Selective oxidation of alcohols by supported gold nanoparticles: recent advances
Anuj S. Sharma, Harjinder Kaur* and Dipen Shah

Industrially, oxidation of alcohols is very important as they are starting materials for a variety of ketones, aldehydes, acids, etc. required to produce plastics, detergents, paints, cosmetics, food additives and drug intermediates. The potential of gold nanoparticles (AuNPs) in oxidation, in general, is immense owing to its tendency to dissociate dioxygen. Supports play a vital role not only in the synthesis and stabilization of nanoparticles, but can also look after the issues of sustainability by facilitating separation, recycling and recovery of catalyst. In the oxidation of alcohols, supports also control the outcome of the reaction. This review aims to systematically discuss the recent developments in the selective oxidation of alcohols catalyzed by supported gold nanoparticles. We draw attention to the impressive progress that has taken place in the oxidation of alcohols in the last thirteen years, leading to several green, sustainable and highly efficient protocols. The effect of a support on the remarkable properties of gold nanoparticles in terms of its catalytic activity, selectivity, recyclability, and stability is discussed at length. Mechanistic aspects of these conversions are discussed in brief.

1. Introduction

Bulk gold typically exhibits a very poor catalytic activity as it is stable and inert in comparison to other transition metals present in the periodic table. After the discoveries that gold in the nanoform is a catalytically active and effective green catalyst for the oxidation of CO and the hydrochlorination of ethylene at low temperature by Haruta and Hutchings respectively, a lot of research has been devoted to its use in various oxidation reactions.1–7 Literature shows that catalysis by supported gold is one of the fastest growing subjects in catalysis science today and a significant portion of the work has been devoted to catalytic oxidation of organic compounds such as alcohols, polyols, carbonyl compounds, alkenes etc.8–11 Oxidation reactions using gold are of relevant interest as it has been shown that oxygen gets chemically adsorbed on nanogold and thus, provides green processes based on the use of stable, selective and non-toxic heterogeneous catalysts with air or pure O₂ as eco-friendly oxidant.12–19 The subject of

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supported gold nanoparticle (AuNPs) catalysed oxidation has been reviewed many times in the literature. The review reported by Rossi and co-workers dealt with the entire work of selective oxidation conducted by supported gold. After that a critical review by Davis and co-workers illustrated the entire field of oxidation conducted by all kind of supported metal nanoparticles. But, with burgeoning new reports on oxidation, it is imperative to focus on a particular group. Alcohols belong to an important class of industrial chemicals that are highly useful starting materials for a variety of chemicals, intermediates, plastics, detergents, paints, cosmetics, food additives, pharmaceuticals etc. There is a huge potential for new catalytic systems that can efficiently convert to alcohols to correspondingly aldehydes with remarkable selectivity, lower energy requirements and without using hazardous reagents. This is evident from the fact that 50% of the reports on AuNPs catalysed reactions are related to oxidation of alcohols. The main objective of this review is to summarize the development in this field.

2. Oxidation of alcohols

Selective oxidation of primary alcohols to aldehydes and restricting its over oxidation to acids is an important issue. Various chromium reagents like chromic oxides, Jones reagent, PCC (pyridium chlorochromate), PDC (pyridium dichromate), activated DMSO (Swern oxidation), carbodi-mide (Pfitzner–Moffatt oxidation), 2-iodoxybenzoic acid, TPAP in presence of excess of NMO (Ley oxidation), TEMPO in the presence of excess bleach (NaOCl) (oxoammonium-catalyzed oxidation), Sarett reagent, Collins reagent etc. have been investigated to accomplish this aim. These reagents and salts are not only toxic but also produce voluminous amount of waste at the end of the reaction. They are also not suitable for highly acid sensitive organic compounds. To overcome these drawbacks research has been directed towards the development of catalytic oxidation reactions. Many homogenous catalysts with well-defined active sites that provide relatively high activity and selectivity have been synthesized and reported e.g. Ru-ionic liquid@silica gel, Co(n), Ni(n), and Cu(n) Schiff base complexes@zeolites, oxo vanadium complexes, Cu–Py, Cu–Phen, Cu–Bipy, CuCl–TEMPO, Cu–diimine, and CuCl–DEBCO, Fe(n)–H2O2, CuBr, phosphinite–ruthenium(n) complexes, etc. Peroxides and molecular oxygen were reported as oxidants. Major disadvantages associated with homogenous catalysts are their poor recycling, stability, and handling in industrial processes. On the other hand, heterogeneous catalysts can easily overcome these problems. Designing a highly active and selective heterogeneous catalyst with the selectivity of homogeneous catalyst is a challenge which has been overcome by the use of nanoparticles in the recent times. Nanoparticles of many transition elements like Ag, Pd, Ru, Au, Pt, Cu, etc., have been reported for the oxidation of aliphatic and aromatic primary alcohols. Among these, AuNPs have become favorites to researchers not only due to their novelty but also due to several advantages. These benefits involve the ability of gold to split elemental oxygen, in general nontoxic nature of gold and its excellent recyclability. In this review, we present growing amount of fundamental research dealing with selective oxidation of alcohols with special reference to the role of support.

3. Type of support

Many natural and synthetic materials such as zeolites, metal oxides, activated carbon, carbon nanotubes (CNT), polymers, resins, proteins, rocks, biological materials, clays, ceramics, metal organic framework (MOFs) and membranes have been used as support to stabilize metal nanoparticles. They have the ability to control the particle growth and reduce the particle aggregation during reaction. One of the significant features of gold catalysis is the dependence of its activity on the size and morphology of nanoparticles and thus, supports play a crucial role in the activity of catalyst (Fig. 1). Role of a support in nano catalysis is manifold:

- They help in facile synthesis of nanoparticles and prevent their agglomeration.
- They provide a framework for anchoring the catalyst that facilitates separation and recycling.
- They influence the microenvironment of the reactants and enhance the reaction rates.

As far as the synthesis of supported nanoparticles is concerned, several approaches are currently available. Among them, three extremely useful methods are (1) impregnation, (2) deposition precipitation, and (3) immobilization. In the impregnation method, the metal salts are dispersed in the existing pores of support and then reduced. The main disadvantage associated with this method is the difficulty in

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**Fig. 1** Schematic diagram of supported gold nanoparticles.
producing gold nanoparticles of required size unless the support has well defined porous structure. In deposition precipitation method, the metal hydroxide or metal hydrate oxide is generally deposited on the surface of the support by increasing the pH of the solution of metal salts in which the support material is added gradually. The obtained precipitate may be nucleated by the surface functional groups, simultaneously allowing the active phase to attach to the support or reduced afterwards. In immobilization method, gold nanoparticles are first synthesized and then dispersed on the support. This method is more commonly used for the preparation of AuNPs on inorganic supports as compared to the other two methods. Literature survey revealed that supports play a crucial role in the performance of gold nanoparticle catalysed oxidation of alcohols. The same quantity of gold deposited on various supports can show different activity towards toward same organic reaction and thus a wide variety of supports has been studied. A summary is presented here.

3.1 Metal organic frameworks (MOFs)

Metal organic frameworks (MOFs) are crystalline porous solids formed by either transition metal ions or clusters of metal ion that occupy nodal positions in a crystalline framework. The most attractive feature of MOFs is the ability to use minimum amount of metal ions and organic ligands to build maximum surface area with predictable, controllable, tailorable, and post-modifiable pores and cavities (Fig. 2). MOFs are a new class of materials at the interface of heterogeneous catalysts and supra-molecules. Excellent thermal stability of MOFs and narrow pore size make them excellent support for the stabilization of metal nanoparticles. The reviews reported by Zhang et al., Su et al. and Corma et al. provide the whole work on MOFs and their various applications.

MOF-5, ZIF-8, ZIF-90, MIL-101, MCM-22 and UiO-66 are the common metal organic frameworks (MOF) that has been used as support for the synthesis of AuNPs. Gold salt precursors such as Me₂Au(acac), HAuCl₄ and ClAuCO has been used to prepare Au NPs with MOFs themselves acting as stabilizing materials as they have inherent cavities suitable for the nucleation of nanoparticles. Chemical vapour deposition (CVD), deposition reduction, in situ synthesis of MOF by solid grinding, impregnation (IP) and solution infiltration are some of the methods used for the preparation of Au NPs@MOFs. In 2008, Haruta et al. reported Au clusters deposited onto porous MOF-5 by solid grinding method (Fig. 3) without using any additional stabilizing agent. However, the Au clusters though less than 2 nm dimension were found to be bigger in size as compare to pore size of MOF-5 and were mostly found on the outer surfaces of the support (Fig. 3). Microporous sodalite-like ZIF-8 (zeolitic imidazolate frameworks-8) and ZIF-90 (zeolitic imidazolate frameworks-90) with pore diameter of 1.2 nm and quite small pore windows of 3.5 Å were used by Fischer et al. to impregnate preformed AuNPs of size 1 to 5 nm in 2010. They reported better stability of nanoparticles in ZIF-90 and owed it to the better matching of the nanoparticle size with the pore size of the support. In the same year, Li et al. and Tang et al. in
a collaborative work reported Au@zeolite-type MOF (MIL-101) by using colloidal deposition (CD) method, impregnation method (IP) and deposition–precipitation (DP) method. MIL-101 has a crystalline framework with two kinds of quasi-spherical cages of 29 Å and 34 Å with a total surface area 4100 m² g⁻¹. Polyvinyl pyrrolidone (PVP) was used as protecting agent for the stabilization of gold nanoparticles in case of colloidal deposition method. HR-TEM study revealed small spherical gold nanoparticles of <3 nm size in the pores of MIL-101.¹⁹

A novel, innovative and highly efficient post functionalization method was developed by Gascon et al. for introducing additional metal functionalities in MOFs through oxamate as chelating agent and triethyl amine as reducing agent. The amine functionalized MOF thus synthesized, was impregnated with AuNPs by sorption reduction method. From the TEM analysis, the author suggested that the stabilized gold nanoparticles were highly dispersed with average size of ≈2.5 nm. However, in the absence of chelating agent bigger Au NPs were observed. Bimetallic gold and copper nanoparticles were synthesized by Ziolek and co-workers on MCM-22. The synthesized bimetallic catalyst was characterized by using different techniques such as XRD, N₂ adsorption/desorption, TEM, SEM, UV-visible, H₂-TPR, FT-IR and ESR spectroscopy. The average size of Au NPs was found to be 21 nm. It was reported that the stability of gold on the MCM-22 surface was improved by the addition of copper species.²⁰

Au NPs supported on MOF UiO-66 were also reported by Voort and co-workers by sorption reduction method. Reduction of precursor with NaBH₄ as well as H₂ was tried and the average Au NP size for the Au@ UiO-66 by NaBH₄ and Au@ UiO-66-H₂ was found to be 7 nm and 5 nm respectively. The stability and size of stabilised AuNPs was determined by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and XPS analysis. The XPS spectrum of Au(0)@ UiO-66-NaBH₄ showed the Au 4f doublet at Au 4f₇/₂ at 83.9 eV and Au 4f₅/₂ at 87.5 eV (Fig. 4). Moreover, two other peaks which were recognized as metallic Au and Au¹⁺ species were observed at 83.8 and 85.1 eV (Au 4f₇/₂).²⁵ Modified UiO-66 (NH₃)
Impregnated with gold nanoparticles by sorption-reduction method was investigated by Wang et al. The group reported that in presence of amino functional group UiO-66 rapidly coordinated with HAuCl₄ which behaved as precursor. This led to better distribution of HAuCl₄ over the outer as well as inner surfaces of the MOF resulting in well distributed gold nanoparticles of average size 2.8 nm (Fig. 5). XPS analysis, confirmed that the AuNPs were in Au(0) state.

In the catalytic oxidation of alcohols by AuNPs supported on MOFs, very high activity was reported but interestingly selectivity for product was different from different supports. E.g. in the oxidation of benzyl alcohol by AuNPs@MOF-5 using molecular oxygen as oxidant, selectivity was for methyl benzoate rather than benzaldehyde. Interestingly, in the absence of base, selectivity for benzaldehyde increased to 31% though conversion was only 69%. Similar selectivity for methyl benzoate was also reported for Au NPs supported on ZIF-8 and ZIF-90. In case of base free aerobic oxidation of benzyl alcohol using Au@MIL-101 (CD/PVP) catalyst selectivity was for benzaldehyde with a TOF value of 258 h⁻¹. High dispersion of AuNPs and the electron donation effect of aryl rings present in the large cages of the MIL-101 support were reported as the reason for its high catalytic activity. Further, in elaborate studies using different stabilizing agents, it was observed that activity was related to the size of nanoparticles (Fig. 6). The versatility of catalyst was investigated and the authors attempted oxidation of various derivatives of benzyl alcohol and hetero aromatic alcohols (Scheme 1). Similar results were reported for the base free aerobic oxidation of alcohols with AuNPs@UiO-66 (NH₂) i.e. 94% selectivity for benzaldehyde at 100 °C in DMF.

Among all MOF supported AuNPs, best results were reported by the AuNPs prepared by Vroot and co-workers using UiO-66 as support that gave 100% selectivity for benzaldehyde with 94% conversion of benzyl alcohol. Though, TON value reported was 35 h⁻¹ and TOF was only 7.5 h⁻¹. This catalyst was highly recyclable, stable and TEM analysis of the reused catalyst did not show any significant change in the Au NP size (8 nm) after the second runs.

Besides, benzyl alcohol oxidation some other alcohols have also been oxidised using MOF supported gold nanoparticles. Haruta et al. investigated the catalytic activity of MOF-5 stabilized gold nanoparticles for the oxidation of 1-phenyl ethanol. Using molecular oxygen 79% yield of acetophenone was obtained in methanol in the presence of base at 80 °C in 23 h. Bimetallic Cu–Au on MCM-22 surface was reported for oxidation of methanol. It was concluded that presence of copper enhanced the mobility of oxygen promoting the conversion of methanol and hence, Au–Cu@MCM-22 showed higher catalytic activity for oxidation of methanol at 523–623 K as compared to gold alone.

MOF and metal oxide mixed supports were investigated for stabilization of gold nanoparticles by Lu and co-workers. Different metal organic frameworks such as MOF-5, ZnO@MOF-5, and TiO₂@MOF-5 were used to produce extremely small AuNPs of size 1–3 nm. The authors reported good reactivity, selectivity and recyclability for the benzyl alcohol oxidation.

3.2 Carbon materials
Carbon is a classical support that has been used since long whereas, associated materials such as carbon nanotubes (CNTs), graphene are very popular and contemporary. Recently, nanostructured carbon materials with well-defined porosities and high surface area has been reported that can be
conveniently modified through different approaches to stabilize catalyst.\textsuperscript{98} Prepared from mesoporous starch by controlled carbonization carbon nanostructure has been reported for the preparation of a wide range of supported metal nanoparticles.\textsuperscript{99–101} 

### 3.2.1 Activated carbon

Activated charcoal (AC) has been impregnated with gold nanoparticles by sol immobilization\textsuperscript{102} and wet impregnation\textsuperscript{103} methods. Generally, capping agents are required to get uniform size of the nanoparticles.\textsuperscript{104} Zhang and co-workers after supporting the nanoparticles on AC removed the protecting PVP by washing. Specially synthesized mesoporous carbon is another popular support for wet impregnation of carbon nanoparticles.\textsuperscript{105} A novel one step method to synthesize gold nanoparticles in mesoporous carbon–silica support was reported by Wan et al. This material was synthesized by using a triblock copolymer Pluronic F127 as structure directing agent, thiol group containing silane as a coordination agent, phenolic resin as a carbon source and HauCl\textsubscript{4} as gold precursor. TEM analysis, showed supported AuNPs (average size 8.7 nm) inside highly stable mesostructured carbon–silica material with hexagonally arranged pores (Fig. 7).\textsuperscript{105} In another novel approach, Shaabani and co-workers prepared a mesoporous carbon by hydrothermal method in the absence of any kind of protecting agent and functionalized it with thiol groups by treating with 3-thiol propyl triethoxy silane (Fig. 8). Au NPs were than impregnated by sorption reduction method using HauCl\textsubscript{4} as precursor and sodium borohydride as reducing agent.\textsuperscript{106}

As far as the catalytic activity of gold nanoparticles towards oxidation of alcohols is concerned, it was observed that the nanoparticles supported on mesoporous carbon were more active and stable compared to those stabilized on activated charcoal. Bimetallic nanoparticles\textsuperscript{107,108} were found to be more active than monometallic. But a detailed discussion of bimetallic is beyond the scope of present review. AuNPs synthesized...
in mesoporous carbon by Shaabani et al. showed excellent activity in water toward benzyl alcohol oxidation using air as oxidant in the presence of a base (K₂CO₃). The best yield of benzaldehyde (>99%) was obtained after 1 h. To evaluate the versatility of this catalyst, the authors investigated some other derivatives of alcohols too (Scheme 2). Besides water, other solvents such as acetonitrile, toluene, xylene, THF gave high yield of benzaldehyde. They checked the activity of this catalyst using various bases such as KOH, triethyl amine, and pyridine. Additionally, the catalyst was reused six times without any significant loss in its activity. After the sixth consecutive runs, the conversion of benzyl alcohol (100%) almost remained constant with slight decrease in selectivity of benzaldehyde (95%).

The gold nanoparticles supported on mesoporous carbon–silica support synthesized by Wan et al. showed excellent catalytic performance in water at 90 °C and with oxygen as oxidant. The catalyst was stable, poison resistant and reusable with little activity loss due to metal leaching. Later on they removed silica and resulting AuNPs were found to be even more active than the earlier one. The catalyst displayed TOF value of 478 h⁻¹ at 25 °C. Both these catalysts showed good conversion of benzyl alcohol but selectivity towards benzaldehyde was poor and even at very low temperatures benzoic acid was the major product.

### 3.2.2 CNT as support

Carbon nanotubes (CNTs) are another carbon material that has been widely used as support for the metal nanoparticles. Their intrinsic properties consisting of high surface areas, unique morphologies and hollow geometry make them extremely attractive as supports for heterogeneous catalysis. However, due to the inertness of the pristine CNTs, metal deposition requires activation. In 2010, Prati and co-workers proposed a novel methodology for functionalising CNTs which included mild oxidation with nitric acid followed by amination by gaseous NH₃. The material was used to synthesize highly dispersed mono and bimetallic gold nanoparticles. Jiang and co-workers reported that introduction of nitrogen groups on the surface of CNT increased the dispersion as well as stability of the metal nanoparticles owing to strong interaction between metal and nitrogen.

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### 3.2.3 Graphene and graphene oxide

Graphene is a two-dimensional, single-atom thick sheet comprising of sp²-
bonded carbon atoms arranged in honeycomb type structure with high carrier mobility at room temperature ($10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), large surface area (2630 m$^2$ g$^{-1}$), excellent optical transparency (97.7%) and significant thermal conductivity (3000–5000 W m$^{-1}$ K$^{-1}$). After its discovery in 2004, it has made a critical change in important fields such as material science and nanotechnology due to its mechanical, electronic, and thermal properties. This interesting, and innovative material has also turned out to be a useful support for stabilization of metal nanoparticles.\textsuperscript{123–126} Graphene oxide (GO) which is the oxygenated form of graphene show very high structure defects as compared to graphene.\textsuperscript{127–131} Both graphene and graphene oxide have many potential applications but production, storage and processing of these materials is a challenge. Commercially, graphene is synthesized by Hummers method which involves an oxidation–reduction process, where the oxidation gives graphene oxide (GO) from the graphite and the reduction converts graphene oxide to graphene (Fig. 10). Though planer in shape, some chemical modification of graphene is necessary; otherwise irreversibly aggregation takes place via $\pi–\pi$ stacking.\textsuperscript{132–134} Besides, chemical inertness of graphene affects the extent of stabilization of AuNPs and achievement of narrow size distribution is difficult. Various modification of graphene such as nitrogen doped graphene,\textsuperscript{135} graphene grafted with polydopamine,\textsuperscript{136} graphene modified with octadecyamine, substituted perylene attached graphene, graphene oxide (GO)\textsuperscript{137} reduced graphene oxide (RGO) and supramolecular ionic liquid grafted graphene\textsuperscript{138} has been reported to overcome this problem and highly stabilized gold nanoparticles (<5 nm) has been synthesized on them for catalytic applications.

In 2012, Wang et al. reported synthesis of AuNPs on nitrogen-doped graphene nanosheets (NG) supported catalyst. The introduction of nitrogen atom to the graphene oxide not only modulated its electronic structure, but also changed the surface properties of graphene oxide significantly by introducing pyrrolic and graphitic N species. This change was evident in the XRD data as graphene showed a weak diffraction.

**Fig. 9** Synthesis of the Au NPs@CNT assembly [reprinted with permission from ref. 119. Copyright (2013) Royal society of chemistry].

**Fig. 10** Basic structural model of graphene and graphene oxide (GO) redraw from ref. 122.

**Fig. 11** XRD patterns of the Au/NG-x composites and NG (A). XRD patterns of the Au/G-x composites and bare graphene (B) [reprinted with permission from ref. 135. Copyright (2012) Royal Society of Chemistry].
line at 26.6° (d = 0.34 nm) corresponding to the (002) reflection which disappeared on N doping. Two new peaks at 16.1° and 22.9° were observed for N-doped graphene. After loading of gold usual peaks at 38.2°, 44.6°, 64.7° and 77.5° equivalent to the (111), (200), (220) and (311) crystal planes of metallic gold (Fig. 11) were reported. XPS results supported that pyrrolic and graphitic N species doped into the graphene lattice played a pivotal role in stabilizing gold nanoparticles by enhancing charge transfer between the two. It was reported that though graphene and NG have same morphology the presence of nitrogen in NG led to the formation of smaller nanoparticles (average size 3.4 nm) as compared to graphene (30–100 nm) with better dispersion.135

Graphene sheets have huge surface area. However, separating them and preventing their restacking is very important to utilize this unique property. A novel layer by layer (LBL) assembly of positively charged 4-dimethylaminopyridine (DMAP) coated AuNPs with negatively charged graphene oxide (GO) nanosheets (Fig. 12) was proposed by Kim et al. Dispersion of Au NPs was much higher on this bilayer assembly of 4-dimethylaminopyridine (DMAP) due to enhancement of surface area. The anodic current peaks were observed at 0.38 and 0.36 V and a cathodic current peak at 0.11 and 0.17 V at 100 and 150 °C respectively.139 Stability of AuNPs on graphene and their dispersion was also enhanced by covalent functionalization of graphene with ionic liquid SIL (Fig. 13) and polydopamine.136

Li et al. synthesized a composite NiAl-LDH with RGO and impregnated this with AuNPs by using sol-immobilization method (Fig. 14). Raman spectroscopy and XPS data was used to propose that NiAl-LDH/RGO composite had both defect sites and oxygenic functional groups in RGO to control the directional growth of Au nanoparticles thus leading to small particle size of Au NPs (2.63 nm). The group was of the opinion that presence of Ni in LDH has a synergic effect that accelerated the electrocatalytic activity for methanol oxidation.140

In 2015, Hutchings et al. reported bi-metallic Au–Pd NPs supported on graphene oxide sheets on graphene oxide sheets separated by the addition of TiO₂. Significant enhancement in the activity of the catalyst was observed by simply hindering the stacking and agglomeration of graphene oxide sheets (Fig. 15).141

Excellent size control and dispensability of AuNPs on various modified graphene has led to excellent catalytic conversion of benzyl alcohol to benzaldehyde as reported by many workers.135,136 Au NPs@SIL-g-G prepared by Shaabani et al. has been reported with remarkable selectivity towards benzaldehyde (99%) with excellent conversion of benzyl alcohol (99%) in 1 h. The catalyst also showed good recyclability and was successfully used for the oxidation of a number of alcohols (Scheme 3).138
In 2013, Wang and co-workers used AuNPs and bimetallic Au–Pd@graphene for the methanol oxidation with 90.2% conversion and 100% selectivity for methyl formate with a TOF of 0.377 h\(^{-1}\) at 70 °C using molecular oxygen as oxidant. From the XPS reports, authors observed lowering in BE (binding energy) both in Au and Pd due to electron exchange between the two. Secondly, maximum shifting of \(-0.5\) eV for Au 4f\(_{7/2}\) and \(-0.6\) eV for the Pd 3d peak in Au\(_{2.0}\)–Pd\(_{1.0}\) graphene was calculated (Fig. 16). This was attributed to conducting property of graphene which brought a strong

![Fig. 15](image-url)  
(A) The systematic method used for preparing GO stabilized Au–Pd NPs on TiO\(_2\). (B) Representative BF-TEM micrograph of the AuPd–9% GO/TiO\(_2\) sample. (Inset) Corresponding Au–Pd particle size distribution (PSD) (100 particles counted) [reprinted with permission from ref. 141. Copyright (2015) American Chemical Society].

Scheme 3  Oxidation of various alcohols by Au NPs@SIL-g-G supported catalyst.
synergism between Au and Pd which resulted in excellent catalytic activity.

AuNPs stabilized on graphene has also been used for electrocatalytic oxidation of ethanol. The catalytic activity was studied in basic medium using cyclic voltammetry and chronoamperometry techniques. The catalyst displayed excellent electrocatalytic activity (13.16 mA cm$^{-2}$ at a working potential of −0.12 V) and higher stability. Recently, Guo et al. has reported highly efficient oxidation of veratryl alcohol to veratryl aldehyde (VA) using AuNps supported on graphene quantum dots. The Au@GQD was prepared through a facile one-pot reaction by using GQDs, HAuCl$_4$ and trisodium citrate as raw materials. From the TEM and HR-TEM study, the author suggested that the AuNPs are coated by GQDs thus making a core shell type structure in Au/GQD. Importantly, the oxygen containing groups on GQDs were reduced throughout during the reduction of Au precursor in presence of reducing agent. The Au@GQD composites showed higher dispersion and stability in aqueous solution resulting in remarkable catalytic activity with excellent selectivity in acidic and alkaline conditions using H$_2$O$_2$ as oxidant (Fig. 17). It was shown that in the case of acidic conditions, singlet oxygen species generated by the reaction of GQDs with H$_2$O$_2$ were the oxidising species whereas, in basic medium, both GQDs and AuNPs contributed to the oxidation by producing superoxide anion and traces of singlet oxygen species.

3.3 Biopolymers and proteins

Biopolymers and biomass-related polymers are indeed attractive candidates for use as supports for catalytic applications owing to their easy availability and low toxicity. At present, commonly used green stabilizing agents for nanoparticles are...
vitamins, citric acid, polyphenols, proteins, enzymes, polysaccharides, carboxymethyl cellulose (CMC), and biodegradable polymers like PLA, gelatin etc. Sorption reduction is the most common method used for preparing AuNPs supported on biopolymers.

Chitosan is the second most abundant biopolymer in nature and widely studied for stabilization of nanoparticles. Sakurainia et al. synthesized chitosan stabilized Au, Au–Pd and Au–Pt nanoparticles and to control the size of nanoparticles they adopted a two step procedure. First ion pairs of AuCl₄⁻ with chitosan were prepared by dissolving gold precursor in a solution of chitosan dispersed in acetic acid, followed by rapid reduction with cold NaBH₄ solution. Nanoparticles with an average size of 2.3 nm with very narrow size distribution were obtained. The interaction between gold and chitosan was
Janus type gold nanoparticles supported on TiO$_2$. This material was synthesized by a sol–gel method using hydrophobic 1-hexanethiolates and hydrophilic 2-(2-mercaptoethoxy) ethanol as capping agents (Fig. 19). This synthesized catalyst was characterized by TEM, HR-TEM and UV visible spectroscopy techniques. From the TEM and HR-TEM analysis, it was shown that most of Au NPs have sizes between 2–6 nm. The material exhibited excellent photocatalytic activity for the oxidation of 0.14 mM methanol to formaldehyde. The group also suggested that the charge separation of photo generated electrons and holes at the Au@TiO$_2$ support was assisted by their close proximity to gold nanoparticles.$^{161}$

In 2014, Li et al. reported a green bioreduction strategy for the synthesis of gold nanoparticles and solvent free oxidation of benzyl alcohol. This group used Cacumen Platycladi extract to assemble bimetallic Au–Pd nanoparticles which were then immobilized onto TiO$_2$ (Fig. 20). This catalyst was characterized by TEM, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and FT-IR (Fourier transform infrared spectroscopy) techniques. From the TEM analysis, author has suggested that all stabilized Au–Pd NPs were spherical in shape and highly dispersed with average size 8 ± 1.1 nm (Fig. 21). This group achieved maximum conversion of benzyl alcohol (74.2%) with remarkable selectivity of benzaldehyde (95.8%) at 90 °C with an oxygen flow rate of 90 mL min$^{-1}$ under solvent free conditions. Excellent yield of benzaldehyde (98%) with remarkable TOF (589 h$^{-1}$) was obtained by this group. The catalyst was highly recyclable and the authors reported that Au/Pd in molar ratio of 2 : 1 showed maximum catalytic activity.$^{162}$

### 3.4 Synthetic polymers

Cross-linked polymers have been adopted as heterogeneous supports for the stabilization of metal nanoparticles for the past several decades.$^{163}$ Their availability, ease of separation, enhanced stabilization of metal nanoparticles makes them popular support especially for solution phase reactions. Many commercially available linear as well as crosslinked polymers such as polyethylene glycol (PEG),$^{164}$ polystyrene (PS),$^{165}$ polysiloxane, polysobutylene,$^{166}$ polyvinyl pyridine,$^{167}$ modified polystyrene,$^{168,169}$ syndiotactic polystyrene-c-o-cis-1,4-polbutadiene$^{170}$ and dendrimers$^{171}$ have been used for the synthesis of AuNPs and used to study oxidation of alcohols. Sorption reduction is the most common method to support gold nanoparticles on insoluble polymers whereas soluble polymers are utilized to synthesize nanoparticle dispersions in water and organic solvents. The letter generally gives a better control over the nanoparticles size. However, former has the advantage of easy recovery from the reaction mixture. Preformed AuNPs were supported on polystyrene by dispersion method.$^{165}$ Polyvinylpyrrolidone (PVP),$^{172,173}$ PANI$^{174}$ are water soluble polymers that have been most widely used to synthesize nanoparticles in aqueous solution with controlled particle size but their separation from reaction mixture is tedious.

Tsukuda et al. developed highly stable and durable gold nanoclusters (4 nm size) in water phase using star like thermo sensitive polyvinyl vinyl ether (Fig. 22). These star like polymers

**Fig. 21 TEM images of bimetallic NPs (preparation conditions:**

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<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>Stirring Rate</th>
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<td>90 °C</td>
<td>1 h</td>
<td>12 000 rpm</td>
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**Inset**

- a) Au(7) Pd(1)
- b) Au(2) Pd(1)
- c) Au(1) Pd(1)
- d) Au(1) Pd(2)
- e) Au(1) Pd(7) NPs

[reprinted with permission from ref. 162. Copyright (2014) American Chemical Society.]
Fig. 22  Preparation and catalytic use of AuNPs [reprinted with permission from ref. 175. Copyright (2007) American Chemical Society].

Scheme 4  Oxidation of various alcohols by AuNPs@poly(EOOVE) catalyst.
were synthesized by living polymerization of 2-2(ethoxy) ethoxy ethyl vinyl ether. The resulting clusters effectively catalyzed aerobic oxidation of benzyl alcohol but with 99% selectivity for benzoic acid. The authors studied the catalytic performance for different alcohol derivatives (Scheme 4). The author suggested that the star-polymer-stabilized Au NPs are existing in hydrophobic layers.

Rider and co-workers synthesised very small and uniform bimetallic Pt–Au nanoparticles of 2–4 nm dimension using polystyrene-block-poly(4-vinylpyridine) block copolymer (Fig. 23) as template. The template was removed by etching after depositing the nanoparticles on electrode which were subsequently used in methanol fuel cell. Self-assembly of copolymer formed micelles of 2–4 nm diameter that controlled the size of nanoparticles. It was seen that the high density Pt–Au core shell bimetallic NPs were electrochemically more active for methanol oxidation as compared to Pt supported nanoparticles and were more resistant to catalytic poisoning too.

Dendrimers are macromolecules with tree-like architecture having a high degree of molecular uniformity, narrow molecular weight distribution, loosely packed interior pockets and highly functionalized terminal surface. Such structural specificity promises uniform formation of nanoparticles with potential applications in catalysis. In 2012, Jiang et al. attached PAMAM dendrimers to polystyrene in order to combine the advantages of both heterogeneous and homogeneous catalysis. From the SEM and TEM analysis, the author has demonstrated that the AuNPs were present both in the interior and on exterior surfaces of the polystyrene beads with sizes 5 to 10 nm. The yield of benzaldehyde (99%) reported by this group under the optimized conditions (Fig. 24).
Recently in 2015, Zang and co-workers developed a new kind of polymer (MCBNs), a brush block terpolymer of [poly(p-chloromethylstyrene)-graft-poly(4-vinylpyridine)]-block-polystyrene [(PCMS-g-P4VP)-b-PS] and used it as a support for the stabilization and of AuNPs (Fig. 25). The immobilized AuNPs on this polymer matrix showed nanoparticles of 1 nm dimension under TEM. This synthesized material exhibited remarkable activity for the aerobic oxidation of 1-phenyl ethanol and it was shown that acetophenone was the main product formed in the oxidation with 96% yield in 6 h.\textsuperscript{179}

PVP stabilized nanoparticles have been studied by many workers and more than 90% conversion with excellent selectivity for benzaldehyde has been reported.\textsuperscript{180} Dyson and co-workers discovered that AuNPs stabilized by carboxylate modified PVP can be separated from the reaction mixture by a new tool i.e. lowering the pH of the solution which caused the NPs to precipitate. The AuNPs form pseudo homogenous aqueous solutions at pH >2.5 and precipitate at pH <2.4. However, during oxidation of benzyl alcohol, this catalyst showed more selectivity towards benzoic acid rather than benzaldehyde (Fig. 26).\textsuperscript{181} Tsukuda and co-workers stabilized AuNPs on this hydrophilic polymer (PVP) and investigated its catalytic activity towards aerobic oxidation of benzyl alcohol in aqueous media at ambient temperatures using molecular oxygen as oxidant. Kinetic measurements were performed to establish reactivity of AuNPs of different sizes.\textsuperscript{182}

Kobayashi \textit{et al.} in 2007, developed a simple and efficient method for the synthesis of a highly controllable gold nanoclusters using AuClPPh\textsubscript{3} complex as gold source and NaBH\textsubscript{4} as reducing agent. They used modified polystyrene as support for the stabilization of gold nanoclusters (AuNCs) (Fig. 27) of 1 nm dimension. This gold supported composite material showed excellent catalytic activity for alcohol oxidation at room temperature using molecular oxygen at atmospheric pressure.\textsuperscript{168,169} Different solvents were studied by the authors and best results were achieved in binary solvent like toluene/water and benzotrifluoride/water. The catalytic activity was also evaluated for various derivatives of alcohols (Scheme 5). All of them gave good conversion (>75%) with >99% selectivity towards aldehyde.\textsuperscript{168} In another report, the same group has used integrated carbon black (CB) in the polymer system (PI/CB-Au), to increase the gold loading on polystyrene resin. The size of AuNCs did not increase much, as the gold loading was increased from 5 wt% to 20 wt%.\textsuperscript{169}

In the same year this group reported a novel gold-immobilized microchannel reactor for the efficient, green
oxidation of alcohols using molecular oxygen. They used a polysiloxane-coated capillary column having 50 cm length and 250 mm inner diameter which contained an inner lining made of 50% phenyl and 50% n-cyanopropyl functionalities on silicon atoms in a film of 0.25 mm thickness. The method for gold-immobilized on capillary column is shown in Fig. 28. The immobilized AuNPs in this column showed 99% conversion of 1-phenyl ethanol to acetophenone in DCM using K₂CO₃ as base. The authors have reported that increasing the flow rate of the aqueous K₂CO₃ solution or oxygen gas did not affect the conversion. They also checked the activity of this catalyst for oxidation of different type of alcohols such as benzylic, aliphatic

Scheme 5 Oxidation of selected alcohols by Au NPs@PI catalyst.

Fig. 28 Immobilization of the gold catalyst. (a) Reduction of the cyano group to an amine. (b) Preparation of microencapsulated gold. (c) Immobilization of the gold catalyst redraw from the ref. 183.
and allylic alcohols. In all cases, high conversion with high yield of product and recyclability was reported.\textsuperscript{183}

Block copolymers are a type of macromolecules that comprise of two separate polymer chains joined together. Such polymers with segregation of hydrophilic/hydrophilic regions can provide better stabilization and dispersion of the nanoparticles.\textsuperscript{184} Kawanami \textit{et al.} derived a versatile, solution based technique with high degree of control over the size and spacing of nanoparticles. AuNPs@amphiphilic block co-polymer (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)) (PEO-PPO-PEO) were synthesized and used for the oxidation of alcohols using molecular oxygen as oxidant at 30\degree C. Interestingly, the block copolymers acted both as reductants as well as stabilizer. The morphology of stabilized AuNPs was spherical with size 4–12 nm. The average particle size of Au NPs is 7.3 nm. The following group has suggested that AuNPs was highly stabilized mainly due to steric factors. 99% conversion of benzyl alcohol was reported but the selectivity for benzaldehyde was only 8%. Benzoic acid and benzyl benzoate were produced as side products during the reaction due to over-oxidation of benzaldehyde.\textsuperscript{185}

Highly active AuNPs@syndiotactic (polystyrene-co-cis-1,4-polybutadiene) multi-block copolymer were successfully used for the oxidation of primary and secondary alcohols by Grassi \textit{et al.} Using molecular oxygen as oxidant. 1-Phenylethanol was oxidised to acetophenone in high yields (96\%) in 1 h, at 358 \degree C, whereas benzyl alcohol was quantitatively oxidised to benzaldehyde with a selectivity of 96\% in 6 h. Nanoporous crystalline form of syndiotactic polystyrene ensured facile and selective accessibility for the substrates to the gold catalyst incarcerated in the polymer matrix.\textsuperscript{179}

Gold nanoparticles of average size 5 nm were synthesised on poly(o-phenylenediamine) submicrosphere of size 700 nm by impregnating with precursor HAuCl\textsubscript{4}. No additional reducing agent was required and PoPD submicrospheres with abundant amino groups and \pi electrons in benzene rings acted as reducing and stabilising agents. The synthesised gold nanoparticles showed good catalytic activity for oxidation of benzyl alcohol to benzaldehyde in water with high yield and selectivity (Fig. 29). TEM images showed gold nanoparticles uniformly deposited on the surfaces of PoPD submicrosphere.\textsuperscript{186} Li \textit{et al.} in 2014 reported AuNPs@PS as highly active catalyst for benzyl alcohol oxidation under atmospheric conditions using potassium carbonate as base in aqueous medium. This composite showed good recyclability and was reused several times without significant loss of activity. The PS microsphere was synthesized using conventional dispersion polymerization. TEM analysis showed gold nanoparticle dispersed on the surface of PS microspheres. The average particle size of the Au NPs was about 3.5 nm, 9.5 nm and 6.7 nm respectively. This catalyst was highly selective for benzoic acid rather than benzaldehyde (Fig. 30).\textsuperscript{165}

Polyaniline commonly known as PANI a conducting polymer was used to synthesise mono and bimetallic gold nanoparticles by Baiker and co-workers. PANI is a charge density donor and its presence enhanced the activity of Au NPs. The size of the mono and bimetallic particles was controlled in a narrow range (2.4–3.7 nm) by using a colloidal preparation route. The authors concluded that if the content of Pd in bimetallic nanoparticles is increased from 1 to 9 mol\% significant increase in the catalytic activity with 100\% conversion of benzyl alcohol and 98\% selectivity for benzaldehyde (98\%) at 100 \degree C can be achieved. As polymer support polyaniline (PANI) was applied owing to its...
3.5 LDH

Clays are another cheap and green material which is frequently used for supporting metal nanoparticles. Among the many classes of clays LDH (layered double hydroxide) is the most commonly used material. It is anionic clay, which belongs to the family of brucite Mg(OH)2 like layered inorganic materials (Fig. 31). It has a number of advantages viz. high versatility in composition, high adsorption capacity, tunable basicity etc. Basicity of the clay has synergistic effect on the catalytic activity of the gold nanoparticles. The ion exchange ability of the clay helps in facile sorption of the precursor. The precursor is generally loaded onto the catalyst by co-precipitation\textsuperscript{196} deposition precipitation\textsuperscript{197} sol immobilization\textsuperscript{198} methods followed by reduction. Besides concentration of the precursor, size of the nanoparticle was also controlled by the nature of reducing agent. The stronger the reducing agent smaller is the size of nanoparticles. Kaneda and co-workers reported that the size of Au NPs decreased more in the following order hydrazine > molecular hydrogen > potassium borohydride. In almost all the cases gold nanoparticles of less than 10 nm were achieved easily.\textsuperscript{196}

In 2011, Zheng and co-workers synthesized a eco-friendly, magnetic separable novel core shell Au NPs@Fe3O4@MgAl-LDH. The authors first synthesized coated negatively charged Fe\textsubscript{3}O\textsubscript{4} magnetic nanospheres with MgAl-LDH. Fe\textsubscript{3}O\textsubscript{4} nanoparticles were of average size 450 nm on which LDH shells of 20 nm thickness were grown. Au NPs with an average size of 7 nm were deposited on this composite material by deposition–precipitation method (Fig. 32). The catalyst was easily separated by magnet and recycled upto five consecutive runs without any drop in yield.\textsuperscript{199}

Li and co-worker synthesized gold nanoparticles on a series of transition metal modified M-HT (M = Cr\textsuperscript{3+}, Mn\textsuperscript{2+}, Fe\textsuperscript{3+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}). They first prepared the HT precursor [MgAl\textsubscript{2}(OH)\textsubscript{4}CO\textsubscript{3}] by homogeneous precipitation method using urea hydrolysis. Later on, HT with different metal ions was produced by calcination–reconstruction process. AuNPs of size 2.7–3.9 nm were deposited by homogeneous precipitation method and used for a base free protocol for the oxidation of various substituted benzyl alcohol.\textsuperscript{200} In 2014, Zhang and co-workers supported glutathione capped gold sol in water on M\textsubscript{4}Al-layered double hydroxide (M = Mg, Ni, Co). The glutathione capped gold nanoparticles of average size 1.5 ± 0.6 were prepared and then different amount of nanoparticles were dispersed in deionized water along with Mg\textsubscript{4}Al-LDH. The dispersion after centrifugation was calcinated under N\textsubscript{2} to remove the capping agent. Highly dispersed gold nanoparticles on LDH were thus obtained (Fig. 33).\textsuperscript{201}

Ni-Al layered LDH is another clay material which has been explored as support by many workers.\textsuperscript{202,203} The basic and redox properties were adjusted by adjusting the ratio of Ni:Al to achieve the best synergistic effects between AuNPs and the support. The activity of the obtained Au catalysts was found to be structurally associated with the arrangements of NiO\textsubscript{4} and AlO\textsubscript{6} octahedrons present on the surface of hydroxide layers. Deposition precipitation method was used to prepare AuNPs of 4.5 nm dimension. XPS studies indicated enhanced interaction between AuNPs and support which was indicated as the reason for better activity of catalyst. A number of studies for benzyl alcohol oxidation using LDH supported gold nanoparticles have carried out and reported at temperatures ranging from 40 °C up to 120 °C with very high TON and TOF using dioxygen as oxidant but in organic solvents. E.g. Kaneda and co-workers reported a turnover number (TON) and turnover frequency (TOF) of 200 000 and 8300 h\textsuperscript{-1} respectively in the oxidation of 1-phenylethanol. Even, less reactive cyclohexanol derivatives were easily oxidized by the AuNPs@HT.
catalyst with excellent yield in basic medium (Na₂CO₃). Wang and co-workers reported best conversion of benzyl alcohol (>99%) with excellent selectivity towards benzaldehyde (99%) in 9 h, in p-xylene at 120 °C using Au NPs@HT as catalyst. To evaluate the activity of this catalyst, authors also oxidized various substituted alcohols, heterocyclic alcohols, and aliphatic alcohols (Scheme 6) with high conversion and selectivity. They observed a unique effect of Au loading on the catalytic activity.

Among the several transition metal doped clays synthesized by Li and co-workers, the best yield of benzaldehyde was achieved in toluene under atmospheric O₂ at 373 K in 0.5 h in case of Cr³⁺ containing Au NPs@Cr-HT support. The activity of the various catalysts was found to decrease in the following order Au NPs@HT < Au NPs@Cu-HT < Au NPs@Zn-HT < Au NPs@Mn-HT < Au NPs@Co-HT < Au NPs@Fe-HT < Au NPs@Ni-HT < Au@Cr-HT. It was shown that the synergy between metallic AuNPs and hydrotalcite support which involved both the basic sites of the surface of the hydrotalcite and the Cr cations was responsible for the increased activity. Highest TOF of 930 with 99% selectivity for benzaldehyde was reported. Versatility of the protocol for various substituted benzyl alcohol as well as 1-phenyl ethanol was also reported.

Hensen et al. also reported that the interaction between gold and Cr content of HT support has synergistic effect on the oxidation of alcohol. As the content of Cr was increased on the HT support, it resulted in an increase in the surface area and basicity of the support. The 1830 h⁻¹ (TOF) was reported by this group and from the kinetic isotope effect, it was concluded that the cleavage of O–H bond was accelerated by the presence of Cr ions (Fig. 34). The size of AuNPs also decreased on increasing the Cr content of the catalyst.
support. From the UV-Raman, X-ray absorption and photo-electron spectroscopic studies, the group revealed that the strong Au–Cr synergy is directly related to a Cr$^{3+}$ → Cr$^{6+}$ redox cycle at the Au/Cr-HT interface, where O$_2$ activation takes place by electron transfer. Recently, Zhang and co-workers reported highest TOF (46 500 h$^{-1}$) for the conversion of 1-phenyethanol with stabilized AuNPs on LDH that also gave acetophenone in 99% yield in toluene under base free conditions in 0.5 h. The activity of this catalyst for different alcohol derivatives was also investigated.

3.6 Zeolites, silica

Zeolites and silicas are the most widely used industrial supports owing to their high thermal stability, variable dimensions of the pores, high ability of absorption, porosity, highly crystalline nature and shape selectivity. Zeolites have an extremely large internal surface area in relation to their external area and an ordered porous structure which make them suitable for supporting nanoparticles. Mesoporous silica with uniform pore sizes or channels (2–10 nm range) is commercially available in well-known phases like MCM-41, MCM-48, SBA-15 and MCM-50.$^{205,206}$ They are highly ordered structures of low cost and their commercial availability makes them highly suitable supports for industrial applications.$^{207–209}$ Moreover, confined void spaces in zeolites restrict the growth of various nanoclusters and lead to an increase in their catalytic performance. Heterogenization of gold nanoparticles on these supports has been reported by deposition reduction, deposition precipitation and impregnation methods.$^{210–226}$

Tsukuda and co-workers impregnated Au clusters ($\approx$ 1 nm) within the mesoporous silica (SBA-15, MCF, HMS) using
triphenylphosphine-protected Au$_{11}$ (Au$_{11}$:TPP) sol as precursor (Fig. 35). After impregnation organic protecting layer was removed by calcination.$^{227}$ Wang et al. modified the surface of SBA-15 with (S)-(−)-2-pyrrolidinone-5-carboxylic acid in order to control the size of nanoparticles (Fig. 36). The average sizes of Au nanoparticles in Au@SBA-15-Py and Au@SBA-15 are estimated to be 2.1 nm and 2.2 nm.$^{228}$

A novel ceria mixed silica was reported by Gong et al. to synthesize gold nanoparticles. An amino functionalized SBA-15 was synthesized and impregnated with AuNps by deposition reduction method. Afterwards, Au@SBA-15 materials was impregnated with different concentrations of cerium nitrate solution and sonicated to prepare Au–xCeO$_2$@SBA-15. The latter was calcinated to obtain the final Au–CeO$_2$@SBA-15. Introduction of CeO$_2$ not only enhanced the stability of the AuNPs but also increased the activity of the catalyst. From the XPS report, authors observed that the Au species existed as Au$^0$ in Au@SBA-15 whereas, on addition of CeO$_2$ to Au@SBA-15, the Au species existed in several oxidation states viz. Au$^0$, Au$^+$ and Au$^{3+}$. This was reported as the reason for large enhancement in the selectivity of catalyst for benzaldehyde from the meagre 2–18% after inclusion of CeO$_2$.$^{229}$ Another mixed support was reported by Gole et al. 2015. The Fe$_3$O$_4$–SiO$_2$–AuNPs was prepared by co-precipitation of iron salts, reduction of gold chloride, and
silica formation in single step (Fig. 37). d-Glucose was added as stabilizing agent for AuNPs. Besides higher stability of the nanoparticles, the catalyst was easily separable owing to its magnetic nature.230

In their extensive research, Hutchings et al. studied the oxidation of benzyl alcohol using various zeolite supports and compared them. They found that selectivities for acidic supports were lower than those for non-acidic supports. The group also concluded that the selectivity towards the benzaldehyde decreased with corresponding increase in side products such as dibenzyl ether and benzyl benzoate. They proposed that the latter is likely to be formed by the oxidation of the hemiacetal intermediate generated by the combination of benzyl alcohol and benzaldehyde (Scheme 7). Further, the addition of Pd into the catalyst improved the activity without loss of the selectivity for benzaldehyde.231 In another investigation by the same group, gold nanoparticles synthesized on hierarchical titanium silicates (TS-1), were reported as better catalysts compared to other commercial silicas. They concluded that the presence of secondary porosities in this material played a crucial role in the catalyst activity as they enhanced the metal dispersion and improved the accessibility to the active sites.232 One again bimetallic Au–Pd was found to be more active than gold alone towards oxidation of benzyl alcohol.

In the case with silica modified with 2-pyrrolidinone-5-carboxylic acid228 the authors reported more than 90% conversions of benzyl alcohol. However, the catalyst showed selectivity for benzoic acid rather than benzaldehyde in water medium. The deposition of nano ionic liquid layer on a porous material and using it to support for catalyst conceptually creates a new fundamental research area that solves certain problems associated with homogenous catalysis.233 The nanoporous ionic organic networks (PIONs) with excellent ionic density were synthesized by substitution nucleophilic bimolecular reaction (Scheme 8) on silica by Dai et al. in 2015. This mixed support was then impregnated with gold nanoparticles of size 1–2 nm. The authors studied the oxidation of a number of secondary alcohols at 60 to 140 °C in toluene with quantitative conversion with >99% selectivity for corresponding ketone. Versatility of both the catalyst was reported by studying a number of examples (Scheme 9).234

3.7 Metal oxides

In general, metal oxides offer high thermal and chemical stabilities combined with a well-developed porous structure having high surface areas, meeting the requirements for most applications. They can also be easily prepared and further functionalised, adding value to their use as supports. Silica,235–238 alumina,239–241 titania,242–245 ceria,246 and zirconia247 are the most commonly employed supports. Depending on the chemical reactivity of the support, metal oxides can be classified as inert (SiO2) or reactive (CeO2). Reactive oxides have been known to participate in the reaction. Lately, super-paramagnetic oxides (e.g. Fe3O4, Co3O4) have also become important materials for the immobilisation of metal nanoparticles owing to their facile separation capabilities. Sol-
immobilization, deposition–precipitation, co-precipitation, hydrothermal deposition precipitation and impregnation are the common methods used for the preparation of supported gold nanoparticles on metal oxides support. A summary of the supports used and the methods used for AuNPs impregnation are tabulated in Table 1.

It has been observed that metallic gold species (Au⁰) are present of inert or non-reducible supports such as alumina.²⁶³ Whereas, gold in three different states (Au⁰, Au¹⁺, Au³⁺) have been observed on the surface of reactive oxides such as CeO₂,²⁶⁴ U₃O₈ (ref. 263) etc. Another support in which gold is reported in different oxidation states is β-MnO₂. Cao et al. synthesized Au

<table>
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<th>Sel. of BZ (%)</th>
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<tr>
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<td>34</td>
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<td>47</td>
<td>Au@MgO* (DP)**</td>
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<td>100</td>
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<td>100</td>
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<td>32</td>
<td>66</td>
<td>100</td>
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*O₂ as oxidant, CP = co-precipitation, IP = impregnation, FSP = Flame Spray Pyrolysis, HD = hydrothermal precipitation, SI = sol-immobilisation, DP = deposition precipitation, WIP = wet-impregnation, WSI = Wet Sol-Immobilisation. b=Toluene using as solvent. * = Methanol using as solvent, Con. (%) = conversion of benzyl alcohol, Sel. (%) = selectivity of benzaldehyde, ** = TBHP as oxidant, *** = base added.
NPs@β-MnO₂ by homogenous deposition precipitation using urea as the precipitation agent and commercial MnO₂ or MnO₂ nanorods as support. From the XPS studies, the author proposed that both reduced and oxidized Au species on the MnO₂ nanorods support before and after the reaction. Significantly enhanced catalytic activity was observed for gold catalyst supported on MnO₂ nanorods, as compared with that on commercial MnO₂ powders. Secondly, the enhanced catalytic activity of the Au/MnO₂–R catalyst was attributed to the beneficial presence of higher amount of oxidized gold species and surface oxygen vacancies resulting from the strong interaction between Au and the more reactive surface of MnO₂ nanorods. TEM images indicated that the MnO₂ nanorods have well defined rod like morphology with diameters of 40–100 nm and length ranging between 2.5 and 4.0 μm. Further, HRTEM studies showed that MnO₂ nanorods are crystalline in nature showing d spacing characteristic of 110 plane of β-MnO₂. The structure feature of MnO₂ nanorods were not altered on depositing gold. Au NPs were highly dispersed on the MnO₂ surface, and the size distribution ranged from 2.0 to 10.0 nm.

Fig. 38 (A) TEM image of pure MnO₂ nanorods. (B) HRTEM image and electron diffraction pattern (inset) of MnO₂ nanorod. In the HRTEM image, the spacing between the lattice fringes is ca. 0.32 nm, which corresponds well with the (110) crystal plane of β-MnO₂ (pyrolusite). (C) TEM image of Au/MnO₂–R catalyst (D) HRTEM image of Au/MnO₂–R catalyst. (E) TEM image of Au/MnO₂–C (F) size distributions of Au nanoparticles obtained for Au/MnO₂–R and Au/MnO₂–C [reprinted with permission from ref. 255. Copyright (2008) American Chemical Society].
with the average size of 4.4 and 5.0 nm for Au/MnO$_2$–R and Au/
MnO$_2$–C (Fig. 38). In addition, the HR-TEM image of the Au/
MnO$_2$–R catalyst also showed that the gold NPs on the surface of
MnO$_2$ nanorods are mainly semispherical in shape.$^{255}$

Another, especially noteworthy synthesis is of magnetically
separable nanoparticles by Rossi et al. in 2009. First oleic acid
coated Fe$_3$O$_4$ NPs and the core shells Fe$_3$O$_4$@SiO$_2$ composite
were prepared as per literature$^{265}$ and then Au$^{3+}$ was
immobilization on the surfaces of core shell silica coated
magnetite NPs. After that the metal was reduced by two
different methods $\text{viz.}$ thermal reduction in air and by hydrogen
reduction at mild temperature. This synthesized material was
modified with amino groups by treatment with 3- amino pro-
pyltriethoxysilane (APTES) in dry toluene under N$_2$ atmosphere
to give amino functionalized support (Fe$_3$O$_4$@SiO$_2$/NH$_3$)
(Fig. 39). After that the material was washed with toluene and

Fig. 39  Schematic preparation of magnetically recoverable Au NPs redraw from the ref. 266.

Fig. 40  TEM images of catalyst 3 (a) and catalyst 4 (b). Histogram showing particle size distribution and lognormal fitting of the Au NPs of catalyst 3 (c) and the Au NPs of catalyst 4 (d) [reprinted with permission from ref. 266. Copyright (2010) Royal Society of Chemistry].
dried at 100 °C. From the TEM analysis, the group reported that the support composed of magnetic cores (≈ 10 nm) which were spherically coated with silica spheres (≈ 40 nm). The average size of stabilized AuNPs was found to be 5.9 nm (Fig. 40). The authors investigated the activity of this magnetic recoverable material for benzyl alcohol oxidation. The best conversion (84.3%) with good yield of benzaldehyde (95%) in the presence of base (K₂CO₃) was reported.

Huchings and co-workers reported very selective, mild, base free and solvent free methodology for the aerobic oxidation of some important aromatic alcohols such as geraniol, benzyl alcohol and some aliphatic alcohols. They synthesized Au@CeO₂ using co-precipitation, deposition precipitation and impregnation methods and achieved 100% selectivity for the oxidation of benzyl alcohol and octan-1-ol with TOF 150 h⁻¹ and 26 h⁻¹ by using this catalyst. For the comparative study, the author also tried various other oxides such as SiO₂ and TiO₂ but Au@CeO₂ was highly selective as well as active. The catalyst was used to explore oxidation of geraniol with excellent conversion. Various products identified during the oxidation of geraniol were linalol, β-pinene, limonene, γ-terpinene, nerol and traces of geranic acid. The selectivity of this catalyst towards citral was poor (Scheme 10).²⁸⁶

In 2007, Chaudhary et al. reported solvent free protocol for the synthesis of chlorine free benzaldehyde. They synthesized U₃O₈ supported gold nanoparticles by four different methods viz. impregnation (IP), deposition precipitation (DP), homogeneous deposition precipitation (HDP) and co-precipitation (CP). The catalyst prepared by HDP method showed much better activity compared to others. Though, different solvents such as toluene, p-xylene, DMF and DMSO were tried best yield was obtained in solvent free conditions. General applicability of the protocol was checked using various substituted benzyl alcohols (Scheme 11).²⁸⁶ Secondly, the author indicated that the stabilized gold atoms were in three different states (Au⁰, Au¹⁺, Au³⁺). Whereas, only metallic gold species (Au⁰) was observed on the

![Scheme 10](image-url) Oxidation of geraniol catalyzed by Au@CeO₂ catalyst.
surface of nano gold deposited on non-reducible metal oxide such as alumina. Corma et al. suggested that the combination of small crystal size gold (2–5 nm) and nano crystalline ceria (5 nm) as a highly active, selective and recyclable catalyst for the solvent and base free oxidation of alcohols to aldehyde and ketones with high TON and TOF using oxygen at atmospheric pressure. XPS analysis revealed stabilized AuNPs having surface atoms in Au3+, Au+ and Au0 state. The Au NPs formed on the Au@CeO2 catalyst interact with the nano-metric ceria surface which stabilizes the positive oxidation states of gold by creating Ce3+ and oxygen deficient sites in the ceria. The TOF value 250 000 h⁻¹ was reported by this same group. Corma et al. and Garcia et al. have suggested that AuNPs supported on nano-crystalline ceria were more active and highly chemo selective for the aerobic oxidation of allylic alcohols (Fig. 41). They were of the opinion that the lattice oxygen vacancies, which are more abundant in nanoparticulated ceria favoured interaction and physisorption of molecular oxygen. Benzylc alcohols either primary or secondary were converted to the corresponding product.

Scheme 11 Oxidation of various alcohols by Au@U3O8 catalyst.

![Scheme 11](image)

Fig. 41 Oxidation of allylic alcohols under solvent free conditions in the presence of gold and palladium catalysts redraw from the ref. 268.

Scheme 12 (A) The proposed intermediates for the formation of the corresponding lactone by oxidation of 1,2-benzenedimethanol. (B) The proposed intermediate for the formation of benzaldehyde by oxidation of meso-hydrobenzoinone.
aldehydes or ketones in quantitative yields. The presence of substituents on the aromatic ring such as NO₂, Cl or OCH₃ influenced the reaction rate but did not affect the selectivity of the product. The Au@npCeO₂ catalyst was also tested for the aerobic oxidation of vicinal-diols. Oxidation of 1,2-benzene dimethanol led to benzofuranone in quantitative yields. However, hydro-benzoin underwent oxidative C=C cleavage to form benzaldehyde as the main product (Scheme 12).

In 2009, Cao et al. reported base free protocol for alcohol oxidation using hydrogen peroxide as oxidant. The group synthesized various metal oxides supported catalyst but Au NPs@TiO₂ gave the best conversion (99%) with excellent yield (98%). It was shown that small AuNPs can substantially facilitate the crucial H₂O₂ decomposition. The synergetic interaction between AuNPs and TiO₂ support was responsible to achieving high activity in the H₂O₂ mediated oxidation of alcohols. TEM and XPS results showed essentially no changes in the mean diameters of the Au NPs and in the metallic state of Au.

Collaborative work done by Li et al. and Hensen et al. showed that gold nanoparticles supported on basic hydrozincite and bismuth carbonate support displayed good activity in solvent free system. The basicity of the support played a crucial role in enhancing the activity of this catalyst. The group checked various supports such as series of metal (Zn, Bi, Ce, La, and Zr) carbonate for the stabilization of gold nanoparticles. Among all, bismuth carbonate and hydrozincite showed excellent activity. AuNPs were loaded on this support by decomposition precipitation of aurochloric acid. Maximum benzaldehyde yield of 54% was achieved in case of hydrozincite based catalyst. This yield was considerably higher than that of Au@TiO₂ and Au@CeO₂. Stucky et al. also explored low cost promoters such as metal carbonates, acetates or borate as support for AuNPs and used them for aerobic oxidation of alcohols under solvent free conditions at 100 °C. By choosing appropriate promoters, product selectivity and alcohol conversion has been simultaneously improved.

4. Mechanism of alcohol oxidation

Outcome of alcohol oxidation is highly dependent on the type of carbon atom to which hydroxyl group is attached. Primary alcohols are easily oxidized to aldehydes but over oxidation leads to formation of carboxylic acids. According to the mechanism, primary alcohols on oxidation form aldehydes, which may get transformed to carboxylic acid on further oxidation through a hydrated aldehyde stage. Secondary alcohols are mostly unaffected by oxidation (Scheme 13).23-27

Controlling oxidation to aldehyde is the most important goal. Several attempts have been made to find out the reaction pathway of alcohol oxidation over supported gold catalyst using molecular oxygen. The adsorption and dissociation of molecular oxygen on extended gold nanoparticles surfaces is energetically unfavourable. There is growing consensus that it is low coordinated gold atoms that can actively adsorb oxygen. Thus oxygen dissociation depends on the morphology of gold nanoparticles more than size, Au(100) facet being most active. There is also evidence of support playing a key role in this.273 As far as oxidation of alcohols is concerned, according to the common mechanism reported by Corma et al.,264 Chechik et al.,274 and Nishimura et al.,275 the oxidation of alcohol generally involves three main steps. In the first step, alcohol molecules are

Scheme 13 General oxidation of alcohols (A) primary alcohol (B) secondary alcohol (C) tertiary alcohol.

Scheme 14 The proposed mechanism for the aerobic oxidation of alcohols redraw from the ref. 264.
adsorbed on the surface of gold nanoparticles. In the second step, \(\beta\)-hydride elimination take place to generate an active carbonyl species and a metal hydride (Au–H). While in the third step, the metal–hydride (Au–H) is oxidized by elemental oxygen to regenerate the gold surface (Scheme 14). Nishimura et al. also reported that the rate of catalytic reaction decreased on addition of little quantity of radical scavengers such as BHT and TEMPO. They believed that the scavengers decreased the rate of the reaction by combining with the radical intermediate species.\(^{274,275}\) Chechik et al. explored the mechanism by using electron paramagnetic resonance (EPR) spectroscopy and spin trapping. With the help of isotope labelling, they proved that the hydrogen in the spin adduct originates from the cleavage of the C–H bond in the alcohol molecule. The formation of the hydrogen spin adducts most likely resulted from the abstraction of hydrogen from the Au surface.

Mullins et al.,\(^{276}\) Yang et al.\(^{277}\) and Li et al.\(^{278}\) investigated the reactivity of oxygen and hydroxyl species on the surface of gold during the partial oxidation of allyl alcohol. The reaction mechanism for allyl alcohol oxidation was influenced by the relative proportions of reactive species on the gold surface (Fig. 42). Activation barrier calculated by DFT studies indicated that the hydroxyl hydrogen of allyl alcohol is readily abstracted by adsorbed oxygen or hydroxyl species on the gold surface to

![Fig. 42](image1.png)  
**Fig. 42**  
The mechanism for dehydrogenation of allyl alcohol to generate allyloxide on the O/Au(111) surface via (a) an oxygen adatom and (b) a hydroxyl species [reprinted with permission from ref. 276. Copyright (2014) American Chemical Society].
generate a surface-bound allyl oxide intermediate. This inter-
mediate on α-dehydrogenation generated acrolein via interac-
tion with an oxygen surface hydroxyl species.\textsuperscript{276}

Li \textit{et al.}, also explained the oxidation of methanol. According
to them molecular oxygen can be activated via a hydroperoxyl
(OOH) intermediate produced by abstracting a hydrogen atom
from co-adsorbed methanol or water (Fig. 43). The formed OOH
intermediate either directly reacts with methanol to produce
formaldehyde or dissociates into adsorbed atomic oxygen and
hydroxyl.\textsuperscript{277,278}

5. Photocatalytic oxidation

Photocatalytic organic transformation, a new reaction way to
carry out organic reactions at room temperature and ambient
pressure are becoming popular. Its biggest advantage is the
product selectivity as compared to thermal reactions where
unstable intermediates produce byproducts. Plasmonic metals
such as gold, with exceptional absorption of visible light have
the potential to photo-catalyse organic reactions.\textsuperscript{279–281} In 2011,
Kominami developed eco-friendly protocol for the oxidation of
benzyl alcohol using Au@cerium oxide as catalyst. Exception-
ally high selectivity (99%) with 99% conversion was reported in
20 h. Versatility of the protocol was also established. This report
inspired a number of other research groups to explore the
photocatalytic properties of supported gold catalyst.\textsuperscript{282} Likewise,
Liu \textit{et al.} reported that Au–Cu/TiO\textsubscript{2}–NB supported material
possessed excellent catalytic activity. A new photo-deposition
technique by galvanic replacement was developed to synthe-
size this catalyst (Fig. 44). The authors reported 93% conversion
with 98% selectivity for benzaldehyde at 240 °C in 8 h when Au/
Cu in the ratio of 1 : 2.3 was used.\textsuperscript{283}

Ke \textit{et al.} reported a novel green tool for the oxidation of
benzyl alcohol to benzaldehyde with high selectivity (99%)
under visible-light irradiation at ambient temperature. This
group synthesized Au@zeolites (Y) catalyst by using reduction
method and checked its catalytic activity for the oxidation of
various substituted benzyl alcohols (Scheme 15). A correlation
of surface plasmon resonance (SPR) effect of gold nanoparticles,
the adsorption capability of zeolite supports and the molecular
polarities of aromatic alcohols, on photocatalytic activity was
demonstrated.\textsuperscript{284} In a similar study by Zhu \textit{et al.} AuNPs@zeolite
were shown to have a strong ability to absorb visible and ul-
traviolet light. The catalyst prepared by impregnation methods
showed 23% conversion of benzyl alcohol with 100% selectivity
for benzaldehyde with molecular oxygen in the presence of base
at ambient temperature. The authors concluded that presence
of base (NaOH) significantly increased the photocatalytic
activity of the supported gold nanoparticles.\textsuperscript{285}

In 2014, Liu \textit{et al.} reported a novel green and highly efficient
methodology for the photocatalytic oxidation of alcohol using
Au@hydrotalcite in the absence of base under visible light. This
catalyst was prepared by a sequential deposition reduction
method. Benzyl alcohol conversion of 57.41% with 93.2% selectivity
for benzaldehyde under visible light in 24 h was
achieved by this group. The catalyst showed good recyclability.
and was easily recovered by centrifugation from the reaction mixture and after washing with deionized water and ethanol it could be reused for the next batch. The authors investigated the effect of solvents on reaction rates and studied solvents like toluene, mesitylene, benzotrifluoride and 1,4 dioxane. The polar solvents did not give good results. More than 40% conversion of benzyl alcohol with excellent selectivity was reported in non-polar solvents. However, best conversion (72.93%) was found in benzotri fluoride. Effect of metal loading and wavelength of light was studied and it was reported that the conversion of benzyl alcohol increased as the wavelength increased mainly due to the strong absorption of gold nanoparticles at 515–535 nm (Fig. 45).

In a collaborative work, Xu et al. and Liu et al. proposed a mechanism for the photocatalytic oxidation of benzyl alcohol275 using Au–Pd bimetallic nanoparticles supported on TiO2 nanobelts (Fig. 46). The proposed photo catalytic mechanism is similar to the aerobic dehydrogenation. Interestingly, it was shown that the presence of PdNPs play more important role for the cleavage of O–H and C–H bonds. Secondly, it was found that the electronic structure of Pd strongly impacts oxygen activation, and electrons transfer ability. In the first step, the activated Au sites transferred electrons to both Pd sites and TiO2 nanobelts. These electrons, which are present in the Pd sites and the heterostructured nanobelts can fill the unoccupied orbitals of oxygen molecules. Thus, transient anion O–O− species are formed which can cleave the O–H bond of the alcohol to form an alkoxide intermediate. While in the second step, the intermediate formed undergoes a hydride transfer from C–H to the positively charged Au to form benzaldehyde and Au−H species. In the third step, the cleavage of the Au−H species take places and the active sites of the catalyst are recovered.

6. Effect of particle size

It is understood that as the size of the nanoparticles decreases, its surface area to volume ratio increases. The free surface area of the nanoparticles is highly important because that increases the contact between reactant molecules and catalytic sites. Highly controllable size, shape and morphology make catalyst more successful and selective in many organic transformations. The effect of size on catalytic activity of AuNPs is even more
The catalytic activity of gold catalyst decreases dramatically with increase in size. In most of the reports, the authors have concluded that very small Au NPs (<5 nm) with low loading are very active as well as selective for the alcohol oxidation as compare to bigger size (>5 nm) Au NPs. The effect of size on the activity of catalyst was studied in detail by Fang et al. They proposed that AuNPs supported on HT exhibited higher conversion of benzyl alcohol (94%) when the gold loading was 0.06 wt% (size 4 nm). However, the conversion decreased as the gold loading was increased up to 0.26 wt% which led to increase in particle size (13.5 nm). In another report, they presented a linear relationship between the size of AuNPs and the TOF values. Similarly, the work done by Zhang et al. and Wang et al. indicated that the catalytic activity of the catalyst in terms of TOF value was depended on the size of AuNPs (Fig. 47) for the oxidation of benzyl alcohol. As the average diameter of Au NPs increased from 4 nm to 12 nm, the TOF decreased from 800 h⁻¹ to 200 h⁻¹.194

According to Corma et al. and Garcia et al. activity of AuNPs correlates linearly with the total number of external gold atoms and with the surface coverage of the support. They reported that during the oxidation of cinnamyl alcohol, TOF value decreased by increasing the size of AuNPs. However, the selectivity towards cinnamaldehyde remains unchanged that indicated that the selectivity is independent of gold particle size. They studied AuNPs having sizes 5–25 nm with cubic shape modelled in fcc crystal lattice and best TOF value was reported for AuNPs of size 5 nm.269 Similar results were obtained by Cao et al. They proposed that the use of smaller Au nanoparticles gave higher activity. Interestingly, the AuNPs having size less than 5 nm substantially facilitate the H₂O₂ decomposition (99% conversion of 1-phenyl ethanol in H₂O₂). The conversion decreased with increasing in size (Fig. 48).270 Similar results were reported by many others too and it can be concluded that activity of gold is directly related to size.

7. Recyclability

In the past few decades, the supported AuNPs have been developed as a sustainable replacement to conventional homo and heterogeneous catalysts as they combine the ease of separation with high catalytic activity. Which are the fundamental requirements for an ideal catalyst or green catalyst. The biggest advantage associated with gold catalyst is its higher stability and remarkable recyclability as compared to supported transition metal nanoparticles (Fig. 49). In solution phase reactions polymeric supported nanoparticles can be separated and recycled more easily compared to zeolites and oxides which are available in powder form. Similarly, nano supports are also not easy to handle. To overcome these problems, several approaches have been developed, such as the immobilization of Au NPs on a magnetic solid support, which rapidly separates nanoparticles from the reaction mixture.

Other important issues that are directly associated with recycling are leaching of the metallic species from

![Fig. 48 1-Phenyloethanol conversion and H₂O₂ decomposition versus gold particle dimension; oxidation of 1-phenylethanol: 10 mmol 1-phenylethanol, Au/TiO₂ (Mintek); 10 mL H₂O, 90 °C, 5% H₂O₂ added dropwise, substrate : H₂O₂ : Au = 100 : 110 : 1; H₂O₂ decomposition: 1.5 wt% H₂O₂ aqueous solution 10 mL, Au/TiO₂ (Mintek) 80 mg, 25 °C for 80 min in open air. The rate of decomposition was calculated based on the amount of H₂O₂ remaining, which was measured by the titration of 0.1 M Ce(SO₄)₂ with 1.5 w/v% ferroin solution as an indicator [reprinted with permission from ref. 270. Copyright (2009) Royal Society of Chemistry].

![Fig. 49 Stability and recyclability of supported Au NPs to the other catalyst.](https://example.com)

![Fig. 50 Catalytic performance of Au NPs@RGO catalysts during the recycling experiment [reprinted with permission from ref. 137. Copyright (2013) Elsevier Publication].](https://example.com)
nanoparticles and agglomeration of nanoparticles. Both lead to decrease in catalytic activity. Among the various supports reported in literature, polymeric supports such as macro porous divinylbenzene cross-linked material have shown excellent recyclability.\textsuperscript{290–292} Nanoparticles attached by covalent bonding to the support are generally sufficiently robust to survive the harsh reaction conditions; this binding and adsorption process minimizes catalyst leaching and allows the catalyst to be reused several times. It has been also observed that the catalyst in which nanoparticles are embedded in the matrix are more stable compared to those where they are present on the surface.

In 2008, Kobayashi et al. have investigated highly recyclable polymer-incarcerated carbon-stabilized gold nanoclusters (PI/CB-Au) for the oxidation of secondary alcohols. The catalyst was easily recovered by simple filtration method and reused without significant loss of its catalytic activity. No leaching was observed in solution. The inclusion of carbon black (CB) to the composition of the catalyst enhances the stability of gold nanoclusters. The catalyst could be recovered and reused up to five times without any loss of its activity. After five runs, the yield for acetophenone was >99%.\textsuperscript{189} Li et al. reported that Au NPs@PS composite with excellent recyclability and stability towards benzyl alcohol oxidation. After the reaction, the catalyst was recovered by centrifugation method and used for the next run. The activity of this composite was maintained up to five runs with same yield.\textsuperscript{185}

Rossi et al.\textsuperscript{186} and Zhang et al.\textsuperscript{199} have reported magnetic separable catalyst to facilitate its from the reaction mixture. But, the conversion decreased and reached 35% after the fourth run though selectivity was unchanged. ICP-AES studies indicated hardly any leaching. Slight change was observed in the size of AuNPs after two consecutive runs. In case of Au NPs@HT catalyst, the size of AuNPs increased up to 0.1 nm. However, size of Au NPs was increased up to 0.5 nm for the Au NPs@G-Al\textsubscript{2}O\textsubscript{3} catalysts and the Au NPs were coagulated in case of Au NPs@MgO catalyst.\textsuperscript{198}

Huang et al. and Ma et al. investigated the reusability of Au NPs@RGO catalysts for the oxidation of benzyl alcohol (Fig. 50). After the reaction, the catalyst was recovered by simple filtration. The filtrate material was dried in vacuum at room temperature for 12 h. After complete drying, it was ready to use for the next batch. After five runs, the conversion of benzyl alcohol (BA) was decreased steadily from 65% to 40% while the selectivity towards benzaldehyde remained more than 90%. The activity of the catalyst was decreased mainly due to the mass loss during the filtration method.\textsuperscript{197}

To conclude supported nanoparticles can be separated using simple filtration, centrifugation and magnetic separation. Recycling upto five cycles is common. Leaching is either absent or negligible. Small increase in size of gold nanoparticles has been reported in some cases.

8. Conclusion and outlook

Heterogenization of nanoparticles using supports is great step in bridging the gap between homogenous and heterogeneous catalysis. Alcohols are an important raw materials for many chemical industries and development of green and sustainable methods for their oxidation is crucial for them. The usage of gold nanoparticles is advantageous in this respect as they show better recycling compared to other transition metals. Especially noteworthy achievements of AuNPs in alcohol oxidation are base free, solvent free reactions using molecular oxygen as oxidant. However, in case of oxidation alcohols designing catalyst that can control the outcome of a reaction in terms of activity and selectivity is the biggest challenge. Activity of gold nanoparticles is largely dependent on the size and greater understanding of nano particle synthesis in recent time has allowed a much better precision in particle size, shape, composition etc. Thus, great improvements in activity of the catalysts is reported. In oxidation of secondary alcohols using AuNPs very high TOFs of the order of 10\textsuperscript{4} or more are easily achieved. But, in oxidation of primary alcohols besides activity, restricting the outcome of reaction to aldehyde stage is rather tricky as enhancement of catalytic activity leads to acids rather than aldehydes. This is where the nature of support has played a key role i.e. optimisation of activity with selectivity.

Many supports starting from conventional C, SiO\textsubscript{2}, zeolites, polymers to more advanced CNTs, MOF, graphenes, nano oxides have been explored to achieve the target of high activity with total selectivity for aldehydes. On one hand this goal has been achieved by enhancing hydrophobicity in polymer supports on the other enhanced interaction of oxides supports such as CeO\textsubscript{2} and TiO\textsubscript{2} has yielded wonderful results. Still others like zeolites have enhanced photochemical oxidations. MOFs are very useful in controlling size of nanoparticles and with many of them oxidative esterification was exclusively achieved. The present review has collected many examples from the literature that clearly prove the intrinsic activity of supported AuNPs for some of the important alcohol oxidations. Oxidation of allyl alcohols to useful 3-hydroxypropionic acid is one of them. Though, some scientists have focused on stabilisation of very small sized clusters (<1 nm) with good dispersion on supports that has not led to selectivity as far as oxidation of primary alcohols is concerned. Recyclability upto five cycles was shown by many catalyst and leaching is negligible from most of the supports probably because of heterogeneous nature of catalysis. With judicious choice of support combining activity, selectivity, accessibility of catalytic sites (low catalyst conc.) and ease in handling AuNPs are certainly promising in the field of alcohol oxidation. As far as industrialisation is concerned challenges in terms of scalability, economy and recyclability of the catalyst still exist.

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