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Transition metal-based nanoparticles catalyzed esterification reactions

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Esters are an important source of aroma due to which they are widely used in cosmetics and food industries. Apart from their fragrance, they are used in textile industries, lubricants, and many other fields. This review paper mainly introduces the overview of research about oxidative esterification using metal nanoparticles. Traditional esterification fundamentally proceeds between carboxylic acid derivatives and alcohols and is regularly a multistep process. Also, research interest in the area of nanotechnology using transition metal nanoparticles is of great interest for application in catalysis for direct esterification of alcohols and aldehydes under oxidative conditions. Transition metal nanoparticles catalyzed esterification process has paved the way to the efficient, sustainable, and environmentally friendly direct oxidative esterification of alcohols and aldehydes.

Keywords: Alcohols; Aldehydes; Esterification; Nanoparticles; Transition metals;

1. Introduction

The aroma of most of the things we come across in our everyday lives is due to esters. From the flavors of fruits to the aroma of perfumes and soaps, esters are everywhere. Leopold Gmelin, a German chemist was the first person to coin the term "ester".[1-4] In addition to good smelling substances, ester groups are widely found in biodegradable polymers like polylactic acid, thermoplastics like polyethylene terephthalate, analgesics. Numerous industrially important products like plasticizers, coatings, perfumes, and resins consist of ester groups.[2] Aromatic esters, in the form of intermediates like liquid crystal polymers, cosmetics, pharmaceuticals, agrochemicals, and food additives, [3] have also been an important contributor in organic synthesis. They are extracted from natural sources such as trees, plants, fruits, and flowers. In the case of seasonal and climate-dependent sources, the process of extraction may become difficult in addition to the high cost of extraction and comparatively lower yields.[4] Methyl esters are of particular importance because they are multifaceted synthetic building blocks, and also intermediates which can be further transformed to form other compounds. They are extensively used as solvents, extractants, diluents, flavoring agents, and odoriferous components as mentioned in table 2. Methyl methacrylate, an industrially important methyl ester monomer is obtained from oxidative coupling of methacrolein and methanol to form poly (methyl methacrylate). Applications of esters have been dealt with in detail in section 8. [3,5,6]

Fischer esterification, named after 1902 Nobel laureate in Chemistry, Hermann Emil Fischer, is a reversible acid-catalyzed condensation reaction and the most common method of esterification.[1] It requires the use of strongly acidic conditions. Baeyer Villiger oxidation is another well-known method of esterification but suffers from low regioselectivity. Most of the esterification reactions require the use of high valent inorganic oxidants like chromate or permanganate which produce numerous by-products and metal waste. Therefore, researchers then started synthesizing esters by carbonylation reactions of aryl halides in the company of transition metal catalysts. These reactions also suffered from the limitation of the requirement of high temperature, high carbon monoxide pressure, and generation of halide ions which was environmentally not suitable.

Later, direct ester formation via oxidative esterification of aldehydes with alcohols in the presence of oxone®, MnO_2, sodium dichromate and peroxides was developed but multiple steps along with the huge amount of by-products were observed.[7–9] Conventional esterification methods are therefore not preferred in the long run since they do not follow the green chemistry principles.[1] As it is rightly said that “great oaks from little acorns grow”, the need for synthesizing esters following green chemistry principles was felt later on by the researchers, even if it was possible on a low scale.[1] So, finally a unitary-step direct oxidative esterification of alcohols catalyzed by transition metals was devised. It was environmentally benign and desirable because alcohols are easily available, stable, less toxic, and easier to handle, hence, making the overall process economical. However, the economy of the process solely depends on the catalyst used. Most of the single-step oxidative esterification of alcohols involves oxygen as an oxidant, which is cheap and abundant and produces harmless water as a by-product. [7,8]

Metal nanoparticles are at the forefront and a very popular choice amongst chemists due to their special physical and chemical properties. Due to their small size in the range of 1-100 nm as is evident from the name itself, they have a high surface to volume ratio, a multitude of active sites which can be utilized for substrate binding and hence, enhancing their catalytic properties. Their high surface energy renders them unstable and so nanoparticles are immobilized on a suitable matrix to increase their stability. Supports like carbon, alumina, hydroxyapatite, graphene, SiO_2, CeO_2 and Fe_3O_4 are mostly used for immobilization of silver nanoparticles and can also be used for other transition metal nanoparticles. The supports also help in easy separation of nanoparticles from the reaction medium. The most commonly used supports for nanoparticles have been discussed in section 5.[8,10]

2. History

Aroma has been associated with perfumes for a very long time. It has played a major role in almost all civilizations, be it Egyptian or Arabic civilization. In ancient Egypt, ointments were used on the body for aesthetic purposes and hence, the perfumes were used in semi-solid or solid form. From then on, the use of fragrances spread throughout the world not only for aesthetic purposes but also for cosmetic and sacred purposes.[11] Jabir ibn Hayyan, also known as Geber, is known as the father of Arab chemistry. He is associated with the development of a laboratory apparatus like the retort and the process of distillation.[12] Soon after, the condenser was invented by Abu Ali Sina, also known as Avicenna. Together, they laid the foundation for the process of distillation which paved the way for the distillation of essential oils and hence, contributing to the development of fragrances. After the mid-19th century, synthetic chemistry became popular and researchers started developing methods for the synthesis of synthetic fragrances or a combination of synthetic and natural fragrances that were even cheaper than natural fragrances. After this, there was no turning back for the fragrance industry, thereby resulting in the rapid growth of the industrial sector.[11]

Apart from the industrial use of aroma in esters, the aroma has also been an important part of aromatherapy. Aromatherapy involves healing a person's mind, body, and soul by using essential oils either for inhalation, massage, or external application on the skin. This rejuvenates the body as it elicits the release of hormones like serotonin, endorphin, and noradrenalin which have a calming effect on the mind, body, and soul. This also lifts a person's mood, thereby improving their health. It has been popular since the late 20th century. The essential oils consist of esters along with other organic compounds like terpenes, ketones, saturated or unsaturated hydrocarbons, etc. For example, Roman chamomile oil, a widely used essential oil, consists of esters of angelic acid, 2-methylbutanoic acid, and tiglic acid.13 The role of esters in imparting aroma has been known for ages and is prevalent even now.

3. Transition metals as catalysts

Most of the transition metals are abundant and comparatively have lower costs. That's why they are best suitable for sustainable heterogeneous catalysis. For enhancing or activating them, numerous bases can be introduced thereby lowering the activation energy of a reaction, which subsequently improves the product yield.[14] Transition metals used as a catalyst for esterification reaction are mainly cobalt, gold, iron, palladium, and silver. Various other combinations of metals are also being explored for the catalysis of such reactions. [8,15]

A reaction where the catalyst exists in the same phase as the reactants is said to proceed through homogeneous catalysis. It is widely employed in several industrially remarkable processes like hydro-formylation reaction, Ziegler-Natta polymerization, Monsanto process and Wacker process to name a few**.**[16] It offers greater selectivity and enhanced activity even under mild reaction conditions as compared to heterogeneous catalysts. In most cases, their mechanism of action is tacit and so can be modified to suit the reaction conditions/ situations. [17]

A reaction where the catalyst exists in a different phase from the reactants is said to proceed through heterogeneous catalysis. Even though homogeneous catalysis exhibits high reactivity and selectivity, heterogeneous catalysis is more preferred. This is due to numerous reasons. The catalyst has a higher surface area, can be easily recovered from the reaction medium by simple filtration and hence is easily recycled. This does not pollute the environment and overall, makes the process cost-effective. On the other hand, homogeneous catalysts suffer from the aggregation of active catalytic sites.[8,18–20] Hence, nanoparticles- based heterogeneous catalysis has been popularly used by researchers around the globe.

In the last decade, a lot of work has been done in the area of esterification by oxidative mechanisms from alcohols and aldehydes employing transition metal nanoparticles. A brief overview of the methods of preparation of catalysts, the different supports used for the catalyst and the recent trends in the field of oxidative esterification by using transition metal catalysts will be given in the subsequent sections.

4. Methods of Synthesis of Nanoparticles

The methods of synthesis of nanoparticles can be broadly classified as Top-down approaches and Bottom-up approaches. The top-down approach is based on dividing the bulk material to form nanoparticles**.** It involves methods like Arc discharge, Ball milling, Inert-gas condensation, Ion-sputtering, Laser ablation, Micro-machining, and Wire explosion.[21] Bottom-up approach also known as the building up approach and involves the formation of nanoparticles from simpler substances**.**[22] It involves methods like Atomic layer deposition, Chemical reduction, Co-precipitation, Electrochemical reduction or oxidation, Sol-gel fabrication and Vapor phase chemical deposition.[21]

From the above paragraph, it is evident that there are a large number of methods of preparation of nanoparticles. However, a few commonly used methods for the synthesis of esters are briefly described. These mainly include methods based on the bottom-up approach.

4.1. Chemical vapor deposition method

In this method, a gaseous precursor is allowed to enter the reaction chamber through a carrier gas. The gas is then allowed to deposit over the substrate which results in the formation of a thin layer of the precursor as depicted in Figure 01. The temperature plays an important role in this method. Firm, uniform, and pure nanoparticles can be formed from this method. The method is best suited for the synthesis of carbon nanotubes. The limitations of the method include the need for distinct equipment, production of harmful gaseous by-products, and carbon impurities. [21,23]

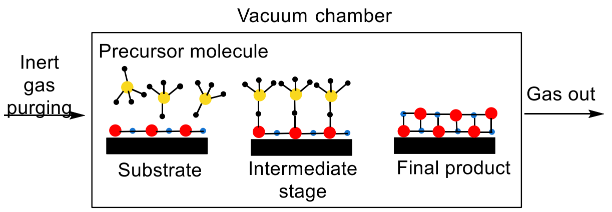


Figure 01:- Schematic representation of Chemical vapor deposition method.[24]

4.2. Sol-gel method

It consists of sol and gel as major components as is evident from the name. The process comprises five steps. The first step is the hydrolysis of the metal alkoxide in the presence of either an organic solvent or an aqueous solvent to form metal hydroxides. The next step involves condensation reaction taking place between molecules resulting in the formation of metal oxide linkages. This increases the viscosity of the solution and leads to the formation of a gel. The solution is then allowed to undergo aging in the third step, to form the colloidal particles of considerable thickness. The gel is allowed to dry using an appropriate method. Finally, it is either heated or calcined at an appropriate temperature to obtain nanoparticles of the desired size as is evident from figure 02. [25] This method is widely used for the synthesis of bimetallic nanoparticles namely Au-Pd and Au-Ag. Since the method is carried out at a relatively lower temperature, the composition of the catalyst is preserved.[26]

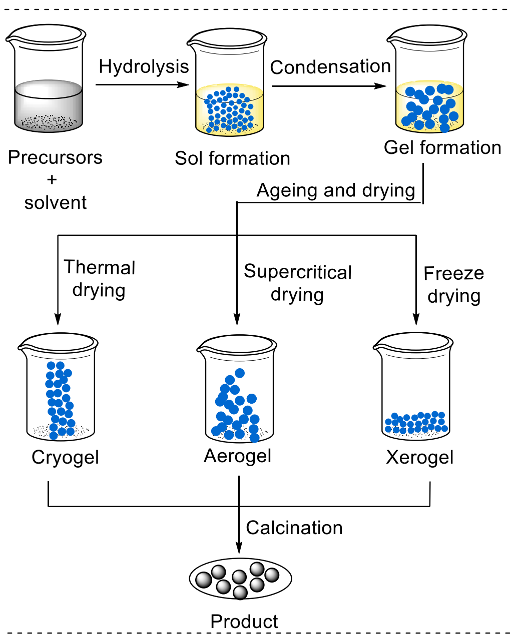


Figure 02:-Schematic representation of Sol-gel method [25]

4.3 Co-precipitation method

It involves the simultaneous nucleation, growth, and agglomeration of nanoparticles.[21] The method is best suitable for transition metal oxides. It is an economic method, requires a temperature of less than 90°C and results in the formation of nanoparticles of desirable stoichiometry which are homogeneous with a high degree of purity. The problem of agglomeration can be eluded by using supports or stabilizing agents.[27,28]

4.4 Wet impregnation method

The method involves mixing of the solid support and the metal precursor with distilled water. It is then thoroughly stirred, dried and maintained at a high-temperature atmosphere to increase the metal-support affinity for each other as depicted in figure 03. The catalyst thus formed is found to be active towards oxidation of alcohols.[29] However, the size and structure of the nanoparticles synthesized using this method cannot be altered easily. [30]

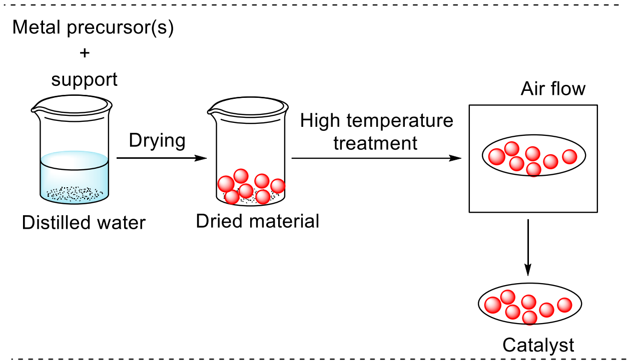


Figure 03:- Schematic representation of the steps involved in the wet impregnation method**.**[30]

4.5 Deposition precipitation method

This method is mainly used for the synthesis of gold nanoparticles supported on metal oxides and was formulated by Haruta and co-workers. The method involves the addition of NaOH solution to $HAuCl_4$ solution resulting in the formation of $[Au(OH)_4]^-$ and $[AuCl(OH)_3]^-$ as the dominant species when the pH is maintained between 7 to 10. Subsequently, $Au(OH)_3$ gets precipitated out on the surface of oxide support which is then reduced to form gold nanoparticles of the size ranging from 1.5−5 nm as summarized in figure 04. Urea is an alternative reagent for NaOH which can be used.[31]

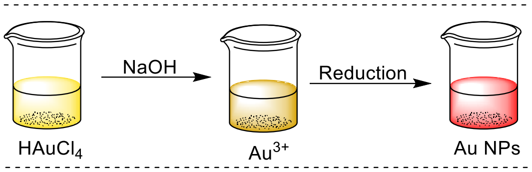


Figure 04:- Schematic representation of the Deposition precipitation method**.**

5. Types of Supports used for Nanoparticles

A supported nanoparticle acts as a heterogeneous catalyst and hence, can be easily recovered from the reaction medium and reused. In certain cases, the support prevents the agglomeration of the nanoparticles by preventing sintering although it does not exhibit a catalytic activity of its own. [32,33]

5.1. Oxide supports

Currently, nano-catalysis by metal/metal oxide supported catalysts has been at the cutting edge as they have given better yields compared to those without support**.**[34] Oxides of numerous metals like zinc, magnesium, calcium, titanium and silicon are used as supports for nanoparticles. The majority of the supports contain silica in some form or the other like zeolites, Santa Barbara Amorphous-type material abbreviated as SBA-15, and sol-gels like Gomasil G – 200. [35]

5.2. Carbon supports

Due to its noteworthy properties like high conductivity, chemical inertness and high surface area, carbon has been a famous choice as support for a very long time.[33,36] Charcoal is the most commonly used form of carbon which is used as a support. Activated charcoal can be modified depending on the requirement by altering its porosity, distribution of pores and surface area. Carbon-based supports are a key component of numerous reactions like Suzuki coupling reaction, Heck reaction, hydrogenation of unsaturated compounds and many others. [33,36]

5.3. Silica, Alumina and Titania

Oxides of aluminium, silicon, and titanium are used as supports. Oxides of aluminium are of two types- alpha and gamma-alumina. Gamma alumina is most commonly used since it exhibits better properties in terms of chemical stability, thermal stability, and porosity. Titania is titanium dioxide and exists in three types- anatase, brookite, and rutile. Anatase is the most frequently used type because it exhibits a higher surface area and networks strongly with the nanoparticles. Of them all, silica is widely used as a support as it is abundant and cheap, especially the amorphous form of silica. SBA-15 is a popular choice as support. F. Rajabi et al. in 2015 synthesized iron oxide nanoparticles supported on SBA-15 for carrying out oxidative esterification of various aldehydes. [33]

5.4. Metal-organic frameworks

Metal-organic frameworks (MOF) are very porous materials that are a blend of inorganic and organic composite materials fabricated from metal ions/ clusters with organic linkers to generate a three-dimensional coordination network. They are a desirable class of supports since they offer tunable porous structures in addition to having a larger surface area. The property of being tunable helps in the formation of a variety of structures with variable pore sizes and different metals/ligands. Since they have low chemical and thermal stability, they pose a limitation for long-lasting usage.[37] MOFs have an extensive microstructure and so, nanoparticles cannot be easily hosted into the pores. This results in the deposition of the nanoparticles on the outer surface instead, which makes the structure unstable. To address this limitation, various strategies have been developed by different groups of researchers. L. Chen and Q. Xu have developed a double solvent method to take care of this limitation and easy fabrication of nanoparticles inside the MOF.[38]

6. Monometallic nanoparticles

Monometallic nanoparticles are composed of just one metal and the properties exhibited by them are solely dependent on that metal. Various monometallic nanoparticles have been extensively employed for esterification reactions in the last few years.[26]

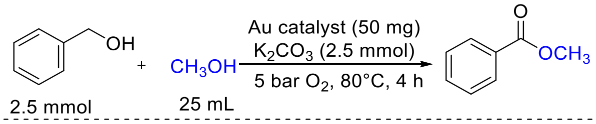
6.1. Gold (Au) nanoparticles catalyzed reactions

Earlier it was thought that since gold is chemically inert it was best used in jewelry and as a coinage metal.[39] Its role in catalysis was explored later by Haruta and Hutchings, who discovered heterogeneous catalysis by gold. They are leading personalities in this field currently.[31] They studied CO oxidation by molecular oxygen at low temperatures on oxide supported gold nanoparticles which lead to the development of the idea that the nanometer range size of gold nanoparticles was the major component responsible for the efficiency of a reaction.[35]

Gold is seen as a kind of ‘Philosopher’s stone’ in catalysis as it is capable of catalyzing a wide variety of transformations.[10] Metallic gold binds very weakly to reactant and product molecules and hence, gold catalysts are highly selective and stable. Their efficiency depends on their size and the support which stabilizes reaction components.[40] Oxidative esterification can equip, as active catalysts, both gold nanoparticles and mononuclear gold complexes. [41]

In 2015, Rohul H. Adnan et al. compared the catalytic activities of two phosphine-capped gold clusters i.e. $Au_{101}(PPh_3)_{21}Cl_5$ [Au_{101}] and $Au_9(PPh_3)_8(NO_3)_3$ [Au_9] having mean sizes of 1.6 ± 0.3 nm and 0.8 nm respectively in the oxidative esterification of benzyl alcohols. These clusters were activated on supports namely fumed silica or titania (anatase) by sol-immobilization method where 0.17 wt.% gold on titania and 0.5 wt% on silica was used.

The catalyst was prepared by mixing the support and gold cluster with dichloromethane which was then either dried or calcined in the presence of oxygen. The catalyst was stored at a 4°C after wrapping the ampoule with an aluminium foil.



Scheme 01:- Gold nanoparticles catalyzed oxidative esterification of benzyl alcohol[39]

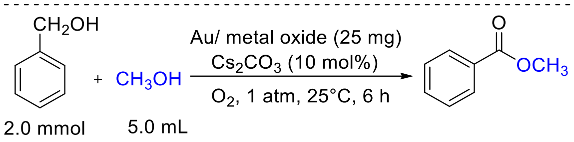
As per their studies, it is found that benzyl alcohol gets oxidized to benzaldehyde and after reacting with methanol to form methyl ester (Scheme 1). There is no formation of benzoic acid and then its reaction with methanol to yield ester. Hence, methyl ester directly gets formed after the benzaldehyde intermediate in the presence of oxygen and methanol. Anisole acts as an internal standard. Nanoparticle size is greater than 2 nm. Au_{101} based catalysts show maximum activity. TiO_2 supported catalysts showed better results than SiO_2 supported catalysts. The selectivity of methyl benzoate was found to change with a temperature change. Au_{101} showed better results as compared to Au_9 even though it had a larger nanoparticle size. This was because nitrate ion reduced the activity of the catalyst significantly. Hence, it was proved that the size of the nanoparticles merely does not define the catalytic activity, counter ions also play an important role.[39]

In 2015, H. Wei et al. synthesized gold nanoparticles supported on metal oxides namely CeO_2, ZrO_2, TiO_2, hydrotalcite (HT) and Al_2O_3 for the oxidative esterification of alcohols (Scheme 2) and aldehydes (Scheme 3). Out of these, Au/CeO_2 and Au/ZrO_2 were found to exhibit the best catalytic activities.

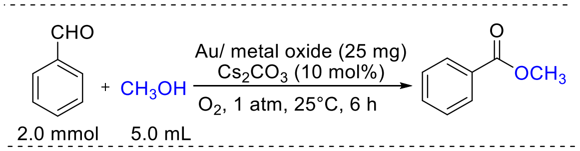
The catalyst was prepared by mixing the metal oxide in distilled water followed by the addition of $HAuCl_4$, L-lysine and sodium borohydride. A pH of around 9.5 was maintained. At the end of 24 h, the precipitate formed was washed and dried. The catalyst can be recycled up to ten times.[42]

Au/support	Size (nm)
Au/CeO_2	3-6
Au/ZrO_2	4-7
Au/TiO_2	5-7
Au/HT	10-13
Au/Al_2O_3	5-7

Table 1:- Size of gold nanoparticles depending on the support used.



Scheme 02:- Oxidative esterification of benzyl alcohol catalyzed by supported gold nanoparticles.



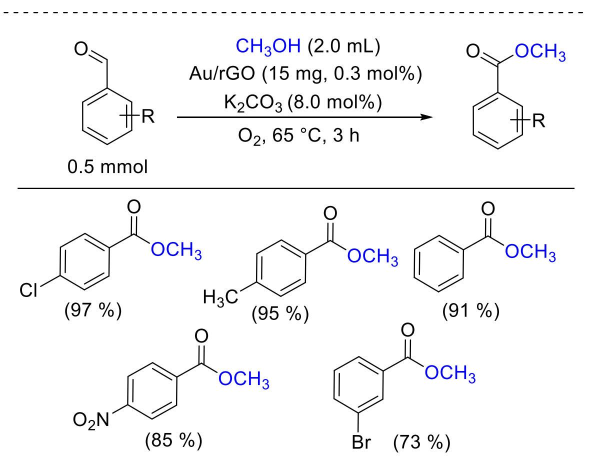
Scheme 03:- Oxidative esterification of benzaldehyde catalyzed by supported gold nanoparticles.

Better yields are always obtained when methanol is used as compared to ethanol because the methoxy group exhibits a higher nucleophilicity than the ethoxy group.

The mechanism proceeds through the alcohol (say primary alcohol) molecule coordinating with the support due to greater affinity between the oxygen atom of the alcohol group and Au metal. Due to the presence of a base (K_2CO_3) in the reaction medium, it abstracts the proton from the hydroxyl group of alcohol. The alcohol moiety then rearranges to form an aldehyde species. Another alcohol molecule adds to the carbonyl group via nucleophilic addition mechanism. Proton abstraction from the formed hemiacetal species, by the base, finally leads to the formation of ester.

In 2016, R. Pocklanova et al. demonstrated that gold nanoparticles deposited on graphene oxide (Au/rGO) can be used for aerobic oxidation of aldehydes to ester (Scheme 4). It was also reported that such supported gold nanoparticles exhibited better catalytic activities as compared to unsupported gold nanoparticles.

The catalyst was synthesized by mixing $HAuCl_4 \cdot 3H_2O$ solution and graphene oxide in distilled water. Sodium citrate solution was gradually added to this solution maintaining a temperature of 80°C. Au/rGO thus formed was washed with distilled water and ethanol and dried.



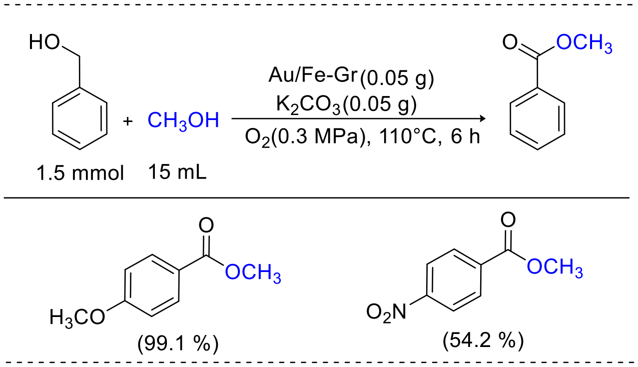
Scheme 04:- Oxidative esterification of benzaldehyde catalyzed by supported gold nanoparticles.

Transmission electron microscopy (TEM) results indicated the size of gold nanoparticles to be 12.5 ± 2.6 nm. Atomic absorption spectroscopy (AAS) analysis showed that the composition of gold was 4 % by weight in Au/rGO. The catalyst can be recycled up to five times. The product yield was not affected significantly by the presence of electron releasing and electron-withdrawing groups. [18]

In 2016, J. Sun et al. synthesized gold nanoparticles supported on iron-doped graphene by deposition precipitation method for the oxidation of benzyl alcohols to yield corresponding aldehydes, acids, and esters (Scheme 5). However, since the objective of the report revolves around esters, only information related to esters has been reported.

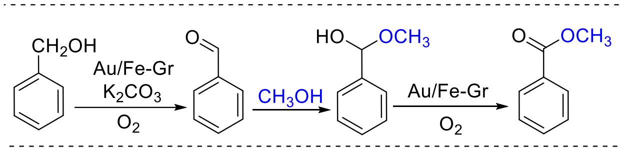
The catalyst was prepared by adding Fe-Gr support to $HAuCl_4$ aqueous solution of pH 9 and heated for 1 h with continuous stirring. The obtained precipitate was then filtered, washed, dried and subjected to calcination which the Au/Fe-Gr catalyst was ready to be used.

Spherical nanoparticles of size in the range of 15 nm-30 nm were detected by Scanning electron microscopy (SEM). The pore diameter of the catalyst was 2.8 - 4.3 nm as determined by the nitrogen physisorption experiment.



Scheme 05:- Oxidative esterification of benzyl alcohol catalyzed by supported gold nanoparticles.[20]

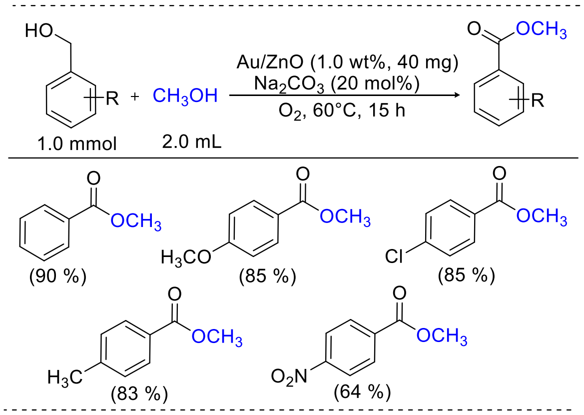
Benzyl alcohol gets oxidized to form benzaldehyde which further reacts with methanol to yield a hemiacetal intermediate. This is followed by oxidation of hemiacetal to form the corresponding ester (Scheme 6).



Scheme 06:- Mechanism of oxidative esterification of benzyl alcohol catalyzed by supported gold nanoparticles.

In 2018, S.M Galani et al reported the synthesis of Au supported on ZnO catalyst for the oxidative esterification of alcohols (Scheme 7). Gold nanoparticle size was found to be in the range of 3-4 nm and polyhedral in shape.

The supported catalyst was prepared by mixing ZnO nanoparticles with distilled water. An aqueous solution of urea and $HAuCl_4 \cdot 3H_2O$ solution was then added to the resulting solution. This was heated, centrifuged, washed with water and the white material was calcined to obtain the supported catalyst.



Scheme 07:- Oxidative esterification of benzyl alcohol catalyzed by supported gold nanoparticles.

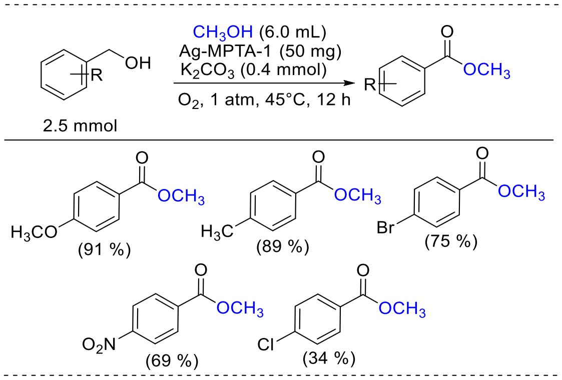
It was found that the presence of electron releasing groups enhanced the product yield whereas the presence of electron-withdrawing groups reduced the product yield. Both methanol and ethanol were found to be good solvents for the reaction. The catalyst can be conveniently detached from the reaction medium by simple filtration due to the larger size of ZnO nano-plates. The procedure for the manufacture of the catalyst and the mechanism behind the reaction was not discussed by the authors.[2]

6.2. Silver (Ag) nanoparticles catalyzed reactions

Although gold nanoparticles based oxidative esterification reactions result in high product yield, silver nanoparticles have an edge over them in being less costly than gold.[8] Silver nanoparticles have already been extensively used for reactions like coupling, cycloaddition, sigma tropic rearrangement, cyclo-isomerization and nitrene transfer reactions. In the last couple of years, different methodologies have been adopted for the fabrication of silver nanoparticles on various mesoporous materials.[3] Like a mesoporous poly melamine formaldehyde offering a high surface area, excellent porosity and a high density of amine and triazine functional groups. [10]

Non-air sensitive silver nanoparticles embedded mesoporous poly-triallyl amine nano-catalyst Ag-MPTA-1 was used for aerobic oxidative esterification of alcohols by N. Salam et al. in 2014. They synthesized silver nanoparticles supported on_mesoporous poly allylamine polymer (MPTA-1) for the oxidative esterification of alcohols (Scheme 8).

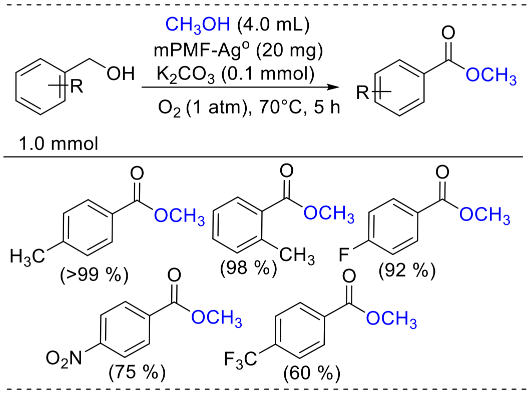
The catalyst was synthesized by mixing TRIS-stabilized silver nanoparticles and template-free MPTA-1 at room temperature. MPTA-1 turned black signifying the stacking of silver nanoparticles which was later recovered after centrifugation, washed with plenty of distilled water and dried.



Scheme 08:- Oxidative esterification of benzyl alcohol catalyzed by supported silver nanoparticles.

Thermogravimetric analysis (TGA) confirmed the stability of the catalyst up to a temperature of 200°C. The catalyst can be reused up to five times. The mechanism of the reaction was not discussed.[3]

In 2015, Islam et al. documented the synthesis of silver nanoparticles embedded on mesoporous polymelamine formaldehyde (mPMF-Ag^0) for the oxidative esterification of alcohols (Scheme 9). The catalyst was synthesized by mixing TRIS-stabilized silver nanoparticles, mPMF at room temperature. mPMF turned black signifying the stacking of silver nanoparticles on the support which was later recovered after centrifugation, washed with plenty of distilled water and dried.

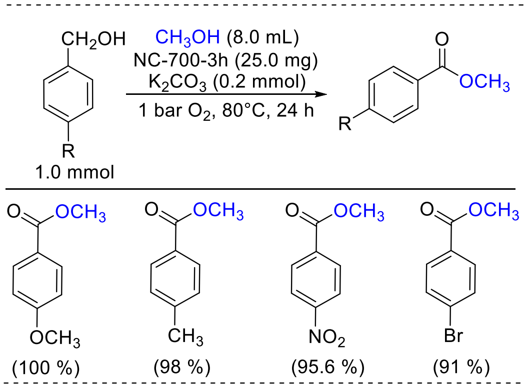


Scheme 09:- Oxidative esterification of benzyl alcohol catalyzed by supported silver nanoparticles.

The size of the silver nanoparticles was found to be 7.8 ± 0.2 nm as reported by TEM. The catalyst was stable up to 500°C and can be recycled up to six times. No mechanistic studies were done by the group. Catalyst is also stable towards oxygen and moisture. [8]

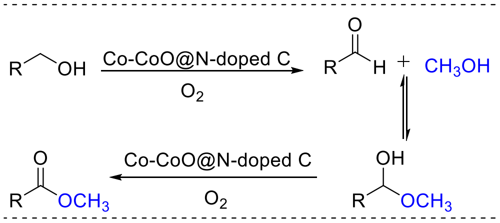
6.3. Cobalt (Co) nanoparticles catalyzed reactions

Cobalt exhibits a variable oxidation state and hence, can efficiently transfer electrons. It is also abundant on the earth and hence, is a good choice for catalysis**.** [14] In 2015, Zhou Y.X et al found in a study that nitrogen-doped porous carbon consisting of cobalt and CoO nanoparticles is capable of oxidative esterification of alcohols in the presence of molecular oxygen, a benign oxidant (Scheme 10). Zeolite type MOF, ZIF-67 nanocrystals were prepared by them. An aqueous solution of $Co(NO_3)_2$ and 2-methylimidazole was thoroughly stirred after mixing at room temperature. The nanocrystals thus formed were then subjected to pyrolysis at different temperatures under nitrogen atmosphere to form Co-CoO@N-doped porous carbon nanocomposites. It was observed that NC-700-3 h, exhibited the best activity for six catalytic cycles under the following reaction conditions: 1 mmol benzyl alcohol, 8 mL methanol, 25 mg catalyst, 0.2 mmol K_2CO_3 and 1 mmol dodecane was added as an internal standard.



Scheme 10:- Oxidative esterification of benzyl alcohol catalyzed by supported cobalt nanoparticles.

The catalyst is comparatively cheaper when compared to noble metal nanoparticles, exhibits good stability and being strongly magnetic, could be conveniently separated from the reaction medium. One-step oxidation of alcohol esters is always preferred as it prevents the formation of numerous by-products and use of too many reagents. This also follows Green chemistry principles to some extent. Based on the above outcomes, a probable reaction mechanism for the oxidative esterification of alcohols over Co-CoO@N-doped carbon nanocomposites is illustrated in Scheme 11.



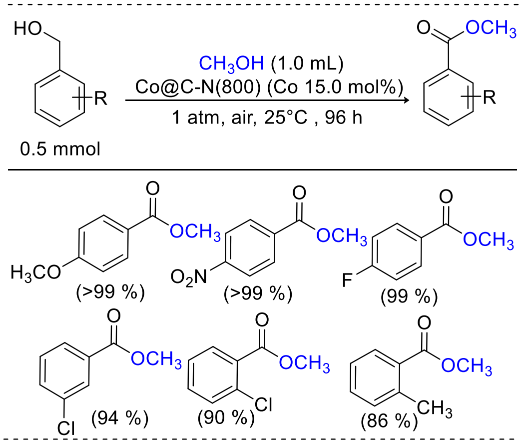
Scheme 11:- Mechanism of synthesis of methyl ester by oxidative esterification of alcohol.

Alcohol is converted to aldehyde in the presence of oxygen. It is the rate-determining step.

This is followed by the formation of a hemiacetal species as a result of the reaction between the aldehyde and methanol. Finally, the hemiacetal species gets converted to ester in the presence of oxygen and Co-CoO@N-doped carbon. [43]

In a similar study by Zhong W. et al. in 2015, it was found that C-N embedded cobalt nanoparticles with ZIF-67 ie. [Co(MeIM)$_2$], MeIM = 2-methylimidazole) as metal-organic framework (MOF) precursor is capable of aerobic oxidative esterification of alcohols (Scheme 12).

To prepare Co@-N, ZIF- 67 was treated under thermal conditions in presence of an inert atmosphere namely argon gas. It was observed that Co@C-N(800) demonstrated the maximum efficiency concerning both conversion and selectivity where the reaction conditions were 0.5 mmol p-nitrobenzyl alcohol, 1 mL methanol, 4 mL n-hexane, Co (15 mol%) catalyst, P=1 atm, 25°C, in air, 96 hr. 4mL n-hexane was used as an internal standard.



Scheme 12:- Oxidative esterification of benzyl alcohol catalyzed by supported cobalt nanoparticles.

They have reported that the percentage conversion and percentage yield with Co@C-N(800) is greater than 99% at room temperature and atmospheric conditions. Even in the nonexistence of any base/basic medium and noble metals, the yield has been phenomenal.

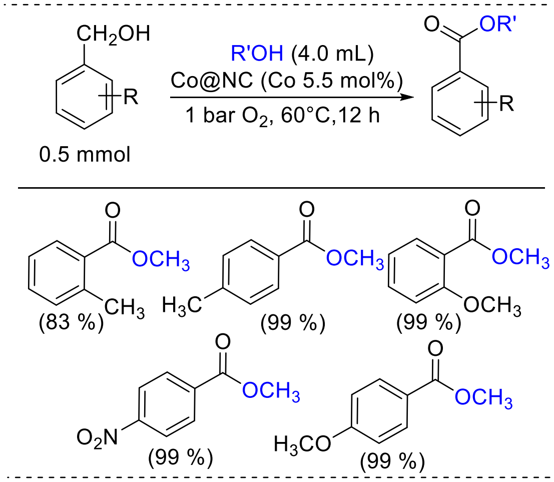
On average, the catalyst can be efficiently used for up to five cycles. If at all reactivity of the catalyst was lost after a few cycles, it was possible to regain its activity by treating it with hydrogen gas at 400°C for 1 h. In powder X-ray diffraction (PXRD) results, diffraction peaks were of high intensity after hydrogen treatment whereas faint without it. Hence, proved that cobalt might get oxidized due to which its diffraction peaks are faint and hence after reduction with hydrogen, back to normal. The mechanism is the same as Scheme 11 where the alcohol is first oxidized to an aldehyde and then the aldehyde reacts with another molecule of alcohol to produce the ester. The only difference is that the latter step is the rate-determining step in this case. [44]

In 2016, H. Su et al developed nitrogen-rich carbon-coated cobalt nanoparticles (Co@NC) for the oxidative esterification of alcohols (Scheme 13).

The preparation of the catalyst, Co@NC-4 required the addition of g-C_3N_4 to a solution containing cobalt nitrate hexahydrate, 1,4-benzenedicarboxylic acid and triethylene diamine in dimethylformamide (DMF). Likewise, Co@NC-0, Co@NC-0.3, Co@NC-2, Co@NC-6 were prepared by adding the corresponding mass of g-C_3N_4. The resulting powder was heated to a nitrogen atmosphere after removing the solvent. The black powder thus formed was then used for the catalytic reactions.

The size of the cobalt nanoparticles in the Co@NC-x samples was found to be between 28 and 30 nm as per TEM analysis. Inductively coupled plasma (ICP) analysis showed that 16 wt% Co is present in Co@NC. High-resolution transmission electron microscopy **(**HRTEM) analysis discovered the carbon layers layered around cobalt nanoparticles resembling a shell and were found to prevent the aggregation and oxidation of the cobalt nanoparticles. Co@NC-4 exhibited the best activity. It was expected that Co@NC-6 would have the best performance, however, it did exhibit good activity and it was concluded that merely increasing the nitrogen content in the support did not increase the catalytic activity.

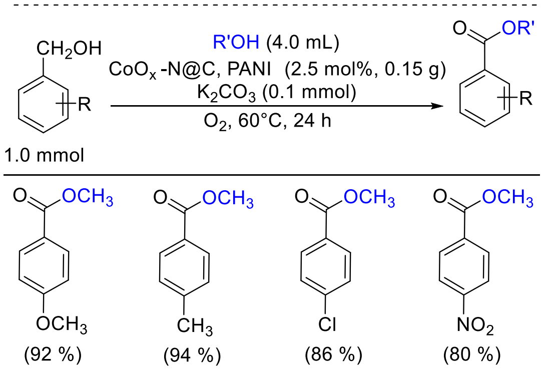
In 2017, Vineeta P. et al developed nitrogen-doped carbon-supported cobalt nanopowder (CoOx-N@C, PANI) for oxidative esterification of alcohols (Scheme 14). The catalyst was prepared by pyrolysis of polyaniline (PANI) grafted cobalt(II) acetate. It is a heterogeneous catalyst for oxidative esterification of alcohols in the presence of oxygen as an oxidant and more efficient than the commercially available cobalt oxide catalyst.



Scheme 13:- Oxidative esterification of benzyl alcohol catalyzed by supported cobalt nanoparticles.[14]

Oxidation of benzyl alcohol derivatives was observed under the following reaction conditions: 1.0 mmol of the substrate, 4 mL methanol, 0.1 mmol K_2CO_3, 2.5 mol%, 0.15 g CoO_x-N@C catalyst. Derivatives containing electron-withdrawing groups like 4- Chlorobenzylalcohol, 4- Bromobenzylalcohol and 4-Nitrobenzylalcohol had yielded between 75-85 % whereas allylic alcohols exhibited a maximum yield of approximately 95 %. The yield of allylic substituted benzyl alcohols was between 80-90 %. Good yields were attributed to the fact that sturdy interactions existed between nitrogen and cobalt atoms which lead to higher stability and hence, greater efficiency of the catalyst. The exact mechanism of the reaction involved is not known currently and needs to be explored in the future.[45]

All of the above-mentioned catalysts have shown remarkable recyclability. On average, cobalt-based catalysts can be recycled up to six times.

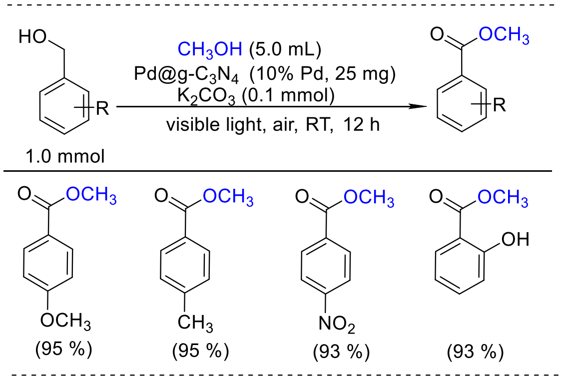


Scheme 14:- Oxidative esterification of benzyl alcohol catalyzed by supported cobalt nanoparticles.

6.4. Palladium (Pd) nanoparticles catalyzed reactions

Palladium is readily available and cheap and so extensively being used.[26] In 2018**,** S. Verma et al. synthesized palladium nanoparticles on graphitic carbon nitride Pd@g-C_3N_4 for direct oxidative esterification of alcohols using atmospheric oxygen as a co-oxidant via photocatalytic C-H activation (Scheme 15).[46] The catalyst shows good activity and can be reused for five cycles. The catalyst was synthesized by mixing $Pd(NO_3)_2$ in water with Graphitic carbon nitride (g-C_3N_4) dispersed in water. The resulting solution was thoroughly stirred and heated. An excess of $NaBH_4$ was added to the solution. The solution turned black resulting in the formation of the catalyst, which is then recovered by centrifuging, followed by washing with methanol and is then dried.

Nitrogenous electron-rich photoactive chromophore accelerates the C-H activation by visible light adsorption. It helps in overcoming the transition barrier by providing the desired activation energy. Aerial oxygen is trapped by Pd@g-C_3N_4 and used in the C-H bond activation and ensuing oxidation esterification. Oxidative esterification by C-H Bond activation gave good yields.



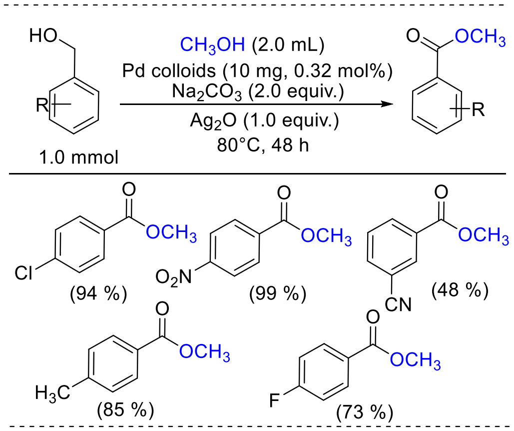
Scheme 15:- Oxidative esterification of benzyl alcohol catalyzed by supported palladium nanoparticles.

Product yield directly depended on the percentage of palladium only till 5 % concentration after which the yield remained unaffected. The product yield remained unaffected by the presence of electron releasing and electron-withdrawing groups**.**

In 2019, Kapdi et al described the oxidative esterification of benzylic alcohols by palladium nanoparticles with Ag_2O as an oxidant (Scheme 16). [47]

The catalyst was synthesized by mixing the palladacycle, K_2CO_3, and 4-chlorobenzaldehyde sequentially to an oven-dried Schlenk tube. Chloroform was added and the resulting mixture was continuously stirred. This was followed by heating the mixture and ethanol were added at the end of 24 h to the cooled mixture. It was then centrifuged to collect a black powder, washed, vacuum dried, and stored safely.[48]

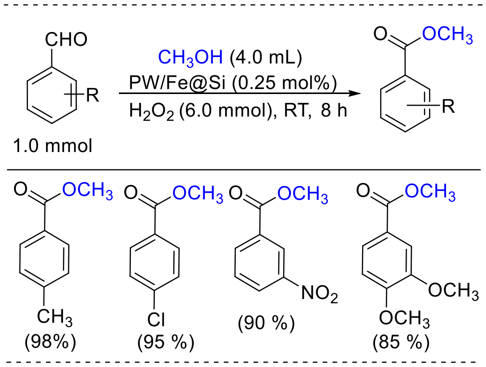
The catalyst was found to be selective towards primary alcohols and the product yields were satisfactory. Due to the synergy existing between silver and palladium, the catalytic activity was found to be enhanced.



Scheme 16:- Oxidative esterification of benzyl alcohol catalyzed by supported palladium nanoparticles.

6.5. Iron (Fe) nanoparticles catalyzed reactions

In 2013, E. Rafiee, S. Eavani developed Keggin-structured $H_3PW_{12}O_{40}$ (PW) which was magnetically separable and had strong acidic sites on the surface of the catalyst. (Scheme 17).[49] Co-precipitation method was adopted for the preparation of γ-Fe_2O_3 nanoparticles. The catalyst was synthesized by mixing an aqueous solution of $FeCl_2.4H_2O$ with an aqueous solution of $FeCl_3.6H_2O$ and the pH of the resulting solution was maintained between 11- 12. This led to the formation of a black dispersion. After stirring, the solution was heated which resulted in the formation of a brown dispersion. The solution was then centrifuged repeatedly four times to get a brown dispersion. Ammonia solution was added to it followed by the addition of tetraethyl orthosilicate (TEOS) and it was stirred. At the end of 24 h, Fe@Si nanoparticles thus formed were recovered using a magnet, washed thoroughly with alcohol and diethyl ether and then dried.



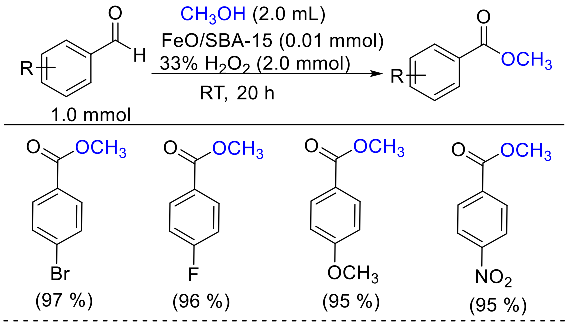
Scheme 17:- Oxidative esterification of benzaldehyde catalyzed by supported iron nanoparticles.

The size of the nanoparticles was 92 nm and they were spherical in shape. The catalyst could be conveniently recovered from the reaction mixture employing a permanent magnet and reused up to four times. The product yield remained unaffected by the presence of electron releasing and electron-withdrawing groups.

In 2015, F. Rajabi et al. synthesized supported iron oxide nanoparticles for the oxidative esterification of numerous aldehydes (Scheme 18). Iron has the advantage of being benign and iron nanoparticles exhibit good catalytic activity.[50]

The catalyst was prepared by adding a solution of salicylaldehyde to the aminopropyl-functionalized SBA-15 materials resulting in a yellow solution. $Fe(NO)_3{\cdot}9H_2O$ was added to it after 6 h and heated on a low flame for 24 h. A dark red color developed as a result of the development of the iron oxide nanoparticles on SBA-15. The produce was thoroughly washed with methanol and water and dried in an oven 8 h.[51]

Under the following reaction conditions: 1 mmol aldehyde, 2 mL of alcohol, 2 mmol of 33% hydrogen peroxide, 0.01 mmol of 10 mol% Fe nanoparticles at room temperature for 20 h, the reaction was monitored by Thin Layer Chromatography(TLC). The reaction was found to be efficient with a majority of aromatic systems as the presence of electron-withdrawing or electron releasing groups did not affect the yield of the products. In the case of sterically hindered substrates, the yield decreased only slightly. Catalyst can be used up to eleven times after which the yield of the product obtained is up to 80 %. This is still very high compared to other catalysts used.



Scheme 18:- Oxidative esterification of benzaldehyde catalyzed by supported iron nanoparticles.

Yields of the esters were obtained mostly above 90 % and the percentage yield of some esters was even 98 %. The reaction can be carried out at room temperature. The reaction favored kinetic products over thermodynamic products due to the presence of numerous catalytic sites present in the catalyst and so the reaction occurs at a higher rate. The detailed mechanism of the reaction was not elucidated. It was thought to proceed through the activation of the carbonyl oxygen by the iron oxide nanoparticles and esterification in the presence of alcohol. The catalyst exhibited both Lewis acidity and redox activities like oxidation as per the reaction conditions.

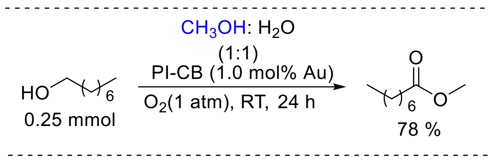
7. Bimetallic Nanoparticles

These nanoparticles consist of two different metals and their properties are dependent on these two metals**.** It is commonly observed that bimetallic nanoparticles have enhanced properties as compared to monometallic because for various reasons. First of all, due to electronic interactions between the metal atoms, a synergistic effect exists between them**.** Secondly, they have additional degrees of freedom. Thirdly, two metals offer a greater surface area. Lastly, the ligand effect and ensemble or dilution effect of bimetallic clusters come into the picture. Ensemble effect refers to the change in the catalytic activity of a metal which happens due to a change in its surface geometry with the addition of modifying metal. Similarly, the ligand effect is the change in the electronic properties of a catalyst due to the addition of another metal. This change in catalytic activity can be monitored by observing the turnover frequency (TOF) of the catalyst. However, there are a few cases where bimetallic nanoparticles do not exhibit better catalytic activities when equated to their monometallic counterparts. For example, Au/Pd bimetallic nanoparticles in water-gas shift reactions, carbon monoxide oxidation, and decomposition of formic acid to CO2 and H2, perform poorly as compared to only gold nanoparticles. Hence, more studies need to be conducted to determine the actual reasons behind such anomalies. [26,32,35]

7.1. Au/Pd nanoparticles catalyzed reactions

Bimetallic nanocluster catalysts in most cases show a distinctive activity when compared with monometallic nanoclusters. In 2010, K. Kaizuka et al found that polymer-incarcerated(PI) Au/Pd is capable of oxidizing alcohols under neutral conditions (Scheme 19).[52] The overall activity is however unequivocally dependent on the combination of metals and solvent systems. The catalyst cluster size was found to be 2-2.5 nm with Au: Pd ratio of either 4:1 or3:1.

When the ratio of Au in PI-CB/Au-Pd was higher, greater selectivity in ester formation was observed whereas its ratio was lower, selectivity for ester formation drastically reduced. The catalyst containing 1:1 ratio of Au/Pd was found to exhibit the maximum ester selectivity. Mechanistic studies were not carried out by the group and hence, not reported.



Scheme 19:- Oxidative esterification of aliphatic alcohol catalyzed by Au/Pd.

In 2017, C.H. Tsai et al. stated the importance of mesoporous silica nanoparticles (MSN) as a better choice for being selected as a support because it has a very large surface area and extremely small pore size. The catalyst can be recycled up to three times.[53]

The supported catalyst was prepared by adding $Pd(OAc)_2$ in dry toluene solution to Au complex MSN. The resulting solution was stirred for 3 h, filtered and washed extensively with methanol and toluene. It was then dried for 24 h under vacuum. The molar ratio between Pd and Au ie. “x” can be altered to form Pd-Au@MSNs-x. The catalyst was prepared by the sequential impregnation method.

Pd-Au@MSN-1.8 exhibited maximum activity with percentage yield and percentage conversion both greater than 99 % in the presence of benzyl alcohol as substrate, methanol, 0.5 mol% catalyst, 1 equiv. K_2CO_3 and 60°C. Performance of the catalyst increased with an increase in the ratio of Pd/Au ratio (Scheme 20).

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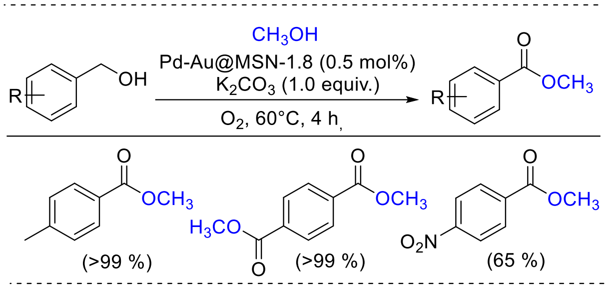


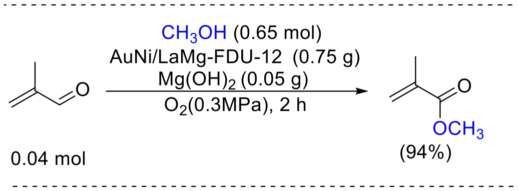
Scheme 20:- Oxidative esterification of benzyl alcohol catalyzed by Pd/Au.

7.2. Au/Ni nanoparticles catalyzed reactions

Nickel is a desirable choice as a component of a bimetallic nanoparticle because it is stable and cheaper than Au which balances the overall cost of the catalyst.[26] In 2014, J. Han et al. synthesized Au–Ni nanoparticles on the La–Mg composite oxide modified FDU-12 which catalyzed oxidative coupling of the aldehyde with methanol to generate esters (Scheme 21).[5] The catalyst had a particle size of 2.3 nm as observed from TEM.

The catalyst was prepared by treating FDU-12 with Lanthanum(III) nitrate and magnesium nitrate solutions after which it was calcined. It was again calculated after the addition of nickel and gold precursors to finally generate AuNi/LaMg–FDU-12 catalyst.

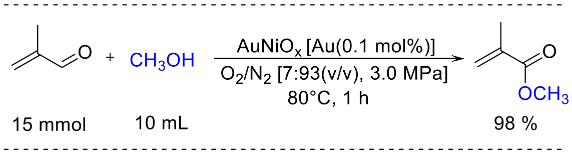
Bimetallic AuNi/LaMg–FDU-12 catalyst was more proficient than monometallic gold and nickel nanoparticles due to the synergistic effect between the two metals. Increase in temperature to 90°C increased the product yield.



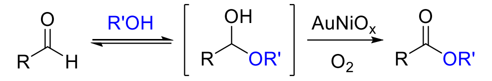
Scheme 21:- Synthesis of methyl methacrylate catalyzed by Au/Ni nanoparticles.

Position of electron releasing groups in aromatic aldehydes did not have any significant effect on the product yield, however, the presence of electron-withdrawing groups at ortho position remarkably reduced the product yield. The exact mechanism behind the catalysis was not mentioned.

In 2019, Suzuki K. et al. stated that the efficiency of oxidative esterification of methacrolein was found to directly depend on the percentage composition of Au and NiO (Scheme 22). Maximum activity was reported at 20 mol % Au.[54] The selectivity and percentage yield of the corresponding esters were fairly good with methanol but relatively poor with n–butane which was attributed to steric hindrance in the alcohol. The reaction conditions maintained were mild and neutral. Size of the nanoparticles was found to be in the range of 2–3 nm and the $AuNiO_x$ had a core-shell structure as reported by the TEM/STEM-EDX, UV-vis and FTIR techniques.



Scheme 22:- Oxidative esterification of aldehydes in the presence of $AuNiO_x$.



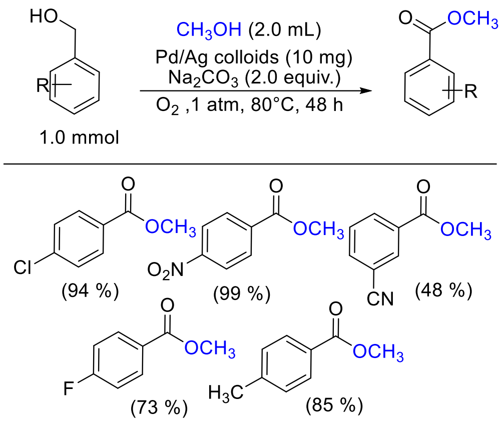
Scheme 23:- Mechanism of oxidative esterification of aldehydes in the presence of AuNiO$_x$.

Aldehyde and alcohol react to form hemiacetal intermediate which subsequently leads to the formation of ester in the presence of AuNiO$_x$ catalyst and molecular oxygen (Scheme 23).

7.3. Pd/Ag nanoparticles catalyzed reactions

In 2019, Sable et al synthesized Pd/Ag bimetallic catalyst for the oxidative esterification of alcohols in the presence of oxygen, a benign oxidant (Scheme 24).[47] The catalyst was prepared by mixing Hermann-Beller palladacycle with 4-chlorobenzaldehyde in chloroform. Silver acetate and potassium carbonate were then added and the solution heated for 24 h. The black powder thus formed was separated by centrifugation, washed with deionized water, suspended in ethanol, and finally dried.

It was found that sterically hindered substrates significantly reduced the product yield. The size of the bimetallic nanoparticles was found to be 2-5 nm by HRTEM analysis. Since the catalyst is easy to synthesize, its inability to get reused does not become a major demerit.



Scheme 24:- Oxidative esterification of benzyl alcohol catalyzed by Pd/Ag nanoparticles.

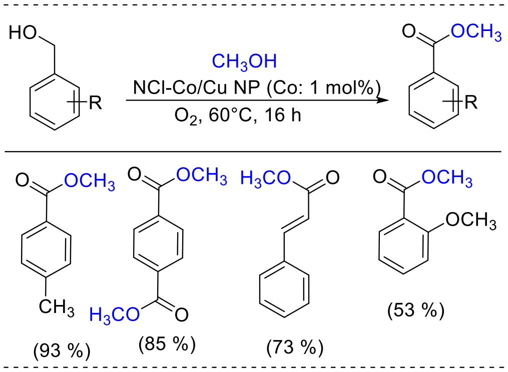
The proposed mechanism is as follows- Ag(0) in the presence of oxygen, gets oxidized to Ag(I) which then oxidizes benzyl alcohol to benzaldehyde. Palladium then gets coordinated to benzaldehyde via an oxidative addition mechanism. Meanwhile, the base abstracts a proton from the methanol. Methoxide ion attacks the carbonyl carbon of benzaldehyde via nucleophilic addition reaction. Pd(0) and the corresponding ester get formed.

7.4. Co/Cu nanoparticles catalyzed reactions

In 2018, T. Yasukawa et al. reported the synthesis of nitrogen-doped carbon-incarcerated (NCI-M) cobalt/copper bimetallic nanoparticle-based catalysts for the oxidative esterification of alcohols and aldehydes (Scheme 25). Both the metals involved in the bimetallic nanoparticles are abundant and hence, a preferred catalyst. [55]

The catalyst was prepared by treating Poly(4-vinylpyridine), Co(OAc)$_2$.4H$_2$O and carbon black with sodium borohydride which resulted in the formation of cobalt nanoparticles. The addition of ethanol to it caused microencapsulation of cobalt on the polymer matrix. Pyrolysis of the encapsulated cobalt resulted in the formation of NCI-Co/M.

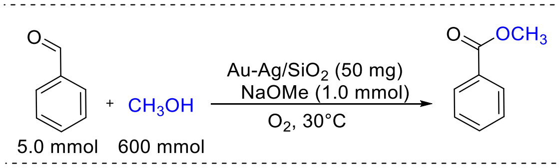
STEM analysis revealed the size of metal nanoparticles was 30 to 200 nm in NCI-Co/Cu 4 and 20 nm in NCI-Co/Cu 5. The catalyst could be recycled up to ten times.



Scheme 25:- Oxidative esterification of benzyl alcohol catalyzed by Co/Cu nanoparticles.

7.5. Au-Ag/ SiO_2 nanoparticles catalyzed reactions

In 2015, R. Vadakkekara et al. reported the synthesis of Au/Ag alloy nanoparticles supported on silica for oxidative esterification of benzaldehyde (Scheme 26).[19] The catalyst was prepared by sequentially adding $AgNO_3$ and $HAuCl_4$ to an aqueous solution of cetyltrimethylammonium bromide. $NaBH_4$ was then added as a reducing agent. The required amount of the Ag-Au nanoalloy and silica were then mixed for 24 h, dried and calcined to obtain the red-colored bimetallic catalyst supported on silica.



Scheme26. Oxidative esterification of benzaldehyde catalyzed by Au-Ag/ SiO_2 nanoparticles.

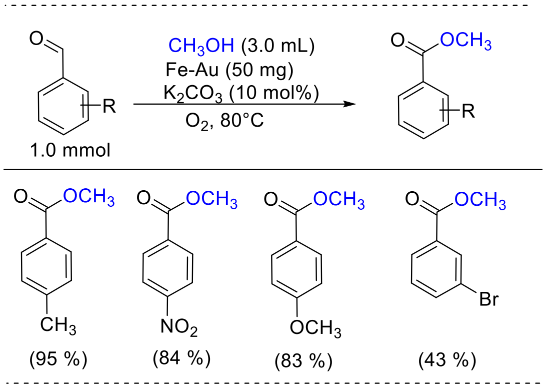
Mechanistic details and substrate scope were not reported. TEM analysis indicated the particle size of the nanoparticles to be up to 14 nm. Product yield was found to depend directly on the weight percentage of silver in the catalyst. Maximum catalytic activity was observed with an Au: Ag ratio of 3:1. The catalyst can be recycled up to five times.

7.6. Fe/Au nanoparticles catalyzed reactions

In 2014, M.B. Gawande et al. reported Fe/Au catalyzed oxidative esterification of aldehydes and reduction of aromatic nitro compounds (Scheme 27).[34] Fe is abundant metal and so preferred for catalysis.

The catalyst was prepared by mixing aqueous solutions of maghemite and gold(III) chloride trihydrate. The resulting solution was then stirred and its pH was adjusted to 12–13. The catalyst was recovered and washed thoroughly with distilled water. It was then dried and stored safely. The catalyst yield was reported to be 98 %.

The size of the maghemite was found to be 17.2 nm and the gold size was 4.0 nm as determined by XRD analysis. ICP-AES analysis revealed the gold content in the catalyst to be 3.94 %. Mechanistic details were not reported. The situation of electron-withdrawing groups on the substrate reduced the product yield. The catalyst can be recycled up to five times.



Scheme 27:- Oxidative esterification of benzaldehyde catalyzed by Fe/Au nanoparticles.

8. Applications of esters

Esters have numerous applications in various industries which contribute immensely to the Gross Domestic Product (GDP) of a country. Some of the major applications are as follows-

8.1. Flavors

Esters have a wide range of applications in the food industry mainly in the bakery items, ice creams, chocolates, jellies, wines and many beverages. The typical aroma enhancing compounds in fruits like apple, banana, grapes and orange are esters only.[56] Some of the esters present in common flavors have already been mentioned in table 2. Encapsulation of esters is a necessity to preserve their active ingredient for a longer time.[4] Beer is a combination of various esters and alcohols. Although the presence of esters in the beer is like a drop in the ocean**,** they are equally responsible for determining the flavor since they have a low odor threshold.[57]

8.2. Cosmetic industries

This includes everyday personal care products like soaps, perfumes, moisturizers, creams, shampoos and shower gels. The fragrances in these products are mainly due to the ester components. Besides providing the aroma, esters may also act as surfactants or antioxidants. Parabens, a group of the alkyl esters of p-hydroxybenzoic acid and methylparaben, ethylparaben, propylparaben, and benzyl paraben are a major component of cosmetic products, toiletries, and pharmaceuticals.[58] They offer low toxicity, antimicrobial activity and being non-volatile is very stable. [59] In 2015, the global market for flavors and fragrances was found to be worth twenty-six billion dollars and is expected to reach thirty-seven billion dollars by 2021.[4]

8.3. Lubricants

Esters that are stable at high temperatures and resistant to oxidation are preferred for being used as lubricants in the turbine engines of airplanes. Neopentyl polyol esters are widely used in jet turbines as well as additives in silicones. Esters of long carbon chain compounds have higher flash points and viscosity and VI value. Therefore, esters of straight-chain carboxylic acids are preferred over branched-chain carboxylic acids.[60]

8.4. Antimicrobial and antioxidant agents

Many esters are widely used due to their antimicrobial, larvicidal, and antioxidant activities. Methyl benzoate, benzyl acetate, and cinnamyl acetate can kill the larvae of the *Aedes aegypti* mosquito. Similarly, eugenol acetate exhibits antimicrobial properties. Benzyl benzoate is not only larvicidal against the *Aedes aegypti* mosquito but is also used to cure scabies, a skin disease. Benzyl benzoate is one of the oldest drugs effective in treating exceedingly contagious skin infections, scabies. However, benzyl benzoate should be properly encapsulated before being administered directly on the skin as it causes a sharp burning sensation. [4]

8.5. Polyesters in textiles and plastics

Polyester is the result of a condensation reaction between ethylene glycol and terephthalic acid. Polyester fabrics became popular in the late 1970s and are still very prevalent amongst the synthetic fabrics in the market. Some notable examples of polyesters widely used in the garment industry are polytrimethylene terephthalate and polybutylene terephthalate. They are widely used since the raw materials for their synthesis are low-cost and the fabric produced is soft, elastic, stable and convenient to dye.

Polyesters are a major component in plastics too. Unsaturated polyesters are synthesized from the reaction between either maleic acid or fumaric acid and ethylene glycol. The reaction is catalyzed by benzoyl peroxide. Such polyesters can also be used as a component in pipes, helmets, furniture, the body of automobiles etc. [64]

9. Conclusion and future perspectives

Numerous research groups have contributed novel ideas in the synthesis of esters by oxidation of alcohols using oxygen, a benign oxidant in the last decade. Synthesis using greener methods is of paramount importance right now. The selectivity of the reactions needs to be increased to prevent the use of alcohols in excess and hence, develop stoichiometric reactions. Currently, the detailed mechanism behind the esterification reactions is not known and hence, more studies on the reaction mechanisms need to be undertaken in the future so that successful variations in the experimental conditions can be done to obtain even better product yields and improve upon the limitations.[41] The stability of the flavors/aroma imparted by the aromatic esters has been a less explored area and hence, more studies in this area would be fruitful

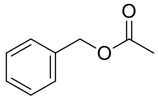
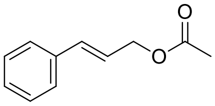
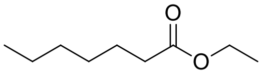
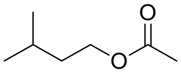
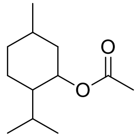
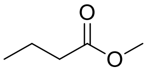
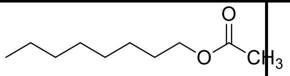
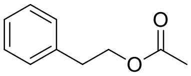
Sr. no	Structure	Name	Source
1		Benzyl acetate	Jasmine
2		Cinnamyl acetate	Cinna-mon
3		Ethyl heptanoate	Grapes
4		Isoamyl acetate	Pear, Banana
5		Menthyl acetate	Pepper-mint
6		Methyl butyrate	Apple
7		Octyl acetate	Orange
8		Phenethyl acetate	Honey

Table 2:- Esters behind the odor of some commonly encountered substances.

for the food and cosmetic industries.[4] The scope of the substrate needs to be explored further in terms of sterically hindered substrates, substrates with electron-withdrawing groups, and more diverse substrates. Consequently, the reaction conditions need to be modified to obtain better product yields. The recyclability of the catalysts needs to be improved further for making the overall process economical especially in the cases where noble metals are used as the catalysts. Attempts to synthesize esters via single pot synthesis methods need to be understood in more detail to make the process facile. Lastly, the reaction conditions need to be modified such that the duration of the reaction is minimal which in turn reduces the cost of the overall process.

Acknowledgements

The authors would like to thank the ICT-IOC, Bhubaneshwar for providing a fellowship to H.S and Chemistry department, ICT-Mumbai for a research project to RB.

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