNTs was attributed to special emulsion formation in the reaction mixture. The Ru@CNTs resides at interfaces of water/alcohol emulsion which enhanced its dispersion in the mixture and quickened the reactions for alcohol oxidation to yield the aldehydes and
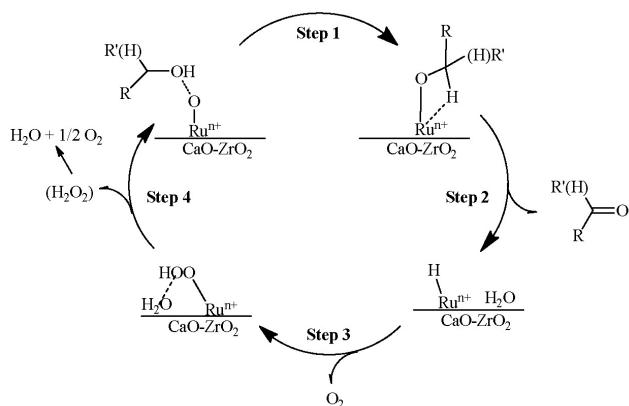
Figure 8. A possible reaction mechanism for alcohol oxidation with Ru@CaO-ZrO$_2$. Ru^{+n} was supposed to be Ru^{3+} or Ru^{4+}.

Figure 9. The interaction of alcohol with the two different Ru-alkoxides existed in two different Ru heterogeneous catalysts.

ketones with high selectivity. Graphene, a two dimensional nanosheet is the opened form of CNT and recently explored in many researches that involve in the various catalytic reactions. Gopiraman et al. described a simple dry synthesis of Ru@Graphene nanocatalyst and its application to the wide range of alcohol oxidation reactions as well as transfer hydrogenation reaction of ketones[101]. The Ru@Graphene showed an excellent stability towards the aerobic oxidation reactions and a small amount of catalyst worked extraordinarily well for complete conversion under atmospheric conditions without any additive. Moreover, the recovered nanocatalyst Ru@Graphene was calcined to form the RuO$_2$ nanorods supported on graphene (RuO$_2$-NR@Graphene). The RuO$_2$-NR@Graphene was applied successfully to the hydrogen transfer reactions of aromatic, heterocyclic, and alicyclic ketones. Ruthenium was immobilized over CaO-ZrO$_2$ surface to form the Ru@CaO-ZrO$_2$ nanocatalysts with varying molar ratios of Ca/Zr[102]. The molar concentration of Ca/Zr affected oxidation state of Ru which was attributed to the changes in the basicity of the CaO-ZrO$_2$ support which ultimately affected the interaction between Ru and CaO-ZrO$_2$ support[24,103,104] and have a great impact on the oxidation of 1-phneylethanol. The highest yield for acetophenone was obtained with Ca/Zr = 0.125 of the support. The reaction mechanism for the alcohol oxidation with Ru@CaO-ZrO$_2$ nanocatalyst is shown in the Figure 8. In this reaction β-hydride elimination and oxidation of Ru-hydride species was rate limiting steps.

3. Room Temperature Oxidation of Alcohols with Supported Metal Nanocatalysts

In the bilateral discussion, we elaborated various supported metal nanocatalysts which demonstrate very high catalytic activity and selectivity towards the desired products. The catalytic oxidation reactions were carried out in the absence of any additive and stoichiometric compounds. In the cutting edge research, there is need to develop the procedures which can carry out the reactions in the environmental benign conditions and most likely at room temperature to economize the system by reducing the energy applied for higher temperature
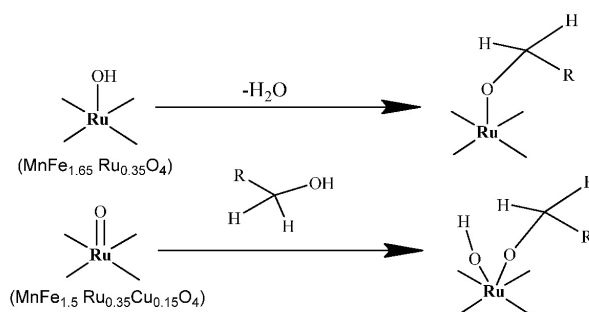
reactions. The room temperature alcohol oxidation with solid supported catalysts is somehow challenging because of the different phased materials used in the reaction mixture. Solubility of the solid alcohol substrates is also another task for the room temperature alcohol oxidation. Therefore a very limited number of supported metal nanocatalysts have been reported for alcohol oxidation at room temperature. We describe the supported metal catalysts for alcohol oxidation at room temperature.

The ruthenium oxide pyrochlore dispersed over nafion ionomer nanocomposite and SiO$_2$'-NH$_2$-Ru nanocatalysts have been described by Venkatesan et al. and Ganesamoorthy et al. respectively for alcohol oxidation at ambient temperature. The catalysts demonstrated excellent yields and selectivity for the aldehydes and ketones and could be recovered with easy work-up. Ru based heterogeneous complex was prepared in different composition[61]. It was found that Ru is an indispensable component for the cinnamyl alcohol oxidation at room temperature as MnFe$_{1.85}$Cu$_{0.15}$O$_4$ showed very less activity than MnFe$_{1.65}$Ru$_{0.35}$O$_4$. The catalytic activity of the two different Ru complexes (MnFe$_{1.5}$ Ru$_{0.35}$Cu$_{0.15}$O$_4$, MnFe$_{1.65}$Ru$_{0.35}$O$_4$) was discussed in detail. The MnFe$_{1.5}$Ru$_{0.35}$Cu$_{0.15}$O$_4$ exhibited an enhanced catalytic activity for the long range of alcohols oxidation at room temperature. It was found that alcohols interact with unsaturated Ru = O sites in these complexes differently as shown in the Figure 9. Moreover, coordinately unsaturated Ru = O species act as the active site for the alcohol oxidation.

A nanocatalyst of Ru over the surface of MnO$_x$/CeO$_2$ mixed oxide was reported for the room temperature oxidation of various alcohols[105]. Although Ru@MnO$_x$/CeO$_2$ nanocatalyst showed TOFs of 4 h^{-1} for benzyl alcohol at room temperature, the reaction at moderate temperature (50 ℃) showed the higher activity and TOFs than other supported Ru nanocatalysts. A Pd-catalyzed alcohol oxidation at room temperature was also described by Schultz et al. for various substrates[106]. Copper-aluminum hydrotalcite/rac-BINOL nanocatalyst has been reported for the aerobic oxidation of benzylic, secondary and heterocyclic substrates under mild temperature conditions[75]. Another Cu/AlO(OH) nanocatalyst showed the excellent catalytic activity for the wide array of alcohol substrates. The Cu/AlO(OH) was found active at room temperature and reactions were carried out in the water as benign solvent. The use of water as solvent and carrying out the re-
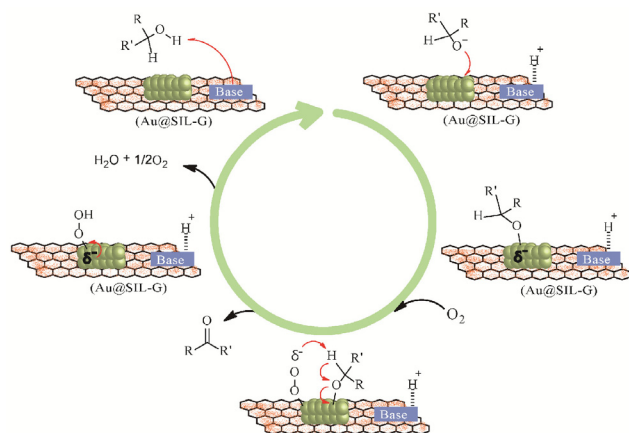
Figure 10. A possible pathway for the oxidation of alcohols with Au@SIL-G nanocatalyst.

Figure 11. A proposed mechanism for the alcohol oxidation with vanadyl sulfate catalyst.

actions at ambient temperature make the protocol important in economic and environmental point of view[74]. The supported gold nanocatalysts are of great interest for various organic transformations even at lower temperature. For instance, Au@CNTs[46], NaAuCl$_4$@Cs$_2$CO$_3$[47], Au@PMO (periodic mesoporous organosilica)[48], Au@LDH (layered double hydroxide)[107], and Au supported on benzene rings of polystyrene derivatives[108] have demonstrated excellent catalytic activity and selectivity towards the oxidation of a range of benzylic, aliphatic, primary, secondary, heteroatomic, allylic alcohols at room temperature under the atmosphere of air/dioxygen. The catalysts maintained their catalytic activity for several cycles of alcohol oxidation and showed their heterogeneous nature.

A green oxidation of alcohols at room temperature and in water was performed with the nanocatalyst of gold supported on supramolecular ionic liquid anchored on graphene (SIL-G)[49]. This system provided a stable solid support to disperse the Au nanoparticles with the controlled particle size in the supramolecular ionic liquid grafted graphene sheets. In addition, graphene provided the good dispersion of catalyst in the water. The catalytic mechanism for Au@SIL-G catalyst is shown in the Figure 10. Reaction started from the Au nanoparticles and OH$^-$ base as shown in Figure 10. The basic sites of SIL-G promoted the dehydrogenation of the alcohol substrates to generate the alkoxide species on Au nanoparticles. Subsequently, corresponding aldehyde/ketone was produced with O$_2$ and H$_2$O$_2$ upon β-hydrogen elimination by the gold nanoparticles. Since the Au@SIL-G system showed the bifunctional heterogeneous behavior with Au nanoparticles and base centers on the support, there was no need of any basic co-catalyst to carry out the reaction under mild conditions.

Very efficient alcohol oxidation at room temperature was reported for with Cobalt(II)@EFNC (Ethylenediamine-functionalized nanocellulose complex) nanocatalyst[78]. A room temperature alcohol oxidation in water was also carried out with the Pt@Ca(Mg)-ZSM-5[30]. In this study, Hong et al. described that metal alcoholate formation was followed by the removal of hydrogen from α-C-H bond of alcohols. The ·OH radicals were formed from the O-O bond breaking in the hydrogen peroxide intermediate which is rate limiting step in the alcohols
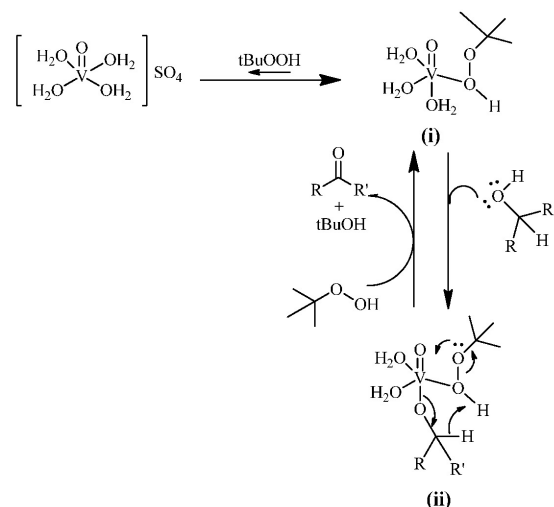
oxidation. A versatile nanocatalyst of vanadyl sulfate with tert-butyl hydroperoxide was applied as a recyclable catalyst for the oxidation of primary and secondary alcohols at ambient temperature[77]. In this reaction, tert-butyl hydroperoxide was employed as green oxidant. The toxomonoperoxo vanadate (V) complex was involved in the reaction mechanism (Figure 11). In the first step, toxomonoperoxo vanadate (V) complex I was produced butyl peroxide group. The intermediate complex II was generated by the nucleophilic substitution reaction of water legand with alcohol. The carbonyl compounds (aldehyde/ketone) were produced in the final step from the intermediate complex II.

4. Concluding Remarks and Future Challenges

The field of supported metal nanocatalysis has grown a lot during the last decade and attracted the researchers owing to outstanding characteristics of the metal nanoparticles. The supported metal nanocatalysts seem to occupy the industry in future to replace the homogenous catalysts which create wastes and make the environment polluted. Alcohol oxidation is one of the pivotal reactions in the chemical industry; therefore, many supported metal nanocatalysts have been reported for this reaction. Although, supported metal nanocatalysts are promising for many reactions, they have some challenges to get a stable position at industrial scale. The properties of nanoparticles are not well understood yet and need more efforts from the researchers to develop the techniques to understand the characteristics of the materials at such small scale. The designing of the supported metal nanocatalysts with appropriate properties for some specific application is still underway and need improvement to describe the reaction mechanisms. In addition, nanocatalysts should have to prove their stability and activity for various cycles at such a large scale to get the industrial applications. However, we believe that the detailed understanding of chemical reactions at nanometer scale and developing the techniques to control the size, shape and design of nanocatalysts will make their way easy towards the chemical industries for various applications soon.

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