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A step forward towards greener aerobic alcohol oxidation: new and revised catalysts based on transition metals on solid supports

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*Dedicated to Prof. Andrea Goti on the occasion of his 60th birthday*

The oxidation of alcohols is a reaction under continuous investigation, due to the importance of the oxidation products and the necessity to perform it in a more sustainable way with respect to traditional procedures. In particular, the combination of a metal catalyst with molecular oxygen or air represents one of the best alternative in the field. New catalysts are continuously proposed in the literature, and it is not often easy to compare their performances owing to the great amount of examples reported. Heterogeneous catalysts represent the best solution to heavy metal contamination of the products, providing that leaching has not occurred. Moreover, they ideally should be recovered without deactivation and reused after reaction. The employ of air or oxygen in non-flammable solvents (ideally, water) is also highly appreciated, for safety reasons. We have tried in this review to focus on some very recent reports on solid supported transition metal catalysts that strive to follow these principles thus performing the oxidation in the more sustainable way while guaranteeing an acceptable substrate scope for synthetic utility.

Introduction

Oxidation reactions are commonly employed by industry to convert petroleum-based feedstocks into chemical reagents commonly used as starting materials. However, they often use polluting and hazardous procedures that deliver toxic wastes (e.g. metal salts in stoichiometric oxidations with metal derivatives or nitrogen oxides in oxidations carried out with HNO3). The pharmaceutical industry has started to limit the use of oxidation reactions for sustainability reasons, such as the disposal of hazardous by-products and safety concerns associated with the use of flammable organic solvents.1

When designing a new oxidation procedure, the principles of green and sustainable chemistry must be carefully considered.2 The traditional oxidation methods are no more acceptable nowadays, and great efforts are constantly made by the scientific community to search for new sustainable oxidants.3 In particular, the oxidation of primary and secondary alcohols to the corresponding aldehydes, ketones and carboxylic acids is a ubiquitous transformation in synthetic organic chemistry and still represents one of the highest investigated reactions, also due to the wide occurrence of these moieties in drugs, vitamins and fragrances.4

There is still an increasing need for systems that are effectively green, scalable and have broad synthetic utility. Ideally, an oxidizing reagent should be able to oxidize a broad variety of different alcohols bearing different functionalities while being as green as possible.5 Enormous efforts have been devoted to the development of aerobic oxidation methods to achieve this transformation. The combination of a metal catalyst with molecular oxygen is certainly the best alternative to the existing methodologies.6,7 Indeed, while catalysis allows reactions to occur under mild conditions in order to save the overall implied energy,8 oxygen in particular (or air, even better), is the cheapest and less polluting stoichiometric oxidant, with the highest active oxygen content (100 or 50 wt%). Moreover, it produces no waste or water as the sole by-product. However, oxygen in combination with volatile and flammable organic solvents can represent a potential risk. This can be reduced if oxygen is diluted with 10% of nitrogen or if air is employed for the oxidation instead of pure oxygen. In alternative, an improved safety profile can be achieved by performing the reactions in non-flammable solvents as water.9 The choice of the solvent is not a trivial task and often is a result of a compromise between sustainability and reactivity. For this reason, we decided to exclude from this review, apart from few significant examples, methods that use pollutant chlorinated solvents.

The field of the aerobic oxidation of alcohols is currently extremely studied, and many good reviews on the topic have already been reported, covering both homogeneous and heterogeneous catalytic systems,10 and also metals in the form of nanoparticles.11 In particular, the interest in metal nanoparticles is also sustained by the prospect of applying aerobic oxidation to biomass conversion, which is an abundant source of alcohols.12

*However, in most cases, it is quite difficult to compare the performances of the different catalysts.* The aim of this review, far to be exhaustive on the field, is therefore to make a critical selection on the most interesting catalytic systems developed in the last few years (2014-2016) that have an effective green potential, up to our opinion. In this regard, *we decided to limit the reported examples to metals on solid supports.* Indeed, the main problem with homogeneous catalysis is the difficulty to separate the catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. Heavy metal contamination of the isolated product is a significant drawback for application in industry. Removal of trace amounts of catalyst from the target product still remains a key challenge that homogeneous catalysis has to be faced out. From a sustainability point of view, we should be aiming to develop systems that are able to recover the metals, and for this reason we decided to focus this update only on supported metals, that can be in principle reused and recycled.

Heterogeneous catalysts can be easily separated from the reaction mixture by a simple filtration or centrifugation of the reaction solution and reused in consecutive reactions provided that the active sites have not become deactivated and leaching has not occurred. We will focus on examples that take this aspect also in account. We further limited the choice of the literature on the basis of some of the well known green chemistry principles8 and in particular we preferred methods with an acceptable substrate scope and that employed mild reaction conditions, such as temperature not higher than 150 °C, no (or low) pressure of oxygen and reasonable reaction times.

Copper Based Catalysts

Copper is a non noble and inexpensive abundant metal. Therefore, its use is highly encouraged to develop new catalysts.

While the practical aerobic oxidation of alcohols using homogeneous copper catalysts is quite mature, and systems combining homogeneous copper with TEMPO and related systems have been recently reviewed,13 copper-based oxidative heterogeneous catalysis has been rapidly developing only in recent times.14,15 Some examples are reported herein.

CuO nanoparticles alone, synthesized following a modification of a previously reported procedures, were able to oxidize benzylic and allylic alcohols without the need of other additives using air as the oxidant, although in quite high amount and with quite harsh reaction conditions (75 mol% of catalyst with respect to the substrate, toluene, 100 °C). Unfortunately, unless the catalyst could be easily separated from the reaction mixture by filtration followed by drying, it maintained the same conversion only for the first two runs, while further reuse led to a gradual decrease in conversions.16

CuO supported on ZnO was reported as an efficient and recyclable catalyst for the aerobic oxidation of several benzylic, primary and secondary alcohols (including unactivated aliphatic ones) in water at reflux temperature, in the presence of 0.5 equiv of base (Cs2CO3) and with oxygen as the oxidant (Scheme 1). The reactions occurred with total selectivity for aldehydes or ketones and no other products were detected in the reaction mixture. Water demonstrated to be the best performing solvent among other tested (EtOH, CH2Cl2, CH3CN, *n*-hexane and toluene). The nanocatalyst CuO/ZnO was prepared with a co-precipitation method and characterized by several techniques. After the reaction, it could be recovered by filtration and reused up to five times without observing appreciable yield decrease.17



Scheme 1. Aerobic oxidation of alcohols by a CuO/ZnO nanocatalyst

An interesting support for a copper-tetrasulfonate phthalocyanine complex was found in nanocrystalline cellulose (NNC), a crystalline form of cellulose that has recently found different applications due to its outstanding physical and chemical properties. NCC is obtained by applying to cellulose a mild hydrolysis with a mineral acid, which selectively breaks amorphous regions in cellulose, while leaving crystalline regions intact giving rise to individual nanocrystallites.18 NCC was made cationic by treatment with (2,3-epoxypropyl) trimethylammmonium chloride (EPTMAC) in aqueous NaOH and then grafted to anionic copper tetrasulfonate phtalocyanine (PC). The resulting NCC-PC catalyst (Figure 1) was applied to the aerobic oxidation of different alcohols including primary and secondary aliphatic and aromatic alcohols, in water as solvent and using air as the sole oxidant without the need of any base requirement.19



Figure 1. Copper-tetrasulfonate phtalocyanine complex grafted to cellulose nanocrystals (NCC-PC)

The catalyst could be recovered by simple centrifugation. Leaching of copper was ruled out by ICP-AES analysis of the supernatant after centrifugation, and 7 consecutive runs could be performed without major decrease in product yield, indicating that the catalyst doesn’t suffer any deactivation during its catalytic process.

A similar strategy was also employed by Shaabani and co-workers, who grafted the same copper(II) tetrasulphonated complex (CuTSPc) by means of ionic interactions to a three-dimensional nitrogen-doped graphene-based frameworks (3D-(N)GFs).20 3D-GFs like graphene aerogels and foams are new generation porous carbon materials recently employed as solid supports for accommodating metals especially for catalytic applications.21 The resulting CuTSPc@3D-(N)GFs worked as a bifunctional catalyst where copper(II) acted as the active site and nitrogen as the base, eliminating the need for other additives. This catalyst (0.4 mol% Cu) was effective in the aerobic oxidation of a large variety (19 examples) of alkyl arenes, primary and secondary alcohols including unactivated aliphatic ones in very mild conditions (water as solvent at room temperature with air as the oxidant) (Scheme 2). The ionic interactions grafting the metal to the support increased the hydrophilic properties of the catalyst by improving its stability and dispersity in aqueous solution. However, recovery of the catalyst was possible through simple filtration, and the catalyst could be reused up to six times. Leaching of copper was estimated to be negligible.



Scheme 2. Aerobic oxidation of arenes and alcohols by copper(II) tetrasulphonated phthalocyanine on three-dimensional nitrogen-doped graphene (CuTSPc@3D-(N)GFs)

Based on the Cu/TEMPO catalyzed homogeneous aerobic oxidation developed by Stahl and co-workers,22 Fernandes and Jensen envisaged that a heterogeneous bifunctional catalyst where both ligand/Cu and TEMPO were immobilized on the same support could afford some benefits through synergistic effects for the aerobic oxidation of alcohols. They used the “click” CuAAC reaction to graft both the ligand and the TEMPO based moieties to a silica platform in different relative proportion in order to achieve an accurate control on surface composition. Aerobic oxidation of benzyl alcohol, in toluene at 80 °C under O2 bubbling was studied with these catalysts. This system, although intriguing in its conception, appear still immature since recycling studied revealed a significant decrease of activity after each run and no substrate scope is reported.23 Even more interestingly, they could incorporate also *N*-methylimidazole (NMI), which is known to accelerate the Cu/TEMPO-catalyzed aerobic oxidation of alcohols by decreasing the CuII/CuI reduction potential, thereby creating a supported trifunctional catalyst that well compete (and even reached better performances) with the corresponding homogeneous catalysts.24 They could recycle and reuse this new catalyst up to five times; however, neither in this case the substrate scope was investigated.

Another interesting solution to graft together both TEMPO co-catalyst and copper(I) in one single molecule was found by Lu and co-workers, who synthesized a bi-functionalized PEG1000 ionic liquid [Imim-PEG1000-TEMPO][CuCl2-] in which a 4-hydroxy-TEMPO was linked to the ionic liquid through a PEG spacer and CuCl2- was the active anion (Figure 2).25 Room temperature ionic liquids (RTILS) have great advantages like negligible volatility and thermal stability.26 Polyethylene glycols are commercially available non toxic and recyclable polymers. These two concepts, combined together, created a new catalytic system (used in 5 mol% with respect to the substrate) where a wide range of primary and secondary benzylic alcohols and two examples of aliphatic alcohols underwent oxidation under air atmosphere at 60 °C, without adding any other organic solvent or additive.



Figure 2. Structure of a bi-functionalized PEG1000 ionic liquid used as catalyst in solvent free aerobic oxidation of alcohols

Even if this is not a solid supported catalyst, we have included it in this review since it could be recycled after extraction of the products (aldehydes or ketones) with ether, dried under vacuum and reused five times in a new reaction with fresh substrate.

Metal-organic frameworks (MOFs) are promising platforms for creating a composite heterogeneous catalyst system.27,28 MOFs are porous crystalline materials, assembled from metallic ions or metal clusters and organic linkers. MOFs have gained popularity as promising supports in heterogeneous catalysis, due to their high porosity and high surface areas, which can accommodate a high concentration of the active catalytic sites, and chemical stability. Furthermore, tailor-made design of the organic ligand and post-synthetic modification procedures (PSM)29 enable a straightforward insertion of the catalytic active site into the MOFs. Consequently, MOFs have been used also as heterogeneous catalysts for oxidation reactions.30 A recent example in the field of aerobic oxidation of alcohols was reported by Lee and co-workers.31 They employed a previously prepared microporous Cu-MOF-7432 for the aerobic oxidation of primary benzylic and allylic alcohols (7 examples) under O2 atmosphere at 70 °C in the presence of TEMPO and DMAP as co-catalysts, in CH3CN as solvent (Scheme 3). All catalytic components were proved to be necessary for the oxidation.



Scheme 3. Aerobic oxidation of benzylic alcohols by copper on metal-organic frameworks (MOF) (Cu-MOF-74)

However, heteroaromatic substrates gave lower yields probably due to coordination to the catalyst, and no oxidation of aliphatic unactivated alcohol is reported. Moreover, the reusability of the catalyst was demonstrated only for benzyl alcohol and for just a second run.

Another example of copper on MOF was reported by Lu and co-workers.33 They immobilized three kinds of Cu(II) salts onto the surface of the previously reported amino-functionalized Zr-MOF (UiO-66-NH2)34 by treatment with salicylaldehyde and then copper salts, and found that the resulting UiO-66-Sal-CuCl2 catalyst was the best choice to perform the aerobic oxidation of allylic and benzylic primary alcohols. The reactions were performed, as before, in CH3CN at 60 °C in the presence of O2, and TEMPO and a base (NaHCO3, in this case) were needed as additives (Scheme 4). The conversion on a secondary benzylic alcohol was significantly lower with respect to primary alcohols in the same conditions.



Scheme 4. Aerobic oxidation of benzylic alcohols by copper on metal-organic frameworks (MOF) (UiO-66-Sal-CuCl2)

The UiO-66-Sal-CuCl2 catalyst could be recycled up to five times without suffering from leaching problems and without change in the structure of morphology of the catalyst.

Among the different MOFs, Cu3(BTC)2 (also known as CuBTC, BTC=1,3,5-benzenetricarboxylate) is one of the most widely used materials due to its high surface area, tunable pore structures and good chemical stability. Nanoscale MOFs of different size and shape of crystals were produced employing Cu2+ salts and BTC as MOFs precursors (and called Cu-MOF-1, Cu-MOF-2 and Cu-MOF-3) and one of them (Cu-MOF-2) was applied to the aerobic olefin epoxidation of alkenes and to the aerobic oxidation of some benzylic and allylic primary alcohols (secondary benzylic did not react), in similar reaction conditions as shown above for other Cu-MOFs based catalysts (CH3CN, 75 °C, 0.5 equiv of TEMPO, 1 equiv of Na2CO3).35 Although the reported substrate scope is quite limited, it is worth noting that the Cu-MOF-2 catalyst demonstrated excellent reusability for aerobic olefin epoxidation and alcohol oxidation (up to 15 recycles) and no leaching of copper.

Wang and co-workers reported a new catalyst in which a functional sulfonated-polystyrene (SPS), a porous Cu3(BTC)2 shell and an active Cu(II) interface between the core and the shell were assembled together via a step-by step assembly method.36 The main function of the SO3 groups on the PS core was to graft Cu(II) ions to generate the catalytically active Cu(II) interface, while the porous Cu3(BTC)2 shell protected the active metal from leaching as well as provided porous channels for mass transfer. These features resulted in high stability and recyclability in the catalysis procedure: the catalyst remained substantially active for over 10 recycles without changing its overall structure (only after 18 cycles the structure of the SPS-Cu(II)@Cu3(BTC)2 was broken). The authors could also demonstrate that the porous Cu3(BTC)2 shell protected the heterogeneous catalyst from metal leaching. The synthesized SPS-Cu(II)@Cu3(BTC)2 catalyst was employed in 2 mol% (Cu amount) for the aerobic oxidation of primary benzylic and allylic alcohols, in CH3CN as solvent at 75 °C and in the presence of 10 mol% TEMPO, with O2 (1 atm) as the oxidant and under base free conditions. Unfortunately, with this system secondary aromatic, allylic or aliphatic alcohols were very difficult to oxidize probably due to steric interactions.

A very interesting study aimed at investigating the performance of a MOF catalyst based on Cu3(BTC)2 synthesized in CO2 expanded DMF was undertaken by Zhang and co-workers.37 They synthesized Cu3(BTC)2 in CO2-expanded *N*,*N*-dimethylformamide (DMF)38 at 30 °C, using copper(II)acetate monohydrate (Cu(OAc)2.H2O) and benzene 1,3,5-tricarboxylic acid (H3BTC) as MOF precursors. They found that a higher CO2 pressure favored the formation of larger mesopores, and this was also reflected in an improved catalytic activity of the material towards the aerobic oxidation (in the presence of 0.5 equiv of TEMPO, 1 equiv of Na2CO3, DMF, oxygen atmosphere, 75 °C) of benzylic and allylic alcohols (5 examples) to the corresponding aldehydes. This catalyst showed no evident drop in catalytic activity after four runs.

Cu3(BTC)2 was also recently immobilized onto superparamgnetic Fe3O4 thereby generating a recoverable catalyst by application of an external magnet.39

A tricky solution to incorporate a nitroxide co-catalyst into the heterogeneous catalyst was developed by Kitagawa and co-workers.40 They synthesized a free-radical decorated PCP (porous coordination polymer) employing an organic ligand for Cu(II) in which a stable free radical isoindoline nitroxide was incorporated. This catalyst was applied to the oxidation, in the presence of 20 mol% TBN (*t*-butyl nitrite) and O2, of several benzyl and aliphatic alcohols (20 examples). Although the simple work up procedure is appealing to industrial application, the main drawback of this procedure is that the reaction were carried out in NMR tube and using a chlorinated solvent (C2D2Cl4) at 80 °C.

The discovery of mesoporous material MCM-41 has given a great stimulus to the research in heterogeneous catalysis and has provided a new possible candidate for the immobilization of homogeneous catalysts.41 A bipyridine copper(I) complex was recently immobilized into MCM-41 (Figure 3) furnishing an effective heterogeneous copper catalyst (pale blue powder) that was able to convert a wide range of primary benzylic and allylic alcohols to the corresponding aldehydes in good yields.42

Appreciable is the use of air as the stoichiometric oxidant (instead of O2). The reaction were run in EtOH at 50 °C in the presence of 5 mol% TEMPO and inexpensive aqueous ammonia as the base. Leaching of the catalyst was ruled out since after hot filtration of the catalyst, no further reaction was observed and no copper could be detected in the solution by ICP-AES analysis. The reaction on 4-methylbenzyl alcohol could be performed on gram scale with 94% yield of isolated 4-methoxybenzyl aldehyde.



Figure 3. Structure of MCM-41-bpy-CuI complex

Finally, TentaGel and Merrifield supported Cu(I)/MeObpy (bipyridyl) catalysts were synthesized and used for the aerobic oxidation of several alcohols in toluene at room temperature using open air vessels. In particular, the Merrifield support showed <1% metal leaching (in contrast to the TentaGel resin) and allowed the good conversion of benzylic alcohols (6 examples), in the presence of 9-azabicyclo[3.3.1]nonane N-oxyl (ABNO) (5 mol%) and NMI (10 mol%) with possibility to be reused up to seven runs.43

Iron Based Catalysts

Iron is the second most abundant metal in the earth’s crust. From the sustainability point of view, iron is in much more advantageous position over copper due to its ready availability, lower price and low toxicity. All these reasons make iron an ideal metal for catalysis. Conversely, iron-based systems for the aerobic oxidation of alcohols have remained relatively underexplored, considering that the first homogeneous procedures dates back to 2002 by Martin and Suárez44 and the first bi-magnetic catalyst composed of Fe and TEMPO supported in an ionic liquid was developed by Zhang and co-workers in 2011.45,46

A novel silica supported iron(III)-based heterogeneous catalyst (called FeCl3-imine@SiO2) was synthesized in two steps starting from 3-aminopropyltriethoxysilane functionalized silica gel (APTES@SiO2), that underwent condensation reaction with acetamide to get an imine-functionalized silica gel (imine@SiO2) containing a bidentate ligand for iron. Final treatment with FeCl3 generated the FeCl3-imine@SiO2 catalyst, which proved to be effective for the aerobic oxidation in water as solvent (using bubbling O2 at 80 °C) of a series (14 examples) of primary and secondary benzylic alcohols and aliphatic primary and secondary alcohols (even if these latter gave more moderate yields) (Scheme 5). Remarkably, although usually immobilized catalysts show lower activity compared to their homogeneous counterparts, in this case the supported catalyst performed better than homogenous FeCl3, suggesting a possible cooperative effect between the metal and supported ligand. The FeCl3-imine@SiO2 catalyst could be reused at least five cycles without significant loss in activity and the hot filtration test indicated that no leaching of the catalyst occurred and that the system is truly heterogeneous.47



Scheme 5. Aerobic oxidation of alcohols by a silica supported FeCl3-imine@SiO2

Graphene oxide (GO) nanosheets were covalently funtionalized with iron phtalocyanine (FePc) (12% w/w FePc). This new catalyst was fully characterized and applied to the aerobic oxidation of alcohols. After a screening of solvents and temperatures, the best conditions for the oxidation of benzyl alcohol as the model reaction with this new catalyst (0.4 mol% Fe) were found using water as solvent at 60 °C, and bubbling oxygen in the presence of K2CO3 (0.5 equiv) as the base (Scheme 6).48 The optimized conditions were applied to the oxidation of a variety of primary and secondary aliphatic and aromatic alcohols and good conversions were obtained with all tested alcohols (21 examples) even if aliphatic ones required prolonged reaction times (around 90 hours). GO-FePc showed good stability and recyclability as the conversion yields for six runs did not decrease significantly.



Scheme 6. Oxidation of alcohols by GO-FePc hybrid material

Magnetic nanoparticles have become increasingly attractive in the field of heterogeneous catalysis as they combine interesting reactivity with an easy, economical and environmentally benign mode of recovery. Indeed, they can represent vehicles for supporting catalytically active nanoparticles or molecules and they can simplify the recovery process of catalysts from liquid reaction mixture by using an external supermagnet.49

In previous works, Liu and co-workers demonstrated that ultrafine iron oxide species supported on carbon were active in the aerobic oxidation of alcohols, although the amorphous nature of these catalysts gave the ultrafine iron oxides particles very low superparamagnetism and thus the catalyst could not be recycled by separation with an external magnet.50 However, more recently, they succeeded in the preparation of a composite of carbon-supported Fe3O4 (called Fe3O4/C) employing an ammonia-assisted precipitation procedure, which accomplished the dual role of catalyst and magnetically recoverable entity.51 This catalyst has high magnetic properties that were attributed to the pure Fe3O4 crystal phase present in Fe3O4/C. Taking advantage of these properties, Fe3O4/C could be easily separated from the reaction solution by using an external magnetic field. The catalytic performance of Fe3O4/C was tested in the oxidation of several benzylic alcohols (7 examples) in toluene at 80 °C with air as the oxidant source. Allylic and secondary aliphatic alcohols such as trans-2-hexenol and sec-butyl alcohol could also be oxidized even if in lower yields and by increasing temperature and reaction time. A hot filtration test confirmed the heterogeneous nature of the Fe3O4/C catalyst, which could be recovered and reused up to five times with no changes in the crystallinity and mesoporous structure of the material.

Highly superparamagnetic nanoparticles (Fe3O4 NPs) were also prepared through a modified co-precipitation method and embedded into a Fe-MIL-101 metal-organic framework. The catalytic activity of Fe3O4/Fe-MIL-101 was investigated in the aerobic oxidation of alcohols and epoxidation of olefins.52 However, regarding the aerobic oxidation of alcohols using O2 as the stoichiometric oxidant, the substrate scope was limited to primary benzylic and allylic alcohols to the corresponding aldehydes (secondary benzylic and aliphatic showed poor conversions) and the reaction required the presence of additives (0.5 equiv of TEMPO, 0.2 equiv of KNO2 in CH3CN at 75 °C). The advantages of this catalyst is its easy recover using an external magnet and its reusability for a total of eight times with only marginal loss in efficiency.

Interestingly, an aqueous-phase aerobic alcohol oxidation was recently reported using non–precious metals (among which not only Fe, but also Cr, Co, Ni and Cu) dispersed throughout a nitrogen-containing carbon matrix. These catalysts, also innovative in their concept, need to be further investigated and improved since for the moment the oxidation works well only for benzyl alcohol and for 1-6-hexanediol (HDO) and 1 MPa of O2 pressure at 80 °C is required.53 A similar cooperative catalysis between nitrogen-doped carbon with various transition metal oxides (Fe, Cu, Co) applied to the oxidation of reactive allylic and benzylic alcohols was reported by Eisenberg, Rothenborg and co-workers.54

Palladium-catalysed reactions

Oxidation of alcohols by palladium has been known for many years, in particular from the early observations by Berzelius that precipitation of Pd metal occurred when K2PdCl4 was refluxed in an ethanol solution.55 A recent review by Lee and Muldoon described the efforts made by the scientific community in the last 15 years on the selective aerobic oxidation of alcohols catalysed by homogeneous and heterogeneous based systems.56 However, in terms of utilizing Pd-based catalysts on a larger scale, the use of a heterogeneous catalyst is undoubtedly preferred, and we describe herein selected very recent efforts made in this field.

Much work has been focused on the use of MOFs27 that are highly promising porous materials for the incorporation of active phases for catalytic applications such as metal nanoparticles (M NPs). Aggregation and leaching of M NPs taking place during catalytic reactions can be minimized in MOF-encapsulated M NPs due to the confinement and electronic effects offered by MOF network. The most employed strategy for creating MOF with embedded M NPs is using MOFs as templates to generate the nanoparticles. However, the main issue is often a random distribution of metal precursors on the MOF material. Luque, Li and co-workers developed a synthetic strategy to encapsulate palladium precursors through ligand design prior to MOF assembly (Scheme 7).57



Scheme 7. Synthesis of Pd0–in-UiO-67

This strategy allowed metal precursors to be evenly distributed within the cavities of UiO-67 MOF. The confined nanoparticles present in this material (called Pd0–in-UiO-67) showed enhanced catalytic activity and stability by comparison to those synthesized by a traditional impregnation method. In particular, the catalyst (1 mol% Pd) was applied to the aerobic oxidation, in toluene at 100 °C, of a series (12 examples) of aromatic and aliphatic primary and secondary alcohols, with good yields also with unactivated alcohols (although 2 mol% of Pd and 120 °C were required in those cases). Reactions were carried out under air atmosphere and base-free conditions. The recyclability of the catalyst was examined in the aerobic oxidation of cinnamyl alcohol. After the reaction, the catalyst was separated by centrifugation, washed and reused for up to ten runs without reduction of catalytic activity nor change in its structure, indicating that the MOF frameworks plays an important role in preventing the encapsulated palladium NPs from aggregation during the reaction. Leaching of homogeneous palladium was also ruled out by a hot filtration experiment, indicating that an effective heterogeneous oxidation takes place.

In terms of security issues, an ideal oxidation process should be performed under mild conditions using oxygen or air as the oxidant in the absence of any solvent or additives. Yu and collaborators made an effort in this direction, demonstrating that palladium nanoparticles supported on a titanate nanobelt (Pb/TNB) are able to oxidize aromatic primary and secondary alcohols to the corresponding ketones in totally solvent-free and base-free conditions, at 120 °C in an oil bath with a continuous oxygen stream bubbled in at a flow-rate of 20 mLmin-1.58 However, this procedure was limited to aromatic alcohols bearing electro-donating groups. Moreover, during the recycling study of the catalyst it was observed that 5.4% Pd content was leached each cycle and TEM images revealed the tendency of Pd nanoparticles to grow larger in the recovered catalyst. Therefore, further studies are needed to improve these aspects.

Some other efforts were reported to perform the aerobic oxidation of alcohols under completely solvent-free conditions using Pd nanoparticles embedded in different supports, although with often limited substrate scope.59

Zamani and co-workers reported a simple preparation of palladium nanoparticles incorporated into a Fe3O4/amino acid nanocomposite. The surface modification of the magnetic nanoparticles with the amino acid allowed trapping of palladium nanoparticles through interactions between the metal nanoparticles and the functional groups of amino acids. In particular, Fe3O4/cysteine-Pd exhibited the highest catalytic performance and excellent selectivity in the solvent-free aerobic oxidation of various primary alcohols (9 examples) to the corresponding aldehydes (including two unactivated aliphatic alcohols) at 50 °C with oxygen bubbling into the mixture. The best performance of cysteine among other amino acids is attributed to the presence of sulphur atom that can act as stabilizer for the palladium nanoparticles. The catalyst was removed by an external magnet on completion of the reaction, and could be reused seven times without any significant loss in activity/selectivity performance.60

Another interesting class of heterogeneous palladium-based catalyst was reported by Karami and co-workers. They formed heterogeneous palladium nanoparticles by reaction of different homogeneous palladium complexes with CB[6] (curcubit[6]uril) macrocycles, and applied this catalyst to the oxidation of a range of aromatic alcohols, in toluene at 90 °C with K2CO3 as the base, under air conditions. The catalyst could be reused at least five times. However, it was completely inactive towards aliphatic alcohols.61

Related to the green solvents issue, Mukhererjee and co-workers contributed with an interesting work focused on the use of ionic liquids.62 The first part of the study is devoted to demonstrate the higher efficacy of a Pd nanoparticles based catalyst (heterogeneous) compared to the soluble Pd complex [PdCl2(PhNH2)2] (homogeneous) in terms of mild conditions employed and substrate scope. However, also the heterogeneous method suffers of poor recyclability (30% conversion with the first recycle *vs* 90% conversion with fresh catalyst) when common organic solvents (THF, CH2Cl2) are used in the oxidation reactions because of Pd nanoparticles aggregation phenomena (as attested by TEM micrographs). Very interestingly, this problem was successfully overcome when an ionic liquid, namely [bmim]OAc, was used as solvent: in this case, longer reaction times are required due to the lower solubility of O2 in this type of solvents at room temperature (2h *vs* 30 min), but the Pd nanoparticles retain their usual catalytic activity (around 80% of conversion) up to the fifth oxidation cycle. Although more substrates should be investigated with these conditions (only the butanol example is reported), the dispersion of Pd nanoparticles in an ionic liquid seems to efficiently prevent the aggregation phenomena, making the heterogeneous catalyst truly reusable. Ionic liquids (namely imidazolium groups) were also incorporated in a novel and very interesting class of catalyst systems consisting of Pd nanoparticles immobilized into periodic mesoporous organosilica materials (PMO) with bridging organic functional groups (1,4-bis(triethoxysilyl)benzene and 1,4-bis(trimethoxysilyl)ethane), reported by Karimi and co-workers.63 These bifunctional systems, overall defined as BFPMO-IL, benefit of important features deriving from their preparation methodology and composition. In particular, the mesoporous organosilica material can be prepared with (*plugged*) or without (*unplugged*) the presence of confinement channels, arising from microporous silica nanocapsules (plugs).

A preliminary investigation on different compositions of *unplugged* systems was carried out, attesting that Pd@BFMO-IL catalyst with a 10% of imidazolium and 15% of ethyl functionalities, respectively, furnished the best result oxidizing benzyl alcohol to benzaldehyde in 90% yield and excellent selectivity (99%). The oxidation reactions were performed at 90 °C for 15 h, by using water as solvent, O2 and K2CO3. Although only benzylic alcohols were employed as substrates, the appealing aspect of this work is that, in the same reaction conditions of the above mentioned example, the analogue *plugged* catalyst furnished benzoic acid in 93% yield and only a 2% of benzaldehyde (95% of conversion), as reported in Figure 4. For the other tested benzylic alcohols, higher conversions but lower selectivity were obtained, even if the corresponding acid is always the major product. This surprising change in the behavior of the two catalytic systems can be ascribed to the hydrophilic nanoregions created by the plugs into the mesoporous material, able to promote the retention of the hydrated aldehyde in the proximity of Pd nanoparticles, thus enabling the overoxidation of this intermediate to the corresponding acid. Moreover, both *plugged* and *unplugged* catalysts were recovered by simple filtration and reused for 4 subsequent reactions without any remarkable decrease in activity and selectivity, and no leaching of Pd species in solution was attested by the hot filtration test. These results pave the way to the design of novel green catalysts, which, combining the variation of hydrophobic-hydrophilic balance with the simultaneous control of plugs technology, will be able to tune the performance and the reaction selectivity of the catalyst, possibly through a synergic mechanism.



Figure 4. Schematic unplugged (A) and plugged (B) Pd catalysts

In the field of mesoporous silica materials, an attempt to develop a highly efficient and recyclable Pd catalyst was reported by Lu and co-workers,64 preparing a nanocomposite shuttle as a precursor for Pd nanoparticles, whose solubility in organic solvents is triggered by pH. In particular, at acidic pH (3-4) the Pd catalyst is water soluble but, when basic pH is reached (NaOH addition, pH = 9-10), the catalyst is transferred to the organic phase, thus combining the efficacy of the homogeneous catalysis with the advantage of an easy recovery of the catalyst, typical of heterogeneous catalysis. The reactions, performed in water/ether mixture with O2 at room temperature, attested an excellent selectivity towards the aldehyde formation for all of the investigated primary alcohols. The conversions were higher for benzylic and aromatic substrates with respect to the aliphatic ones and several secondary alcohols were also studied, reporting good conversions (20 total examples). When the reaction was over, few drops of diluted HCl were added to the reaction mixture, allowing the catalyst to be transferred to the water phase (after stirring) and the product to be recovered from the organic layer. In addition, the catalyst could be reused at least for 5 runs, without any loss or decomposition: leaching test demonstrated that the catalyst phase transfer is complete and that the whole catalyst is stable, as attested by the fact that Pd, N and C contents after a 4 times recycle are similar to those of the fresh catalyst.

Gold-catalysed oxidation of alcohols

Nowadays, gold is no longer considered as a noble, not reactive metal but, conversely, it has been demonstrated a powerful tool to develop green oxidation of alcohols65,66 with molecular oxygen upon heterogeneous catalysts combining Au nanoparticles and different solid supports. With respect to other metal based catalysts, the nature of the support and the particles size showed to play a more important role in gold catalysis. In addition, the interaction between the support and the catalyst is a crucial factor for controlling reactivity, as emerged from many studies.

Among supports, metal-organic frameworks are currently widely explored as supports also for Au NPs encapsulation. Since MOFs themselves are inherent heterogeneous catalysts, due to their inorganic−organic hybrid composition and polymeric nature, the incorporation of MOF-supports with Au NPs usually leads to enhanced or even novel catalytic properties compared to their pristine counterparts.67 For these reasons MOFs have emerged as a highly practical and efficient platforms to engineer multifunctional catalysts for one-pot cascade organic transformations.68

In these regards, Wang and co-workers, presented an Au@UiO-66(NH2) catalyst, based on a MOFs substrate functionalized with amino groups in order to better stabilize the gold NPs. The catalyst (1.8 wt %) was demonstrated for the aerobic oxidation of benzyl alcohols (5 examples) in base free conditions and using DMF as solvent and O2 as oxidant. More interestingly, the authors demonstrated the same catalyst to be effective in oxidation/imine formation/reduction reaction sequences (Scheme 8).69



Scheme 8. Oxidation/imine formation/reduction reaction sequences

Using a different MOF support, but still taking advantage of its functionalization by amino groups, Wang and co-workers presented an Au@MIL-53(NH2) catalyst for an efficient one-pot alcohol aerobic oxidation/Knoevenagel condensation sequence. The role of Au NPs and amino groups in the one-pot cascade reaction was systematically investigated. Furthermore, a variety of benzyl alcohols were tolerated under the optimal reaction conditions (1.0 mol% of Au, toluene, 100 °C, O2, 1 atm, 13 to 18 h) for the synthesis of 2-benzylidenemalononitrile and its derivatives. The catalyst could be recycled five times without significant loss of catalytic activity in the one-pot reaction (Scheme 9).70



Scheme 9. One-pot aerobic alcohol oxidation/Knoevenagel condensation

The catalyst could be easily filtered after reaction and washed with DMF before reuse. For the aerobic oxidation of benzyl alcohol, only slightly lower yield were observed after over five runs while preparation of secondary amine showed almost no loss of reactivity after five runs. No leaching of Au was detected analyzing the mother liquor by ICP-AES.

The same oxidation-condensation reactions were presented step-wise by Dong and co-authors using Au@Cu(II)-MOF as catalyst (Scheme 10).71



Scheme 10. Step-wise aerobic alcohol oxidation/Knoevenagel condensation

Slightly increasing the catalyst amount (3 mol% Au) and the temperature in the first step, and adding a MeOH solution of malonitrile (0.17 M) in a second step, extending the reaction times to 7 hours, resulted in an increasing of both conversion and selectivity when *p*-F or *m*-OMe benzyl alcohols were used as starting materials. After each catalytic run, the solid catalyst was easily collected by centrifugation, washed with acetonitrile, dried at 90 °C, and reused in the next run under the same conditions. Yields between 98% and 94% were obtained within five recycling runs for the aerobic oxidation of benzyl alcohol while the same range of yields was obtained within three runs for oxidation/Knoevenagel condensation sequence.

Development of MOF-supported Au catalysts toward solvent-free aerobic alcohols oxidation was investigated by Lu and co-workers.72 Although the authors do not expand their evaluation towards the substrate scope, they performed an interesting evaluation of the water role demonstrating its promotion effect when added in appropriate amount (which is established in 0.05mL for 10 mL of benzyl alcohol), due to the hydrophilic nature of the inner face of UiO-66 support. In fact, best results are obtained when the amount of water is similar to the pore volume of the catalyst.72

Interestingly, Wang, Su and co-workers presented a yolk-shell Au@ZIF-8 nanoreactor, prepared via a sacrificial template strategy and having up to 15 reactive units in each MOF shell, able to provide fine control over selective mass transfer of reactants through the MOF shell. The catalyst showed excellent selectivity in the catalytic aerobic oxidation reaction of 1-butanol and 1-hexanol with respect to 3-phenylpropanol when the reaction was performed in water, at 70 °C and in presence of KOH. Both 1-butanol and 1-hexanol showed a conversion of over 40%, while 3-phenylpropanol showed zero conversion.73

A different class of widely studied supports for Au NPs is composed of metal oxides. Great attention is paid to the study of the specific role that active sites play in the oxidation reaction and on the mechanisms based on the activation of oxygen atoms on the gold surface, focusing on the role of the contact boundaries between gold and oxide supports in the catalytic mechanism.74 New efforts in this regards have been recently presented by the use of composite metal oxide. An interesting example, reported the use of a nanocomposite CuO–ZnO support loaded with Au NPs by a deposition–precipitation method.75 The 2Au/1CuO–ZnO catalyst (where 2 and 1 are the weight amount percent of Au and CuO in the catalyst, respectively) showed good performance for the oxidation of a wide range of alcohols including benzylic, primary and secondary alcohols (24 examples), with O2 as the oxidant and C2CO3 as base, in water at reflux temperature. All the reactions were absolutely selective to aldehydes or ketones and the catalyst was recycled and reused for at least 6 consecutive runs with relatively sustained catalytic activity.

Interestingly, Ding and co-workers presented a novel gold catalyst prepared by depositing gold nanoparticles on the mixed NiAl-oxide derived from the calcination of the corresponding layered double hydroxide (LDH) precursor.76 In comparison with Au/Al2O3 and Au/NiO, the Au/NiAlO-2.5 (having the molar ratio of Ni to Al of 2.5) catalyst showed better performances being able to catalyze the oxidation of several alcohols in *o*-xylene at 80 °C, using 0.006 mmol Au and 20 mL/min O2. The authors also suggest the enhanced catalytic property of the Au catalyst to be mainly originated from the synergistic effect between the Au and the support on reaction mechanism, besides the contribution of the electronic interaction. They suppose that the support loaded with Au NPs undergoes structural interconversion between the mixed oxide and the layered double hydroxide upon the water exchange during the reaction, affording a fast removal of water from the Au surface and then accelerating the restore of the Au active sites for the oxidation of alcohols (Figure 5).76



Figure 5. Proposed mechanism for Au/NiAlO-2.5 catalyst

By changing the support with SrTiO3, the reaction on benzylic alcohols proceed toward the carboxylic product when performed in water at room temperature and in the presence of air instead of pure oxygen.77

Imura, Komatsu and co-workers presented Au in the form of nanoflower supported on γ-Al2O3 (Au NFs/ γ-Al2O3) consisting of small crystallites, which have higher proportion of edge and corner sites as well as higher surface area than a spherical nanoparticle with the same particle size. They demonstrated how removing the capping agent (used for the NF preparation) by water extraction, resulted in an increased catalytic activity in the oxidation of 1-phenylethyl alcohol at 60 °C in the presence of K2CO3 and under air atmosphere. After 5 extractions the authors reported an 11-fold increase (after) over the un-extracted catalyst for acetophenone formation.78

Moving to carbon as support, an interesting example took advantage from the environmentally friendly hydrothermal condensation of d-fructose synthesised Au NPs on thiol-functionalized fructose-derived nanoporous carbon (Au NPs@thiol-Fru-d-NPS). The catalyst preparation is itself a green process since it started from an inexpensive natural precursor and it was performed in water and relatively low temperatures (e.g. 130 °C) and pressures (<10 bar). The result is an inexpensive, biocompatible, thermally stable and recyclable functionalized nanostructured carbonaceous material able to stabilize noble metals and heterogeneous catalysis because of its high surface (Figure 6).



Figure 6. Catalyst preparation

Once used in water in the presence of a base, Au NPs@thiol-Fru-d-NPS (0.1 mol% Au, 0.001 g) allowed the aerobic oxidation of various primary and secondary aliphatic and aromatic alcohols (22 examples) to the corresponding aldehyde and ketone derivatives at room temperature. Slightly lower yield were showed when air was used instead of O2. The catalyst was easily recovered and reused several times without leaching of metals or loss of activity.79

Also ordered mesoporous silica (OMS) has emerged as an active material to support metal nanoparticles for catalytic applications due to their high surface area, tunable and confined mesopores, diverse morphology, and large adsorption capacity. Moreover, the channel confinements of mesopores can be utilized as template for the size-controlled synthesis of Au nanoparticles. Yang and co-workers curiously demonstrated how the MCM-41 supported Au nanocatalyst with lower Au loading, displayed higher catalytic activities than other catalysts (having higher weight ratio of Au) for the aerobic oxidation of 1-phenylethanol and benzyl alcohol in toluene at 100 °C and in the presence of Na2CO3 as base, proving the dimension of the Au nanoparticles size (the smaller the better) to be more important than the Au amount for the catalytic activity.80

As previously mentioned, another important aspect is Au NPs dimensions: the reactivity for alcohol oxidation is generally increased with reduced sizes of Au NPs.81 This is why ultrasmall (≈1 nm) metal clusters are promising candidates for novel catalytic sites owing to their unique geometrical and electronic structures. In particular, it is possible to prepare gold clusters (Au NCs) composed of less than 100 atoms with diameters smaller than 2 nm.82 In this case, not only the nature of the support plays an important role but also the presence of organic ligands on the cluster surface imposes steric restriction on the accessibility of reactants and modulate the electronic states of the cluster driving or poisoning the catalyst activity.83 An interesting example in this regard, was reported by Tsukuda and co-workers.84 The authors described differently covered by dodecanethiolates (C12S) Au25 clusters supported on hierarchically porous carbon nanosheets (HPCSs), and demonstrated how the amount of ligand affects both the catalytic activity and the selectivity in the aerobic oxidation of benzyl alcohol (BA). In fact, the fully covered Au25 clusters were inert owing to the site-blocking effect, the thiolate-free Au25 clusters oxidized BA efficiently but with poor chemoselectivity, while selectivity for benzaldehyde formation was significantly improved by the presence of residual thiolates on Au25, although the activity was reduced. The authors also proposed that the role of thiolates is to reduce the oxidation ability of Au25 by electron withdrawal and to hamper the esterification reaction on the cluster surface by site isolation.

Another interesting example of Au NCs as aerobic alcohol oxidation catalysts was reported by Zhang and co-authors having layered double hydroxides (LDH) as support.85 LDH, also known as hydrotalcite, is a layered anionic clay consisting of a positively charged two-dimensional brucite layer with interlayer anions such as carbonate, hydroxide, and/or other desired anions,86 and has progressively received attention as catalyst or support due to its unique surface acid-basic property and potential redox nature.87 The author demonstrated the preparation of several supported Au NCs, varying the metal in the LDH support (M3AL-LDH, M = Mg, Ni, Co), by using water-soluble gluthatione-capped Au nanoclusters as precursor and obtaining ultrasmall Au NCs (~ 1.5 nm) finely dispersed on the support (≤ 0.23 wt %).85 Using oxidation of 1-phenylethanol in toluene as the model reaction, they highlighted the remarkable performances of the catalysts able to selectively oxidize the substrate to the carbonyl corresponding compound under base-free conditions (toluene, 80 °C, 1 h, 0.015 mol% Au, bubbling O2 20 mL/min), with atmospheric O2 as a sole oxidant. Moreover, for Au NCs/Mg3Al-LDH the wide substrate scope without basic additives and the reusability (at least five runs without any loss of activity or selectivity after simple solvent washing of the catalyst) were demonstrated. The presence of transition metal cations on the LDH supports further enhanced the alcohol oxidation activities of the catalysts and Au NCs/Ni3Al-LDH showed the highest activity for the model reaction with a TOF of 5687 h-1, attributed to its strongest Au–support synergy among the catalysts studied. Zhang and co-workers further explored Ni–Al layered double hydroxides (LDHs) to get inside of the support role.88 Combining data from different characterization techniques applied on LDHs having different ratios between Ni and Al, the authors underlined how the arrangements of NiO6 and AlO6 octahedra in the surface hydroxide layers affected directly the synergistic effect of Au NPs and Ni–Al–LDHs supports. The fully ordered arrangement (Ni2AlOH hydroxyl environment), that is, a honeycomb-like Al distribution generated a uniform charge density, resulting in the optimization of the synergistic effect. Additionally, the nanocrystalline sizes and weak basic hydroxyl groups on the surface of Ni–Al–LDHs promoted both the uniform dispersion of Au NPs on supports and proton abstraction from the hydroxyl groups of alcohols, which facilitated the liquid-phase aerobic oxidation of alcohols as well. On the basis of these finding, they also proposed a possible mechanism with Au NPs and Ni2AlOH structure as synergistic active sites, illustrating that the aerobic oxidation of alcohols should be performed by cooperation between the Au NPs and Ni2+ as well as hydroxyl on the surface of the Ni–Al–LDHs (Scheme 11).88



Scheme 11. Cooperative mechanism proposed

A further investigation was performed by the same authors, synthesizing a series of Ni-based LDH supported Au25 clusters catalysts *via* a modified electrostatic adsorption method of Au25Capt18 onto pre-dispersed Ni-based LDH followed by proper calcinations.89 They underlined how activities increase in an order of Au25/Ni4Al-LDH < Au25/Ni2Al- LDH < Au25/Ni3Al-LDH for aerobic oxidation of 1-phenylethanol under no adventitious base with molecular oxygen as a sole oxidant. After activities and kinetics studies, they found the catalyst Au25/Ni3Al-LDH to show the highest activity thanks to the strongest Au25-LDH synergistic effect between the ultrafine Au25 clusters (~0.9 nm) with the negative charge on the clusters’ surface and the LDH support with most Ni-OH sites from the best layer orderliness. They assume that the layer orderliness of the LDH supports directly affects the synergistic effect of Au25 and Ni*x*Al-LDH: the higher is the orderliness of the LDH supports, the stronger interaction between Au25 and supports is observed. In addition, the higher activity of 1-phenylethanol oxidation besides the ultrafine clusters facilitate the aerobic oxidation of alcohols.89 The substrate scope has to be implemented but first evidence of the effectiveness of the catalytic system towards aliphatic alcohols is provided.

Cobalt-based catalysts

Since our last review, where only two examples of Co-based heterogeneous catalysts were reported,10k research for catalysts based on this non-precious metal had a great improvement. While both previous examples involved Co(II) Schiff base complexes, newly published researches are mainly focused on Co NPs or Co containing porous nanocomposites.

Li and co-workers explored the preparation of Co/C-N heterogeneous catalysts by one-step thermolysis of Co-containing MOFs under inert atmosphere.90,91 They demonstrated the materials to possess high specific surface areas and the presence of N to be beneficial for the improvement of basicity and metal dispersion of the Co-carbon nanocomposites. The system prepared from [Co9(BTC)6(TPT)2(H2O)15] (BTC = 1,3,5-benzenetricarboxylate, TPT = 2,4,6-tris(4-pyridyl)-1,3,5-triazine), showed good performance in the aerobic oxidation of secondary alcohols, both benzylic and aliphatic (21 examples), when used in 10 mol% Co/C–N700 (where 700 indicates the pyrolysis temperature) as the catalyst, H2O as the solvent, air as the oxidant, at 110 °C for 48 h. After the reaction, the catalyst could be easily separated with the assistance of an external magnet and reused for at least five times without any significant loss of activity, after being reduced in H2 at 400 °C for 1 h. The authors demonstrated no significant leaching of the active Co during the reaction process.90 When ZIF-67 (Co(MeIM)2, MeIM = 2-methylimidazole) was used as the starting MOF for the preparation of Co@C-N(800) catalyst and the reaction was performed in methanol or p-nitro benzyl alcohol, at 25 °C in air with 40 mol% Co, the resulting products were the corresponding methyl or *p*-nitro benzyl esters. When diols were used as substrates and *n*-hexane as solvent, the reaction produced the corresponding lactons in very good yields (Scheme 12).91 Of course the system should be implemented towards less amount of catalyst.



Scheme 12. Lactone formation

Using the same ZIF-67 MOF as starting material, but preparing the catalyst by a different thermal decomposition method, Jiang and co-workers prepared a Co-CoO@N-doped porous carbon nanocomposites with regular shape, in which crystalline Co NPs with surface-oxidized CoO species are well dispersed throughout the N-doped porous carbon.92 The reaction, performed in MeOH, under 1 atm O2 at 80 °C and in presence of K2CO3 afforded prevalently the corresponding esters.

A different and simple thermal condensation method, using a metal salt (exemplified by Co(NO3)2), and low-cost organic molecules (terephthalic acid and triethylene diamine) as the precursors was presented for larger-scale production of Co@NC catalysts for the oxidation of benzyl alcohols to the corresponding esters.93 The authors investigated the role of the nitrogen-rich carbon support on the reactivity highlighting the key role of the Mott−Schottky effect at the interface of the heterojunction in modifying the electron density and thus the final catalytic activity of Co particles. The Mott−Schottky effect in solid-state physics is, in this case, the electron transfer between nitrogen-rich carbon, having a flat band potential (or work function) relatively higher than that of metallic Co materials, and electrons from Co nanoparticles. Moreover, they demonstrated the support to act as a built-in and strengthened Lewis base able to accelerate the deprotonation process and the reaction to proceed via the superoxide radical anion.93

Preparing Co@NC by pyrolysis of Co(OAc)2 with 1-methyl-3-cyanomethyl-1*H*-imidazolium chloride ([MCNIm]Cl) in activated carbon (carbonation at 800 °C under N2 for 2h), Huang and co-workers obtained a Co@NC-(800-2h) catalyst able to promote oxidation, esterification or ammoxidation of benzylic alcohols simply by changing the reaction conditions (Scheme 13).94 The oxidative esterification in presence of methanol proceeded with 3.0 mol% Co at 60 °C and in presence of base (19 examples of primary aromatic alcohols), while slightly increasing the catalyst amount to 5.0 mol% and performing the reaction in EtOH at 80 °C in base-free condition the oxygenation of alcohols to aldehydes was demonstrated (13 examples of primary and secondary aromatic alcohols). Using the same catalyst amount and *t*-amyl alcohol as solvent but increasing both temperature and oxygen pressure, ammoxidation of alcohols to nitriles was reached. The reusability of the catalyst was evaluated for the three reactions. The recovered catalyst was reused after filtered, washed and dried after vacuum at room temperature, for at least 8 times without no evident loss in activity and selectivity. Moreover, no leaching of the catalyst was underlined by ICP-AES analysis.



Scheme 13. Oxidation of alcohols to ester, aldehyde and nitrile promoted by Co@NC(800-2h)

Co NPs, prepared using TBAB (tetra butyl ammonium bromide) as surfactant were demonstrated as quite good catalysts for oxidation of primary and secondary aliphatic and benzylic alcohols using O2 as source of oxidant, without the use of additives. While the best results in terms of yield and conversion were obtained with common, not environmentally friendly solvents, increasing the reaction times comparable results were obtained using ionic liquid as solvents. Such longer reaction times are probably due to the lower oxygen solubility in these solvents at room temperature. Furthermore, the combination of ionic liquids as solvents and Co NPs resulted in easy separation and recyclability of the catalyst for at least four times.95

Moving towards inexpensive and biodegradable natural polymers as supports, Shaabani et al. presented cellulose whiskers (the needle-like structure of crystallite cellulose) to prepare Co(II) supported on ethylenediaminefunctionalized nanostructured cellulose (Co(II)-EDANC). The catalyst was demonstrated effective only for benzylic alcohols, using *o*-xylene as solvent at room temperature, in the presence of KOH and bubbling air.96 Even if a broader substrate scope would be appreciated, the recyclability (at least 5 runs) and the use of a bio-support make the article promising for further investigations.

Bimetallic catalysts

Recently, bimetallic nanoparticles have been found to be more advantageous in terms of activity and selectivity compared to their monometallic counterparts.97-100 These better performances can be ascribed to synergistic effects arising from electronic or geometrical interactions between the two metals.99 In the preparation of a bimetallic catalyst, a support is required to prevent aggregation of the metals and easy recovery by filtration of the catalyst.101

Li and co-workers described the preparation (and thorough characterization by means of ICP-OES, TEM, UV-vis, EDX and XRD X-ray analyses) of polystyrene (PS) microsphere decorated with gold-platinum alloy nanoparticles. Surface pre-treatment was not required for the deposition of alloy nanoparticles, which were formed upon a co-reduction method of HAuCl4 and H2PtCl6 with NaBH4 in the presence of sodium citrate.102 The resultant PS/Au1.25Pt1 composite particles (3.6 nm size with a narrow size distribution) proved to be effective in mild and green conditions (air as the oxidant, in water for 24 h at 40 °C) for the 99% conversion of 1-phenyl ethanol to acetophenone. No base addition was required for this bimetallic catalyst, in contrast to the PS/Au and PS/Pt composite particles taken as reference catalysts, thus demonstrating a synergistic effects resulting from the combination of the two metals. Non activated alcohols such as cyclohexanol and 1-octanol were also oxidized in these conditions, even if with minor conversions (80-84%).

Hollow porous shell encapsulated with metal nanoparticles have recently attracted the interest of many researchers. The permeable shell protects the catalytically active nanoparticles from sintering and provides a homogeneous micro-environment for the catalyst and reactants which greatly improves the catalytic activity and stability.103 These systems are also referred to as nanoreactors. With the aim of performing the reactions in water (the greenest solvent), one has to deal with the catalyst/substrate solubility issues. While hydrophilic silica porous shell well disperse in water, many hydrophobic substrates have poor solubility in this solvent. In contrast, hydrophobic polymer catalysts allow fast diffusion of the reactants and products but have poor aqueous dispersion. To overcome this problem, Wang, Qiu and co-workers proposed an amphiphilic hollow porous shell (made of –Pd–bridged periodic mesoporous organosilica, Ph-PMO) encapsulating catalytically active Au@Pd bimetal nanoparticles.104 In the catalyst preparation Pd was introduced by a simple seed growth process to a previously prepared Au@Ph-PMO material. The obtained nanoreactor (Au@Pd@Ph-PMO) showed a good aqueous dispersion and a good reactivity with hydrophobic substrates in water, as evidenced by the oxidation of a series of primary and secondary alcohols (11 examples, including non activated aliphatic ones), using air as the oxidant, in 5-24 h. With such nanoreactor, the substrates are supposed to be stored in the hollow interior of the Au@Pd@Ph-PMO particles. Leaching and sintering of catalytically active nanoparticles can be effectively prevented, thus leading to excellent catalytic stability. The reusability of the Au@Pd@Ph-PMO catalyst was demonstrated up to ten recycling runs. No leached gold and palladium species were detected in the reaction medium after filtration of the catalyst, and the recovered catalyst was characterized again showing that the yolk-shell nanostructure did not changed.

The enhancement in activity for alcohol oxidation resulting from alloying Au with Pd was demonstrated by Hutchings and co-workers around 10 years ago.105 The same Hutchings proposed, last year, a new method for the stabilization of Au-Pd alloy NPs using exfoliated flexible graphene oxide (GO) sheets, that were afterwards dispersed with TiO2 as shown in Scheme 14.



Scheme 14. Cartoon for the method of preparation of GO stabilized Au-Pd NPs on TiO2 (AuPd-GO/TiO2)

This “ternary” catalyst (gold-palladium/graphene oxide/titania) demonstrated to be a highly efficient, stable, recyclable catalyst for the solvent-free oxidation of alcohols (7 examples) with molecular oxygen (1 bar).106 The GO acted as a two dimensional stabilizer for Au-Pd NPs, and the addition of TiO2 further improved the activity for the oxidation of benzyl alcohol. This was attributed to the inhibition of excessive agglomeration of the Au-Pd-GO sheets, to allow for fast diffusion of oxygen and reactants.

We have previously seen (in the iron section), an example of Fe3O4/C catalyst that could be magnetically recovered.51 A similar bifunctional catalyst (with the dual role of oxidation catalyst and magnetic entity) was developed by exploring the giant magnetic moment of Co-Pd alloys.107 The bimetallic Co-Pd alloy nanoparticles were prepared by the reduction of CoCl2 and Pd(OAc)2 (1:1 molar ratio) with LiEt3BH in THF in the presence of different capping agents. The formed nanoparticles had small average diameter with narrow distribution (2.9-4.1 nm). The Pd:Co ratio was determined to be 1:1. The oxidation of non activated alcohol 1-octanol was investigated in water at 60 °C for 24 h with Pd-Co nanoparticles and different capping agents (Scheme 15).



Scheme 15. Oxidation of non activated alcohols by Pd-Co bimetallic catalyst

The best reactivity was found for the catalyst with the capping agent bearing the isocyanide group, which is supposed to give the best back donation of Pd enhancing the catalytic activity. The substrate scope was extended to benzylic and other aliphatic less reactive alcohols (11 examples). As a weak point of this procedure, recovery of the catalyst by an external magnet and reuse experiments worked well only for two runs, while from the third one the yield dramatically dropped to 18%. TEM images registered on the recovered catalyst established a growth of the nanoparticle dimension from 2.9 nm to 5.0 nm, consistent with leaching of Co and aggregation of Pd(0).

The synergistic effect between different metals not always takes place. An extensive investigation of Pt, Pd and Au NPs and the corresponding bimetallic NPs supported on hydrotalcite (HT), prepared by a sol-immobilization method, was recently reported, and the activity compared with the same NPs on different supports such as MgO and TiO2.108 The synergistic effect between different precious metals were investigated in the aerobic oxidation of octanol, a substrate commonly taken as model to determine the effectiveness of a catalyst in the oxidation of aliphatic alcohols. The activity of these catalysts was tested under base- and solvent-free conditions, at 100 °C and with pressure (3 bar) of oxygen. The Pt/HT catalyst gave the highest activity and selectivity towards the aldehyde. However, no synergistic effect was observed upon addition of a small amount of Pd or Au to this Pt/HT catalyst. Conversely, alloying the gold catalyst with palladium resulted in higher activity and selectivity toward octanal. Catalyst reusability of the monometallic Au-, Pd- and Pt-/HT catalysts was not possible, due to possible deactivation of catalyst by binding of the products to the catalyst themselves.108 The synergy between gold and palladium in Au-Pd catalysts supported on hydrotalcites (HT) (Au60Pd40-PVP/HT) in the oxidation of 1-phenylethanol was thoroughly investigated by means of X-ray photoelectron spectroscopy (XPS), X-ray adsorption near-edge structure (XANES), and kinetic studies, indicating an electron transfer from Pd to Au atoms strongly contributing to the rate-determining step in the alcohol oxidation.109 A range of primary and secondary benzyl alcohols were oxidized with Au-Pd/sodium titanate nanotubes (NaTNTs) that worked well in alkali- and solvent-free conditions at 120 °C.110 However, the conversion of furfuryl alcohol and cyclohexanol was not higher than 20%. Recycle up to five times was possible. Physicochemical studies revealed that the particles of Au were smaller and uniformly dispersed on the support in the presence of Pd.

The synergy between gold and the heterogeneous support was clearly evident in study carried out by Zhang and co-workers.111 They prepared a series of 3D honeycomb-like nanostructured magnetic catalysts, among which -Fe2O3@Ni3Al-LDH (layered double hydroxide)@Au25-x (x≈0.2) showed the best performance in the aerobic oxidation of alcohols in toluene at 80 °C with a flux of oxygen as the oxidant. The oxidation strongly depended on the size of Au25NCs, with the smaller NCs guaranteeing the best TOFs of the catalyst. The catalyst could be recovered employing an external magnet and reused up to ten times without loss of efficiency.

Methods to carry out two or more transformation in one pot reaction are highly desirable from the viewpoint of sustainability, since they avoid tedious purification procedures of intermediates resulting in higher efficiency and elimination of wastes.

The group of Kobayashi and co-workers has established a method for immobilizing metal NPs onto a polymer support and they have demonstrated that these polymer-incarcerated (PI) metal catalysts, also using carbon black as a second support (CB), facilitate a series of reactions without the leaching of metal from the polymer support.112 In particular, Kobayashi and co-workers recently reported very nice examples of TOP (tandem oxidative process)113 using bimetallic PICB Au-Pd catalysts. For instance, they were able to achieve the selective formation of imines from alcohols and amines using PICB Au-Pd catalyst (1.5 mol%) in a 9:1 THF/TFE (trifluoethanol) solvent mixture using oxygen or air at 30-60 °C, showing that several aromatic and aliphatic alcohols (18 examples) react with several primary amines or anilines giving the corresponding imines in good yields (Scheme 16).114 The effectiveness of the bimetallic system with respect to the isolated Au or Pd NPs was demonstrated by control experiments.

The catalyst could be recovered and reused up to 5 times after a pre-treatment (washing with THF/H2O followed by heating at 170 °C for 4 h).



Scheme 16. Tandem oxidation-condensation catalyzed by PICB Au-Pd to afford imines

By coating a polymer supported chiral organocatalyst (OC) with a styrene-based copolymer able to immobilize and incarcerate Au-Pd alloys NPs, they were also able to produce a heterogeneous bifunctional chiral catalyst that achieved the sequential aerobic oxidation-asymmetric Michael reactions between primary allylic alcohols (10 examples) and dibenzyl malonate (Scheme 17).115



Scheme 17. Tandem oxidation-asymmetric Michael addition of allylic alcohols catalyzed by PI(Au-Pd)-CO

No leaching of Pd or Au was detected (by ICP analysis). However, the possibility of recover and reuse this catalyst was not reported. Addition of 20 mol% of acetic acid as an additive was required to achieve good yields.

Finally, an integrated three-step process involving alcohol oxidation, C-C unsaturated bond formation and asymmetric 1,4-addition reaction in a one-pot manner was achieved by means of the PI/CB-Au-Pd bimetallic NPs combined with chiral Rh NPs to achieve highly enantioenriched (ee’s >93%) esters with the chiral centre at the  position (Scheme 18).116 This reaction required 3 equiv of K2CO3 and 60 °C temperature in H2O/toluene 2:1 solutions. Several aromatic and heteroaromatic alcohols (11 examples) gave satisfactory yields (34-84%) of the corresponding -substituted esters (calculated on three steps).



Scheme 18. Three step integrated process in one pot reaction using PI Au-Pd NPs and enantiopure Rh based NPs

The growing focus of the scientific community on the utilization of visible light as a source of renewable and sustainable energy has prompted towards new photo-catalysts that can be active in the visible light spectrum. Very recently, Varma and co-workers reported the used of titanium clusters (TiC) with a reduced bang gap in order to harness visible light to undergo alcohol oxidation.117 In the proposed catalytic system, Pd nanoparticles were dispersed on TiC and the obtained catalyst was used for the oxidation of a range of benzylic alcohols and other aromatic and heteroaromatic substrates (8 examples) using air as the sole oxidant in CH3CN at room temperature under a visible light source. In this catalyst, titanium clusters perform the dual task of providing the required activation energy and transmitting oxygen in the oxidation step.

Aerobic flow oxidation of alcohols

The development of organic transformations under continuous flow conditions is becoming an increasingly important topic in different fields of synthetic organic chemistry.118

The application of flow chemistry to oxidation protocols that use molecular oxygen or air is highly interesting, since the application of these sustainable and gaseous oxidants in conventional batch reactors is often associated with severe safety risks and process challenges especially on larger scales. Continuous flow technology offers the possibility to minimize these safety hazards and concurrently allows working in high-temperature/high-pressure regimes to access highly efficient oxidation protocols.119

However, the catalytic aerobic oxidation of alcohols in continuous-flow systems with heterogeneous catalysts are still limited and have not yet reached a practical synthetic utility.120 For these reasons, new efforts in this direction are desirable, especially those that try to address the oxidation of less-active aliphatic alcohols.

Uozumi and co-workers, based on their previously reported catalyst ARP-Pt (obtained by dispersion of platinum nanoparticles in amphiphilic polystyrene-poly(ethylene glycol) resin (PS-PEG), which was effective in the oxidation of even less reactive primary alcohols in water under mild conditions and proved to be stable and recyclable,121 tried to apply it in a continuous-flow system for the oxidation of alcohols. They used a commercially available X-CubeTM flow reactor system (ThalesNano Nanotechnology Inc.). A range of benzylic and aliphatic secondary alcohols were oxidized in water (or in 7:3 mixtures of water and *tert*-butyl alcohol in case of low solubility of the resulting ketones) in a continuous flow reactor where the substrates were sequentially passed through two catalyst cartridges each charged with the ARP-Pt catalyst (in total 0.17 mmol Pt), for a total contact time of 55-73 seconds, at 100-120 °C and with a 50 bar pressure of O2. Good yields were obtained even with unactivated aliphatic alcohols.122 The scope of the reaction for various primary alcohols was also investigated under the aerobic flow conditions and it was found that in the presence of one equivalent of sodium carbonate (or 2, in case of diols) the reaction proceeded to the selective formation of carboxylic acids, while in the presence of 1 equivalent of trimethylamine the reactions selectively gave aldehydes. It was postulated that the oxidation of aldehydes to carboxylic acids is suppressed by deactivation of the platinum nanoparticles by the amine (Scheme 19). To demonstrate the practical utility of this process, they also performed a gram-scale oxidation (40-57 g) of two surfactants starting from the corresponding oligo(ethylene glycol)monododecyl ethers for 36-113 hours, also demonstrating that the catalytic activity was retained at 100 °C for quite a long period.122



Scheme 19. Aerobic flow oxidation with ARP-Pt-charged cartridges

The groups of Stahl, Root and co-workers, after having demonstrated safe and scalable processes for aerobic alcohol oxidation using homogeneous Pd(OAc)2/pyridine123 and Cu/TEMPO124 catalytic systems, became interested also in the possibility of applying the heterogeneous Ru(OH)x/Al2O3 catalyst (developed by Yamaguchi and Mizuno)125 in a continuous-flow process using a packed bed reactor. They employed 8% O2 mixture in N2 to ensure that the reaction mixture, which employed toluene as solvent, was nonflammable throughout the process. After having optimized the system with benzyl alcohol, they applied this procedure to the oxidation of some (4 examples) aromatic alcohols also bearing heteroatom functional groups such as 2-(hydroxymethyl)thiophene and 2-(hydroxymethyl)pyridine, that did not poisoned the catalyst.126

In order to improve the mechanical strength of the support, Martín-Matute and co-workers127 surrounded their Pd nanoparticles embedded in MOF (Pd@MIL-88B-NH2) with a silica support and called this new catalyst Pd@MIL-88B-NH2@nano-SiO2. This new material was applied to the oxidation of several secondary benzylic alcohols (14 examples) in *p*-xylene at 150 °C, obtaining the corresponding ketones in good yields and reasonable times (<20 h). Interestingly, the use of bubbling oxygen in the reaction mixture containing the flammable organic solvent was avoided and the reactions were performed in tubes open to air. No additional oxidants or additives were required. The reaction was also adapted to a continuous flow process in which a much better mixing of air and starting materials was achieved, thus allowing to decrease the temperature to 110 °C while maintaining the same performance. Under these conditions, Pd@MIL-88B-NH2@nano-SiO2 could be used for at least 7 days, showing no signs of deactivation.

Conclusions

The development of novel heterogeneous catalysts able to selectively oxidize alcohols in eco-friendly conditions is a continuously growing topic. This is essentially due to importance of the oxidation products (aldehydes, ketones, carboxylic acids and esters), which occur widely in drugs and vitamins. Only in the last two years hundreds of papers have been published reporting encouraging results in the search for more sustainable methods and rather strict parameters were chosen for the selection made in this review, with the aim of identifying the guidelines to be followed for the future progress of new green catalysts. While there are many examples reporting the use of O2 as the only oxidizing agent, a few Cu, Au, Co and bimetallic catalysts are able to efficiently work with air as oxidant and water as solvent, which means real green conditions. Some examples where the use of ionic liquids as solvent allowed to achieve better results than with common organic solvents have been also reported for Cu, Pd, Fe and Co catalysts.

Recycling the catalysts is usually possible at least for five times, while some examples, namely using Fe, Co or bimetallic systems, reported most efficient recyclability with the catalyst reused up to eight or even fifteen times. Also the catalyst recovery can be obtained in a green way by filtering and washing with environmental friendly solvents, or even better, by exploiting magnetic properties of the catalysts or their pH sensitivity.

Looking at the substrate scope, aliphatic alcohols still present the major challenge. Only few examples are reported showing high yield and good selectivity towards such substrates using catalysts based on Co, Au, Pd, bimetallic systems or by means of flow chemistry.

Interestingly, many papers investigate the synergistic effects between the metal and the support and many efforts to understand the mechanism of the catalyzed oxidation were done. In particular, the costs related to the use of precious metals to activate oxygen remain too high for the use of such reactions in industry. For this reason, a great improvement in the investigation of N doped graphitic supports to be decorated with non-precious metals was achieved. Even if these studies are still in their infancy, they may pave the way for a new generation of efficient catalysts. The last years showed a great increase in the number of papers presenting heterogeneous catalysts based on copper, and even more remarkable, on Fe and Co, highlighting how the research community is moving towards such class of catalysts, which were almost unexplored in their heterogeneous fashion up to 2012.

In conclusion, we think that this field will find space for new horizons in the next future, together with the improvements in the material science and in the design of new catalysts.

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